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Hydrogel Microneedle Arrays for Transdermal Drug Delivery

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Abstract: Stratum corneum is the main obstacle for drugs to pass through the skin. Microneedles are composed of arrays of micro-projections formed with different materials, generally ranging from 25-2000 µm in height. Microneedles straightly pierce the skin with its short needle arrays to overcome this barrier. Microneedles can be divided into several categories, for instance, solid microneedles, coated microneedles, and hollow microneedles and so on. However, all these types have their weak points related to corresponding mechanisms. In recent years, pioneering scientists have been working on these issues and some possible solutions have been investigated. This article will focus on the microneedle arrays consisting of hydrogels. Hydrogels are commonly used in drug delivery field. Hydrogel microneedles can be further divided into dissolving and degradable microneedles and phase transition microneedles. The former leaves drug with matrix in the skin. The latter has the feature that drugs in the matrix are delivered while the remaining ingredients can be easily removed from the skin after usage. For drugs which are required to be used every day, the phase transition microneedles are more acceptable. This article is written in order to summarize the advantages of these designs and summarize issues to be solved which may hinder the development of this technology.

Keywords: Hydrogel; Microneedle; Phase transition; Dissolving and degradable

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Introduction

Microneedle (MN) technology, a minimally invasive drug delivery system, has the potential to be an alternative to hypodermic needle tech [1]. Generally, MNs are composed of arrays of micro-projections formed with different materials, generally ranging from 25-2000 µm in height [2], with different tip shapes and tip intervals, being attached to a base support [3]. When applied to skins, they puncture the epidermis and reach the dermis. Since the depths of needle insertion is within the non-innervated layer of the skin, this technique would allow painless delivery and improve patient compliance [4]. This kind of structures help to overcome the weaknesses of traditional transdermal delivery systems, which only allow small and lipophilic molecules to be delivered by passive diffusion, while keeping the strengths of accessibility, safety, painless drug administration, potential for self-administration, and avoidance of enzymatic degradation in the gastrointestinal tract or liver as well as needle phobia [5-7].

Hydrogels are polymers with a three-dimensional structure that exhibit the ability to swell in water and keep significant amount of water within the structures [8]. They can be divided into natural hydrogels and synthetic ones. Natural hydrogels include agarose, methylcellulose, hyaluronic acid, chitosan, starch, collagen and other naturally derived polymers while synthetic ingredients include polyvinyl alcohol, sodium polyacrylate, acrylate polymers and copolymers with an abun-
dance of hydrophilic groups [9]. Additionally, hydrogels that do not exhibit any significant volume transition to environmental changes (pH, temperature, photo field, ion concentration, composition of the solvent, etc.), which are generally obtained from hydrophilic monomers, are defined as “conventional” hydrogels, while others, which can change their volumes abruptly in response to the changes of the external environmental factors are classified as “intelligent” hydrogels [10-13].

Problems of non-hydrogel MNs

There are several kinds of MNs, namely, solid MNs for skin pretreatment to increase skin permeability, MNs coated with drugs, hollow MNs for drug infusion into the skin, polymeric or polysaccharide MNs that encapsulate drugs and partially or fully dissolve in the skin [14-17].

Solid MNs, which do not contain drugs themselves, enhance the permeability of drugs, for instance, small molecules, proteins and nanoparticles, by creating pores into the skins [18]. They are the first generation of MNs and generally fabricated with silicon or metals [19]. However, this requires a two-step application, which is not convenient for patients. Skin is a self-regenerating organ which heals itself [5] and the different recovery rates caused by individual differences significantly affect the bioactivity administration of drugs. In order to retard the recovery of skin, some additional drugs are applied to the skin including diclofenac sodium. Brogden et al. [20] suggested that the micro-pore lifetime could be prolonged with simple topical administration of a non-specific cyclooxygenase inhibitor. Ghosh et al. [5] utilized naltrexone (NTX) with diclofenac co-drugs for systemic delivery of NTX into the treated skin and the results indicated that the co-drug approach could be used for the development of a 7-day transdermal system. These results showed the possibility for better delivery of drugs after the skins were treated with solid MN-enhanced delivery, thus expanding the transdermal field to a wider variety of clinical conditions. On the other hand, if some of the needles happen to break and are left in the skin, irritation is inevitable. The fabrication cost is high and the disposition of wastes is also a question. Some materials, for example, silicon, require clean room processing and are not FDA-approved biomaterials.

Drug coated solid MNs was a simple, versatile, and controllable method to coat microneedles with DNA, proteins, microparticles and viruses for rapid delivery into the skin [21], which solve the problem of two-step application. Moreover, the drug coated MNs may also combined with hydrogel. M Pearton et al. [22] showed the ability of micro-fabricated needles to create some channels and a mediate reporter gene expression in viable human skin by using pDNA loaded the hydrogels. This is another kind of drug coating. The skin was first treated with pDNA loaded hydrogels and then punctured with MNs. Further in vivo studies with these formulations will research the ability of these systems controlled-release pDNA expression. But the results showed that the total number of positive expression was less than solution prescription in 24 h. However, due to the design, the drug can only be loaded onto the surface of MNs, so the drug loading amount is relatively low [23-25]. The cost of fabrication is also another concern.

Hollow MNs usually require very precise and high cost manufacturing technology, which prevent them from large scale production [26]. In this approach, large scale reproduction with low costs is pursued sometimes based on self-assembly and molding of soft materials. Polydimethylsiloxane (PDMS) is an elastomer used in micro fabrication, but it is to some extent with low stiffness. However, Matteucci et al. [27] investigated re-usable poly vinyl alcohol (PVA) masters, which were found to be easily obtainable and perform better in fabrication of needle pillars where aspect ratios higher than five are needed. PVA masters also show advantages of higher stiffness, hydrophilic behavior and resistance to poly methyl methacrylate (PMMA) developers for the fabrication of PMMA structures. However, if hollow MNs are occasionally broken in the skin, significant leakage or uncontrolled drug release may occur [2]. There are also risks that the body tissue blocks the narrow channels which interfering the drug dosage.

The advantages of hydrogel MNs

Hydrogel MNs are one kind of polymeric or polysaccharide MNs according to the definition of hydrogel. Besides the hollow MNs which are fabricated with polymers or the hydrogel coated the surfaces of solid MNs, there are three kinds of drug-loading methods. Some MNs only have drugs in the tips; some in the patches; others have drugs in both of them. All of these methods provide large spaces for drugs to be loaded. The drug loading amount is better than the solid MNs and drug coated MNs as well as the hollow MNs. Polymeric and polysaccharide MNs include a variety of MNs with different characters. Some polymers and polysaccharides are drawing increasing attentions because of their excellent biocompatibility, degradability, and nontoxicity [28-29]. Polymer microneedles also offer the benefits of ease of fabrication, cost-effectiveness, and the capacity for mass production, as well as controlled drug release with the help of water solubility and degradation properties of polymers [30]. Hydrogel MNs are overall easier and more economical to be fabricated from materials which are more likely to be biocompatible and with
FDA approvals. The fabrication methods often include the photolithographic process and micro-molding process [30]. For micro-molding processes which are lower cost, centrifugation and vacuum method have been developed to obtain polymer microneedles with the proper shapes; it is obvious that the latter is more suitable for mass production of MNs. Thus there is a new research field to find an inexpensive, easy to be manufactured, waterproof while air permeable mold to achieve mass production of MNs. According to the function mechanism of hydrogel MNs, they are divided into two categories.

The first is dissolving or degradable MNs. They bear common features in the mechanism that the drug release pattern is related to the dissolution or degradation of the MN matrix, i.e. the polymer or polysaccharide themselves [30-32]. These MNs dissolve or degrade in the skin and thereby leave no sharp medical waste after use [33-35]. The common process is shown in Fig. 1. Jeong W. Lee et al. [36] applied FDA-approved ultra-low viscosity carboxymethylcellulose and amylopectin to present a dissolving MN design involving preparation under mild conditions that may be suitable for protein delivery.

Dissolving microneedles can dissolve within the skin safely and need not be removed from the patient’s skin when applied. After the insertion to the skin, dissolving microneedles dissolve quickly and release the loaded drugs in a short time. Ming-Hung Ling et al. [37] presented a dissolving microneedle patch, which is composed of starch and gelatin and carried insulin as the model drug. Regarding the in vitro drug release test, the dissolving microneedles released almost all the insulin carried into the skin within 5 minutes. Consistent with the in vitro skin insertion test, the starch/gelatin microneedles dissolved completely within 5 minutes after insertion into the porcine skin. The dissolving microneedles have enough mechanical strength and stable encapsulation of bioactive molecules, which is promising for the transdermal delivery.

Biodegradable MNs degrade in the skin after application, whereby the release of incorporated drugs can be sustained up to months by choosing the proper polymers. Mei-Chin Chen et al. [38-39] investigated that drugs loaded in chitosan carriers can be released through swelling and degradation of the chitosan matrix, leading to a clear sustained-release effect. Chitosan with suitable molecular weight can be cleared by the kidney in vivo, whereas excessive molecules can be cleaved by proteases into fragments to be suitable for renal clearance. They used OVA as a model antigen to be loaded in the microneedles. The release profile result showed an initial burst within one day and a slow release followed for at least 7 days, with almost 90% of the OVA released. The in vivo degradation of VOA-loaded chitosan microneedles also showed that even 14 days after application, small residual fragments of the microneedle still can be found. The slow degradation rate demonstrated that the embedded chitosan microneedles degrade gradually and may lead to a sustained antigen release.

Some biodegradable MNs leave the needles in skin to deliver bolus drugs or sustained release of drugs by separating the needles from the patches in the skin. Min Kim et al. [40] demonstrated MN separation mediated by hydrogel swelling in response to contact with body fluid. In such cases, the tips of biodegradable polymeric MNs were separated because of hydrogel microparticles, which were fabricated between the needle tips and the patches, expand quickly and lose mechanical strength rapidly by swelling and absorbing body fluid. Besides, there were also hydrogel MNs combined with metal shafts to form biodegradable ones. Leonard Y. Chu et al. [41] investigated separable arrowhead MNs which upon insertion in the skin, the sharp-tipped polymer arrowheads induced hydrogel part which contained drugs to separate from their metal shafts. Due to rapid separation of the arrowhead tips from the shafts within seconds, administration using arrowhead MNs can be performed rapidly, while the release kinetics profiles of drug can be independently controlled based on separable arrowhead formulation.

The second is phase transition MNs in which drug release as a result of the polymer swelling when absorbing body fluid. This kind of MNs leaves few or no residuals after application. These MNs preserve the advantages of other MNs, such as the drug permeating amount and rate improvement, large drug loading amount and relatively easy to be fabricated. They also have the potential to be daily used since few non-drug residuals will be left in the skin, which may increase the patients’ compliance. They are so far a very promising MN technologies. Ryan F. Donnelly et al. [42,43]
developed MNs made of Gantrez®, a copolymer of methyl vinyl ether and maleic anhydride, which could be removed completely and intact from the skin. The needle tips swell in skin to produce continuous, unblockable conduits from patch-type drug reservoirs to the dermal microcirculation, thus allowing prolonged transdermal drug administration. According to their findings, delivery of macromolecules was no longer limited to what can be loaded into the MNs themselves and transdermal delivery drug was controlled by using the crosslinking density of the hydrogel system rather than the stratum corneum. The materials they chose were biocompatible, non-irritant and raised no safety concerns in human volunteers. The MNs can be fabricated in a wide range of patch sizes and MN geometries by adjusting the molds used. Furthermore, they can also be easily sterilized. It is reported that Young’s modulus and hardness of non-toxic Gantrez® AN-139 MN were noted as 6.56 ± 0.56 GPa, 385.6 ± 12.00 MPa, respectively, which indicates it as a stiffness microneedle base material [44]. PVA is a well-known polymer, which can generate hydrogels by physical or chemical crosslinking and is applied in the field of controlled drug release [45,46]. Sixing Yang et al. [47,48] developed PVA MNs, which compared to other hydrophilic MNs, would not dissolve in the skin, but swell and therefore diffusion channels were opened for drug release. The microneedles were adequately swollen after embedding into human skin and were strong enough to penetrate skin. The results showed that the MNs were embedded reliably into the skin using a force of about 5 N with one thumb. The easy application method is also helpful for the self-administration of patients.

Biodegradable polymeric poly(lactic-co-glycolic acid) (PLGA) MNs and dissolvable MNs, for instance, sodium alginate MNs are proved to create micro-holes in the skin layers without breaking, although the former one have more resistance and mechanical stability [49,50].

MN could be combined with other methods such as electroporation and iontophoresis (ITP) to enhance the delivery of drugs [51-53]. Electroporation is the transitory structural perturbation of lipid bilayer membranes due to the application of high voltage pulses. Its application to the skin has been shown to increase transdermal drug delivery by several orders of magnitude [54]. Iontophoresis was often used combined with hydrogel MNs, which was reported to broaden the range of drugs suitable for transdermal delivery, as well as enabling the rate of delivery to be achieved with precise electronic control [55]. Martin J. Garland et al. [51] found that whilst the combination of MN and ITP did not further enhance the extent of small molecular weight solute delivery, the extent of peptide/protein release was significantly enhanced when ITP was used in combination of the soluble PMVE/MA MN arrays.

Micro- and nanoparticles were also applied. Cherng-Jyh Ke et al. [56] managed co-delivering of two model drugs trans-dermally, Alexa 488 and Cy5, in sequence, based on a system of polyvinylpyrroldione (PVP) MNs that contain pH responsive poly (D,L-lactic-co-glycolic acid) hollow microspheres (PLGA HMs). The key component of this system was NaHCO₃, which could be easily incorporated into HMs. After HMs are treated with an acidic solution (simulating the skin pH environment), a large number of CO₂ bubbles were formed to generate pressure inside the HMs and creates pores inside their PLGA shells, releasing the encapsulated Cy5 (as shown in Fig. 2).

**Existing problems of hydrogel MNs**

Whilst hydrogel MNs are more promising technologies over non-hydrogel ones, they also have problems to be solved. Firstly, although the dissolving or degradable MNs comparatively carry more drug amounts, the matrix, which accounted for a large portion of the needles, dissolve or degrade in the skin. The process is not the best choice since the MNs are transdermal administration methods. However, since the matrixes dissolve or degrade in skins, this kind of MNs is not suitable for drugs which require daily administration. The retention of matrix in the skin will cause low patients compliance and other potential side effects if the drugs are applied every day or within short intervals through MNs. The most suitable active ingredients to be loaded are vaccines, for they are used only once or just several times and thus the amount of matrixes deposit in skin will be much more acceptable.

As mentioned above, scientists developed phase transition MNs in order to solve this problem. Poly methyl vinyl ether/ maleic acid (PMVE/MA) and poly(ethylene glycol) 10,000 (PEG) were utilized by Donnelly et al. [42] to fabricate MN. The diffusion of body fluid caused controlled swelling of the MN arrays to form an *in situ* hydrogel conduit (as shown in Fig. 3). This further resulted in liberation and diffusion of drug molecules from the adhesive patch through the hydrogel MN into the skin. The striking feature was that the hydrogel MN arrays remained intact, even after removal from the skin, thereby leaving no polymeric material in the skin following drug delivery. They developed adhesive patches, containing the molecules at defined loadings, were then attached to the upper base plates of hydrogel-forming MN, with the novel composite system termed as “integrated MN”. However, according to the experimental details, for example, the delivery of insulin from the MN (with 600 µm height, 300 µm width at base, 50 µm interspacing, & 19 × 19 arrays, i.e., about 0.45 cm²) was investigated in a diabetic Sprague-Dawley rat model. Positive controls were
Fig. 2 The design of PVP MN microneedles. pH-responsive PLGA HMs and their mechanism for two model drugs Cy5 and Alexa 488 in sequence transdermal. After the HMs were inserted into skin, the first Alexa 488 rapid release and HMs using Dil-labeled were accomplished because the PVP quickly dissolve. And then the second Cy5 release was stimulated by using the acidic environment of skin. PLGA HMs: poly(DL-lactic-coglycolic acid) hollow microspheres; PVP MNs: polyvinylpyrrolidone microneedles [56].

performed by subcutaneously injecting bovine insulin solution in PBS pH 7.4 at a dose of 0.2 IU per animal. The integrated MN was at a loading of 5 mg/cm² insulin, which equaled to about 2.2 mg or more than 60 IU insulin. The dose in the MNs was over 300 times comparable to that of the positive control. The results showed that the blood glucose level (BGL) dropped to about 90% of its original level within 2 h and fell further to about 37% by the end of the 12 h experimental period if the MNs were applied alone: Even the combination of integrated hydrogel MN and anodal ITP (applied for a 2 h period, after which the electrodes and MN/insulin patch were removed) led to a rapid reduction in BGL, dropping to approximately 47% within 2 h and 32% within 6 h compared with the positive control. According to the doses in the MNs, the bioactivity of this method was quite unsatisfactory. The combination of MN and anodal ITP led to the increase of MN cost and inconvenience of drug administration by patients themselves. The decrease of BGL level in the first 2 h period by MN alone was insignificant, which meant that it could not release sufficient drugs in a short period of time.

The phase transition PVA MNs developed by Sixing Yang et al. [46] was made with the application of the purple-sand female mold. Purple sand was traditionally used by Chinese to make teapots [57,58]. Although this mold had the advantage of being air permeable but water resistant [59], and in coordination with a vacuum on the opposite side, it perfectly met the demand of hydrophilic microneedle patch preparation. However, since purple sand was hydrophilic, the concentration of the polymeric solution might change during the fabrication process when a vacuum was applied. The purple sand absorbed the water in the polymeric solution and it was hard to control the concentration, as well as the drug loading amount. The MN was 0.8 mm in length and 0.3 mm in base, while the length inserted into skin was 0.4 mm. It can be calculated that the volume inserted into skin was only 12.5% of the total...
Drug-containing patch
Hydrogel-forming microneedles
Stratum corneum
Viable epidermis

(A)

(B)

(C)

(D)

Fig. 3 The design of hydrogel-forming MNs [60].

needle tip. This should be improved in order to achieve better release rate and amount of drugs.

Ryan F. Donnelly and Juntanon et al. [60-63] realized that MNs had the possibility to carry microorganisms into the skin and did related tests which indicated that microorganisms could penetrate skin beyond the stratum corneum following microneedle puncture. The numbers of microorganisms crossing the stratum corneum following microneedle puncture were greater than $10^5$ cfu in each case while no microorganisms crossed the epidermal skin. When using a 21G hypodermic needle, more than $10^4$ microorganisms penetrated into the viable tissue and $10^6$ cfu of Candida albicans and Staphylococcus epidermis completely crossed the epidermal skin in 24 h. However, the MN applied in the test was shorter than 280 µm. In a variety of cases, the needle tips were longer than 500 µm, so the experiment did not cover this part. The anti-microorganism effect should be investigated further.

Overall, the hydrogel microneedles are more promising compared with their solid or hollow counterparts. There are also some weaknesses related to the dissolving or biodegradable mechanisms. The most prospective MN type is the hydrogel MN which does not dissolve or degrade in skin but with a controlled or sustained release of drugs. The application of other methods, including ITP or electroporation, may enhance the drug release rate, but they also increase the costs of MNs while lower the patients’ compliance.

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Introduction

In the past few decades, polymer-based drug vehicles have attracted significant interests in the development of drug delivery system mainly owing to the tailorability, easy-functionalization and biocompatibility of polymers [1-5]. Polymeric drug vehicles such as nanoparticles, micelles, nanogels, micro/nano capsules are very advantageous in the control of drug distribution in the living organism, prolonging the biological activity of drugs, improving the therapeutic effect and reducing the administration frequency [6-10]. It is revealed that capsule-like drug carriers could easily realize high drug payload and achieve a better sustained release behavior due to their larger inner cavities [11-14], hence many efforts have been devoted to the synthesis of polymeric capsules. Layer-by-Layer (LbL) assembly is a widely used route to the preparation of polymeric capsules with well-defined chemical and structural properties, which potentially afford a large degree of control over functional properties of polyelectrolyte containers, such as their permeability to low molecular weight compounds or macromolecules [15,16]. For example, Möhwald’s group has reported a series of pH-sensitive LbL capsules, of which the wall could be triggered by pH or ionic strength to switch on and

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off between ‘open’ and ‘closed’ state for guest macromolecules [17-19]. Caruso group has recently found that when disulfide links are used for cross-linking the hydrogel capsules system, a disulfide exchange reagent can be used to trigger release of a model drug [20-22]. However, there are some intrinsic shortcomings in the LbL approach, e.g., difficult to achieve high yield owing to the multistep preparation, absent of structural robustness of the shell upon template removal, and great challenge to refill the hollow interior with functional substance. As a result, a convenient fabrication procedure to the capsules with satisfactory loading capacity and expected stimuli-responsive behavior is highly desired in terms of practical applications of the capsules in biomedical area.

Recently various approaches have been developed for the massive preparation of polymeric capsules [23-25], and template method is especially attractive by precipitating polymers on the surface of granular templates or removing selectively the core of the templates [26-28]. Kozlovskaya group developed a series of weak polyacid based cross-linked capsules by hydrogen-bonded self-assembly as drug carriers [29-31]. In our previous work, various poly (acrylic acid) (PAA)-based micro/nanogels were prepared by using the precipitation polymerization method [32-34]. The obtained nanogels showed a high drug loading capacity and a sustained release feature for water-soluble drug molecules. In this study, in order to enlarge the inner space of the PAA-based particles and gain further high drug loading capacity, we optimized the synthetic strategy in which HPC-PAA was performed as templates followed by the surface polymerization of N-isopropylacrylamide (NIPAm) and the removal of HPC cores, leading to the PAA-PNIPAm hydrogel capsules finally. These capsules exhibit a new high drug loading of ~280% for anticancer drug Doxorubicin hydrochloride (Dox). The in vitro release and anticancer effect on the human intestine cancer cell LoVo show a responsive behavior upon the change in temperature and pH value of the surroundings. In combination of the convenient preparation, high drug loading, dual responsivity as well as the sustained release feature, this polymeric hydrogel capsules show potential application in drug controlled-release system. Importantly, the multiple carboxylic groups on the capsules surface allow functionalization on the capsules with a variety of macromolecules at mild conditions, such as targeting group. This makes the capsules ideal candidates for the target therapy.

Experimental Section

Materials

Hydroxypropylcellulose (HPC, $M_w=100,000$ Da), N, N'-Methylenebisacrylamide (MBAAm) and N-isopropylacrylamide (NIPAm) were purchased from Acros Chemical Company. Sodium dodecyl sulphate (SDS) and Acrylic acid (AA) were purchased from Shanghai Guanghua Chemical Company. Doxorubicin hydrochloride (Dox) was purchased from Beijing HuaFeng United Technology Company. All the other reagents were of analytical grade and used without further purification. Distilled water was used for all polymerization and treatment processes. Human intestinal cancer LoVo cells were obtained from Shanghai Institute of Cell Biology (Shanghai, China).

Preparation of the HPC-PAA template particles

The HPC-PAA template particles were synthesized by direct polymerization of AA in HPC aqueous solution. In a typical run, 0.20 g of HPC was dissolved in 35 mL aqueous solution containing 0.20 g of AA. The solution was stirred at room temperature until it became clear. Then 500 µL of ascorbic acid (0.10 mol/L) and hydrogen peroxide ($H_2O_2$) (0.10 mol/L) solution were separately added into the above solution to initiate the polymerization of AA at 35°C under the protection of nitrogen gas. When the polymerization of AA reached a certain level, opalescent suspension occurred, indicating the formation of HPC-PAA template particles. The reaction was allowed to proceed at 35°C for 1 h.

Preparation of PAA-PNIPAm hydrogel capsules

The PAA-PNIPAm hydrogel capsules were prepared as follows: 15 mL aqueous solution containing 0.20 g of NIPAm, 0.15 g of MBAAm and 0.05 g of SDS was added into the HPC-PAA template particles suspension. Then the polymerization of NIPAm was carried out at 35 °C under a nitrogen stream and magnetic stirring. The reaction kept on for another 2 h before being cooled down to the room temperature, resulting in the HPC-PAA-PNIPAm complex particles. Appropriate amount of HPC-PAA-PNIPAm particles were redispersed in water and the pH of the suspension was adjusted to 8.0 using 0.1 mol/L of NaOH [34]. The PAA-PNIPAm hydrogel capsules were finally obtained after several centrifuging/washing cycles with water.

Preparation of Dox-loaded PAA-PNIPAm hydrogel capsules

The Dox-loaded PAA-PNIPAm hydrogel capsules were prepared by an incubation method at pH = 7.0. A certain content of PAA-PNIPAm hydrogel capsules were mixed with the Dox solution of a predetermined concentration (0.4, 0.8, 1.2, 1.6, 2.0 mg/mL) at room temperature. The mixed solution was incubated at 37°C for 12 h to allow Dox entrapment in the hydrogel capsules to reach an isothermal equilibrium. The drug loading efficiency and loading capacity of PAA-
PNIPAm hydrogel capsules were determined by separating capsules from the aqueous medium containing free Dox via centrifugation (12,000 rpm, 20 min). The amount of free Dox was measured on a UV-vis spectrometer at 495 nm. The loading efficiency (LE) and loading capacity (LC) were calculated with the following equations:

\[
LE (\%) = \frac{\text{weight of drug entrapped in hydrogel capsules}}{\text{weight of drug initially}} \times 100\%
\]

\[
LC (\%) = \frac{\text{weight of drug entrapped in hydrogel capsules}}{\text{weight of dry hydrogel capsules}} \times 100\%
\]

**In vitro release**

The Dox release from the hydrogel capsules was evaluated by the dialysis method. Dox-loaded PAA-PNIPAm hydrogel capsules were placed in a dialysis bag (MWCO = 14,000 Da) and dialyzed against the PBS solution with predetermined pH value (pH = 4.0, 5.0 and 7.4) at particular temperatures (T = 25, 30 and 37°C), respectively. The released drug outside the dialysis bag was sampled at selected time intervals and measured with a UV-vis spectrometer.

**In vitro cytotoxicity**

The cell viability for free Dox, empty and Dox-loaded PAA-PNIPAm hydrogel capsules on the LoVo cell lines were evaluated by MTT assay. LoVo cells (5000 cells/well) were cultured in RPMI 1640 containing 10% fetal bovine serum in a 96-well multiplate. Afterwards, the cells were exposed to free Dox, empty and Dox-loaded PAA-PNIPAm hydrogel capsules respectively for 48 h (at 37°C, 5% CO2), and the medium was replaced with MTT solution (0.50 g/L), and cells were incubated for another 2 h. The resulting blue formazan was solubilized in DMSO, and the absorbance at 560 nm was measured with a plate reader. The MTT reduction of untreated cell was set as 100%, and that of treated cells was expressed as a percentage of untreated cells.

**Cell uptake**

4T1 mouse breast cancer cells were incubated with PAA-PNIPAm hydrogel capsules in a humidified atmosphere with 5% CO2 at 37°C. After incubation for 2 h to allow the 4T1 cells to internalize the capsules, the noninternalized capsules were removed through washing three times with PBS solution. Cell nucleolus was stained by 2-(4-Amidinophenyl)-6-indolecarbamidine dihydrochloride (DAPI). Cells were observed using a laser confocal scanning microscope (LCSM, Zeiss LSM 710, Germany) at an excitation wavelength of 543 nm.

**Characterizations**

The morphology of particles and capsules was observed by transmission electron microscopy (TEM; JEOL TEM-1005) and scanning electron microscopy (SEM, HITACHI S-4800). The samples were dripped onto nitrocellulose-covered copper grid at room temperature without staining. The hydrodynamic diameter (Dh) and size distribution of particles and capsules were measured by dynamic light scattering (DLS) using a Nano ZS system (Malvern Instruments Corporation, UK). Each sample was diluted to the appropriate concentration with water and repeatedly conducted for 3 times at 25°C, obtaining the mean diameter. Zeta potential of the PAA-PNIPAm hydrogel capsules was determined by Zetasizer (Malvern Instruments Corporation, UK). All analyses were performed on samples adjusted with 0.01 M NaCl solution in order to maintain a constant ionic strength. Each measurement was triplicated and the result was the average of three runs.

**Results and discussion**

The strategy to prepare the PAA-PNIPAm hydrogel capsules is proposed in Fig. 1. The HPC-PAA template particles are prepared by the direct polymerization of AA monomers in HPC aqueous solution according to the method reported by Hu et al. [35]. Hydrogen bonding interaction between hydroxyl groups of HPC and carboxyl groups of PAA induces the formation of HPC-PAA particles in the aqueous solution. The size of the templates can be readily tuned from 100-1000 nm by varying the feed ratio of HPC to AA from 10:1 to 1:2.5 [33]. In this study, the [HPC]:[AA] was fixed at 1:1. After polymerization and cross-linking of monomer NIPAm on the surfaces of the HPC-PAA templates, cross-linked HPC-PAA-PNIPAm complex particles with core-shell structure were formed. It should be noted that increasing the pH of system could cause ionization of PAA as well as dissociation of hydrogen bonds and consequently the HPC component of the templates would re-dissolve in the solution and thus the templates would be broken. Hence, cross-linked PAA-PNIPAm hydrogel capsules could be obtained easily just after adjusting the pH of the solution to 8.0.

Figure 2 illustrates the TEM and SEM images of particles at each step. As shown in Fig. 2(a), HPC-PAA template particles possessed morphology of round shape with an average diameter of about 135 nm. After the polymerization and cross-linking of PNIPAm on the template surface at the second step, the size of the particles increased to about 230 nm. Close observation of the particles were indicative of core-shell feature with a dark core and a dusky shell (Fig. 2(b)). After the removal of the template, the particles still kept the sphere morphology as seen in Fig. 2(d). By further TEM
measurement, they were characterized by a thin shell and a fairly large inner cavity (Fig. 2(c)). The wall thickness is about 50 ± 12.5 nm according to the TEM image. More interestingly, some mesopores penetrating from shell to the hollow interior of PAA-PNIPAm hydrogel capsules can be seen in the Fig. 2(c), which were probably the molecular imprint left by HPC after stripping from the HPC-PAA-PNIPAm particles. Compared to the HPC-PAA-PNIPAm particles, the size of PAA-PNIPAm hydrogel capsules increased significantly to about 560 nm, which maybe result from the intense swelling and the electrostatic repulsion generated by the complete ionization of PAA at pH = 8.0. Additionally, in virtue of removing the core, the restriction imposed by the hydrogen bonding between HPC and PAA was gradually released. This induced the particles to swell as well, accounting partially for their size increase. The size distributions of the particles in three steps
measured by DLS are shown in Fig. 3, which illustrates the agreeable trend of particles size with the TEM observations. The diameters from DLS measurements obviously greater than those from TEM measurements could be attributed to the stretching PNIPAm chains in the aqueous solution of 25°C and the shrinking PNIPAm chains under ultrahigh vacuum condition [36].

Considering the large space inside the capsules, the PAA-PNIPAm hydrogel capsules are expected to be drug carriers with superior loading capacity which is regarded as an important factor for the performance of drug carriers [37]. Here, a water-soluble antitumor agent, Doxorubicin hydrochloride (Dox), is selected as a model drug to evaluate its drug loading ability. The drug loading process proceeds easily by incubating the PAA-PNIPAm hydrogel capsules in Dox water solution at 37°C for 12 h. The excessive Dox was removed by centrifugation, followed by repetitive washing with distilled water, leading to the drug-loaded hydrogel capsules. The UV-vis spectrum with the Dox characteristic absorption peak 495 nm (Fig. 4(a)) and LCSM section image of the Dox loaded PAA-PNIPAm hydrogel capsules (Fig. 4(a) inset) confirmed a successful entrapment of Dox into the capsules. Figure 4(b) depicted the loading capacity (LC) and loading efficiency (LE) of the PAA-PNIPAm hydrogel capsules corresponding to different feeding Dox concentrations at pH = 7.0. Along with the rise of the feeding drug concentration, increasing in the LC was observed. The maximum LC of ~280% was exhibited at the feeding Dox concentration of 1.6 mg/mL. Compared to analogous PAA-PNIPAm polymer particles [34,38], the PAA-PNIPAm hydrogel capsules show higher loading capacity for Dox. The high loading of Dox in the PAA-PNIPAm hydrogel capsules may arise from the charge controlled permeability mechanism, i.e., negatively charged PAA in the capsules shell at neutral medium induces positively charged Dox to penetrate through the capsule shell and then deposit spontaneously into the interior of the capsules [39,40]. As previously reports, the incubation process usually exhibited lower loading capacity compared to the encapsulation method. However, the PAA-PNIPAm hydrogel capsules herein still show high loading capacity using the incubation method, which suggests their convenient and low-cost loading procedure for drugs in future application.

Upon changing the environmental conditions, the loaded drugs were released from the capsules in a controlled manner. Figure 5 described the release profiles of Dox from PAA-PNIPAm hydrogel capsules in different pH and temperature, showing a low-rate but sustained release characteristic compared with free Dox.
For instance, at pH = 7.4 and the temperature of 37°C, about 27% of the loaded Dox was released in the early 10 h and 33% of the total Dox was liberated continuously in the next 100 h. This implied that the utilization of the PAA-PNIPAm hydrogel capsules as the Dox carrier was favorable for low-toxic and long-term therapy for cancer.

Figure 5 revealed that the release behavior significantly correlates with the pH of release medium. The release rate of Dox from PAA-PNIPAm hydrogel capsules accelerates with the pH decreasing. This could be explained by the following two aspects. On one hand, the electrostatic interaction between PAA and Dox was actively responsive to the pH variation. At pH = 7.4, PAA chains and Dox molecules were fully ionized with opposite charges and the electrostatic interaction between them was too strong to make the entrapped Dox escape out rashly. As the pH drops down to 4.0, PAA chains were mainly protonated and the bonding force would be weakened greatly, boosting Dox to get off the cavity with ease. On the other hand, deswelling/swelling of the hydrogel capsules also had a certain effect on Dox release. In order to confirm the influence of pH on the size of hydrogel capsules, PAA-PNIPAm hydrogel capsules were incubated in a set of buffer solution with different pH values (pH = 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0) for 24 h. The size and zeta potential of samples at each pH were shown in Fig. 6. It could be found that as the pH increasing from 2.0 to 6.0, a remarkable increase in the size of PAA-PNIPAm hydrogel capsules was observed from 365 nm to 578.4 nm. This could be explained that the ionization degree of PAA chains gradually enlarges and the electrostatic repulsion between COO− groups of PAA causes the whole sphere to be swelling increasingly. Particularly, in the pH range from 4.0 to 6.0, the size showed a dramatic increase possibly being associated with the pK_{a} of 4.75 for PAA. When the pH was beyond 6.0, there was little change in the size due to the complete deprotonation of PAA. Meanwhile, the zeta potential also revealed a similar variety trend. The gradual shrinking of the capsules could undoubtedly narrow their inner volume and force more entrapped Dox to release out of the cavity. This pH-dependent releasing behavior was favorable for the antitumor drug delivery system, since tumor cells were often at a lower pH level of 5.7-7.8 [41], which would induce a faster drug release in the diseased cells than in the normal cells.

It is noteworthy that PNIPAm belongs to thermo-responsive polymers, so the PAA-PNIPAm hydrogel capsules serving as drug carriers are expected to exhibit a thermo controlled-released character. In order to verify this inference, the Dox-loaded hydrogel capsules were dialyzed in PBS (pH = 7.4) at different temperatures. The release profiles at different temperatures depicted in Fig. 5(b). Based on the previous analysis, it was concluded that the obtained PAA-PNIPAm hydrogel capsules, of which the drug release was dual-responsive to both temperature and pH, and could be able to intelligently distinguish between normal and pathological tissues, achieving better targeting efficiency.
and treatment efficacy, and foreseeing an application to the drug controlled-released system.

To investigate the potential toxicity of the PAA-PNIPAm hydrogel capsules and the pharmacological activity of Dox released from the hydrogel capsules, empty and Dox-loaded PAA-PNIPAm hydrogel capsules solution were incubated with human intestine cancer cell line LoVo cells to examine their effect on cell viability with a positive control of free Dox. The MTT assay (Fig. 7(a)) showed that, even at high concentrations of 128 µg/mL, PAA-PNIPAm hydrogel capsules still have no significant cytotoxicity. In vitro cytotoxicity of Dox-loaded hydrogel capsules and free Dox against LoVo cell were exhibited in Fig. 7(b). It could be observed that the cytotoxicity of Dox-loaded hydrogel capsules was almost equivalent to that of free Dox, implying that the drug efficacy released from the hydrogel capsules was scarcely influenced by the process of drug loading, which was in agreement with our previous work [32,34]. LCSM characterization was used to further examine cellular uptakes of PAA-PNIPAm hydrogel capsules. Figure 8 showed the section images of 4T1 mouse breast cancer cells after incubation with the Dox-loaded hydrogel capsules at 37°C for 2 h. As shown in Fig. 8 (a)-(c), the Dox-loaded hydrogel capsules with red fluorescence arising from Dox were observed to mainly distribute in the cytoplasm of cells, indicating that the hydrogel capsules could overcome cellular barriers to enter the intracellular region, although it carried negative surface charges, which was consistent with the results reported by Savic et al. [42]. Moreover, the red fluorescence in the nuclei came from the Dox migrating and accumulating in the nuclei after releasing from the hydrogel capsules localized in the cytoplasm. These results firmly confirmed that the PAA-PNIPAm hydrogel capsules as a drug carrier had an excellent biosecurity and a high pharmacological activity.

Conclusions

We have demonstrated the convenient preparation of PAA-PNIPAm hydrogel capsules in this work, which were fabricated by a templated strategy in aqueous solution. Hydrophilic antitumor drug Dox was successfully entrapped in these hydrogel capsules based on charge controlled permeability mechanism, leading to a new high loading capacity of ∼280% to the weight of the
carriers. More encouragingly, the release of drug from the PAA-PNIPAm hydrogel capsules exhibited a slow-rate but sustainable feature, and behaved the thermo and pH dual-responsivity. In vitro cytotoxicity assay indicated that the Dox-loaded PAA-PNIPAm hydrogel capsules have high antitumor activity. Considering the simple and mild preparation procedure, high drug loading capacity as well as the desired dual-responsive controlled release property, the PAA-PNIPAm hydrogel capsules may serve as a promising candidate for intelligent drug delivery system.

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Research Progress in Improving the Rate Performance of LiFePO$_4$ Cathode Materials

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Abstract: Olivine lithium iron phosphate (LiFePO$_4$) is considered as a promising cathode material for high power-density lithium ion battery due to its high capacity, long cycle life, environmental friendly, low cost, and safety consideration. The theoretical capacity of LiFePO$_4$ based on one electron reaction is 170 mAh g$^{-1}$ at the stable voltage plateau of 3.5 V vs. Li/Li$^+$. However, the instinct drawbacks of olivine structure induce a poor rate performance, resulting from the low lithium ion diffusion rate and low electronic conductivity. In this review, we summarize the methods for enhancing the rate performance of LiFePO$_4$ cathode materials, including carbon coating, elements doping, preparation of nanosized materials, porous materials and composites, etc. Meanwhile, the advantages and disadvantages of above methods are also discussed.

Keywords: LiFePO$_4$; Lithium ion battery; Rate performance

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Introduction

In recent years, one of the greatest challenges is to make use of renewable energies to deal with the limited oil storage and global warming threats [1]. The development of electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs) is imperative. Currently, challenges remain in designing and manufacturing high safety, high performance and low cost rechargeable batteries for vehicle applications. The large scale lithium-ion batteries (LIBs) have become the prime candidate for the next generation of EVs and PHEVs because of its high operative voltage and energy density [2, 3]. For LIBs, the cathode material has significantly impact on battery capacity, cycle life, safety and cost, on which a lot of attentions are drawn. Since the olivine LiFePO$_4$ was reported by Goodenough and coworkers in 1997 [4], it has been considered as the most promising cathode candidate for the next generation large-scale LIBs used in PHEVs or EVs, because of its inherent merits including low toxicity, low material cost, flat voltage profile, long cycle ability and high safety compared to other cathode materials including LiCoO$_2$, LiMn$_2$O$_4$, and Li(NiCoMn)O$_2$ etc. [5-7]. Meanwhile, the olivine LiFePO$_4$ exhibits reversible electrochemical lithium insertion/extraction reactions at about 3.5 V (vs. Li/Li$^+$) with a theoretical capacity of 170 mAh g$^{-1}$ [8]. However, with the deepening of the study, researchers find that the pristine LiFePO$_4$ exhibits poor rate capacities. The low intrinsic electronic conductivity and low Li$^+$ diffusion coefficient of LiFePO$_4$ are the main shortcomings that limits its electrochemical performance and commercial applications of LiFePO$_4$ [9]. At room temperature, bare LiFePO$_4$ is an insulating with an electrical conductivity of about $10^{-9}$ to $10^{-10}$ S cm$^{-1}$, which is much lower than that of LiCoO$_2$ (about $10^{-3}$ S cm$^{-1}$) and LiMn$_2$O$_4$ (2 $\times$ $10^{-5}$ to 5 $\times$ $10^{-5}$ S cm$^{-1}$) [10-12]. Meanwhile, the intrinsic ionic diffusion coefficient is found to be as low as $10^{-13}$ (LiFePO$_4$) to $10^{-16}$ (FePO$_4$) cm$^2$ s$^{-1}$ depend-
ing on the Li\(^+\) concentration and the characterization method such as the electrochemical impedance spectrometry. It should be noted that the diffusion coefficient calculated is related to the state of charge and on the composition of Li\(_x\)FePO\(_4\) [13]. Obviously, such a diffusion coefficient is also lower than that of LiCoO\(_2\) (about 5 \times 10\(^{-9}\) cm\(^2\) s\(^{-1}\)) [14]. Hence, how to overcome these drawbacks has become an important factor of study.

**Structure of pristine LiFePO\(_4\)**

The olivine structure of LiFePO\(_4\) belongs to the family of lithium ortho-phosphates which is shown in Fig. 1. Its space group is Pnma. The lattice parameters are \(a = 10.33\) Å, \(b = 6.01\) Å, \(c = 4.69\) Å and \(V = 291.2\) Å\(^3\). The O atoms occupy a slightly distorted, hexagonal-close-packed arrangement. The P atoms are located in tetrahedral sites; and the Fe and Li atoms are located in octahedral 4a and 4c sites, respectively. A corner-shared FeO\(_6\) octahedron shares edges with two edge-shared LiO\(_6\) octahedrons and a PO\(_4\) tetrahedron. It is notable that the delithiated phase FePO\(_4\) has essentially the same structure as LiFePO\(_4\). This structural similarity not only avoids capacity degradation resulting from severe volumetric changes during the charge-discharge process, but also effectively compensates the volume changes of the carbon anode during lithiation and delithiation. This explains the excellent electrochemical cyclability of the system to some extent [15]. However, in this structure, there is only one-dimensional tunnel formed by the edge shared Li octahedra, where the Li\(^+\) are mobile in this tunnel. These one-dimensional channels are easily blocked by defects and impurities, which may hinder the ion diffusion rate of Li\(^+\), resulting in the poor ion conductivity of LiFePO\(_4\). Meanwhile, such structure cannot form a continuous FeO\(_6\) network, leading to low intrinsic electronic conductivity [16].

Obviously, the low electronic and ionic conductivities seriously restrict the rate performance of LiFePO\(_4\). In recent years, various methods have been proposed to solve these problems in order to improve its performance.

**Approaches to improve the rate performance of LiFePO\(_4\)**

**Carbon coating**

Carbon coating on the LiFePO\(_4\) particles is one of the most important techniques to improve its electrochemical performance with respect to the specific capacity, rate performance, and cycling life [18-22]. The main role of carbon coating is to increase the electronic conductivity on the surface of LiFePO\(_4\) particles [23]. Meanwhile, carbon coating reduces the particle size and alleviates to aggregation of LiFePO\(_4\) particles by inhibiting particle growth [24-27]. In addition, carbon can play the role of a reducing agent, avoiding the oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) during sintering and thus simplify the atmosphere requirement during synthesis [28, 29]. The beneficial effect of carbon coating has been observed varying depending on the structure, precursor, uniformity, loading and thickness of the coating [30-32]. Different carbon sources have different effects on the electrochemical properties of LiFePO\(_4\).

The conventional synthesis route, in which the carbon source materials are simply mixed together with LiFePO\(_4\) precursor, yields a non-uniform distribution of carbon in the final LiFePO\(_4\)/C products. Recently the chemical synthesis routes are widely adopted to achieve homogeneous carbon coating around the surface of

![Fig. 1 The crystal structure of olivine LiFePO\(_4\) in projection along [001] [17].](image)

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LiFePO⁴ particles. Nazar et al. [33] prepared LiFePO⁴-conductive carbon by polymerization of resorcinol-formaldehyde and then heated at 700°C for 10 h under flowing N₂. The discharge capacity reached about 120 mAh g⁻¹ at 5 C. Zhao et al. [34] synthesized core-shell LiFePO⁴/C composites from FePO⁴/C precursor. They used a chemical vapor deposition (CVD) assisted solid-state route with polyvinyl alcohol (PVA) and benzene vapor as the reducing agent and carbon source. The LiFePO⁴ particles were encapsulated within thin graphite shell with a thickness of 3 nm, which prevented the agglomeration of the LiFePO⁴ and improved the conductivity of the whole electrode materials. The composites exhibited a high specific capacity of 115 mAh g⁻¹ at discharge rate of 5 C. However, generally the polymers are difficult to be dissolved and dispersed, which will lead to inhomogeneity in the process of carbon coating. In order to solve these problems, Wang et al. [35] prepared a LiFePO⁴/C composite by an in situ polymerization restriction method, formed from a highly crystalline LiFePO⁴ core with a size of about 20-40 nm and a uniform semi-graphitic carbon shell with a thickness of about 1-2 nm (Fig. 2). Aniline was polymerized in situ on the outer surface of the newly generated FePO⁴ precipitate to form a green polyaniline shell that can effectively restrict the growth of the FePO⁴ particles. The unique structure combined with its full coating of conductive carbon, effectively enhanced the electrochemical performance of LiFePO⁴. The as-prepared LiFePO⁴/C composite delivered a capacity of 90 mAh g⁻¹ at the rate of about 60 C.

In addition to using polymer, various sugar and organic carboxylic acids are also adopted as the carbon precursor. A LiFePO⁴/C composite synthesized by adding sugar before the heating steps was reported by Dahn et al. [36]. The particles of LiFePO⁴/C were of uniform size and well coated by carbon. These characteristics apparently assured LiFePO⁴/C of a good rate capability. The capacity of LiFePO⁴/C showed 125 mAh g⁻¹ even at 5 C discharge rate. Zhang et al. [37] reported a LiFePO⁴/C composite cathode synthesized via a mechanochemical activation/sintering process by adopting citric acid as the carbon source. The formation of carbon consisted of two processes i.e. pyrolysis of carbon precursor to CH₂ and subsequent formation of carbon. Compared with different carbon contents, the cathode with 6.0 wt% citric acid showed the highest initial rate discharge capacities of 92 mAh g⁻¹ at 20 C. Manthiram et al. [38] synthesized highly crystalline LiFePO⁴ nanorods via a rapid microwave-assisted solvothermal approach employing tetraethyleneglycol as the solvent. Then they adopted an ex situ coating of carbon by heating the nanostructured LiFePO⁴ with sucrose in 2% H₂-98% Ar at 700°C for 1 h. The as-prepared LiFePO⁴/C possessed excellent rate capability of 110 mAh g⁻¹ at discharge rate of 10 C, which could be attributed to the formation of highly crystallized sp² carbon. Manthiram’s group also presented a one-pot microwave-assisted hydrothermal method to synthesize carbon-coated LiFePO⁴ with a more uniform particle size (220-225 nm). The carbon coating was uniform and found to be 5-12 nm in thickness, which uniformly cover the surface of LiFePO⁴ (Fig. 3). The composite exhibited high capacity with excellent cyclability and rate capability, which reached at 110 mAh g⁻¹ at discharge rate of 10 C [39].

Other carbon sources are also studied. Sides et al. [40] reported a new type of template-prepared nanostructured LiFePO⁴ electrode. This electrode consisted of uniformly dispersed nanofibers of the LiFePO⁴ electrode material mixed in an electronically conductive carbon matrix. Because of this unique nanocomposite morphology, these electrodes delivered high capacity of 150 mAh g⁻¹ at a rate of 5 C. Meanwhile, even at rates exceeding 50 C, these electrodes still maintained a substantial fraction of the theoretical capacity. Due to the conductive carbon matrix, this new nanocomposite electrode solved the problem of the inherently poor
intrinsic electronic conductivity of LiFePO₄.

Fig. 3 TEM image of LiMPO₄/C nanocomposites obtained by the MW-HT process after heat-treatment at 700°C for 1 h: (a) TEM image of LiFePO₄/C, (b) HRTEM image of LiFePO₄/C [39].

So far, the application of carbon coating on the LiFePO₄ particle surface by various strategies is the most effective way to increase the conductivity of LiFePO₄. However, some authors find that carbon coating still have some disadvantages, including reduced tap density and high production costs, which may cause low energy density and high energy cost of the battery [41]. Meanwhile, the high rate capacity and cycling stability of LiFePO₄/C materials are still dissatisfactory [42].

**Doping**

Carbon coating is an efficient way to enhance the conductivity between particles [33, 36, 43]. However, this method obviously has little effect on the chemical diffusion coefficient or lattice electronic conductivity of lithium within the LiFePO₄ crystal [44]. The doping of heterogeneous ions, at either cation (Li⁺ and Fe²⁺) or anion (O²⁻) sites of LiFePO₄, can greatly improve the intrinsic electronic conductivity of materials in terms of capacity delivery, cycle life, and rate capability [45-48].

**Li site doping**

Many studies have demonstrated that Li-site doping can cause LiFePO₄ lattice defects, which is conducive to the proliferation of Li-ion [9]. The Li-site doping with supervalent cations was inspired by Chung et al. [10]. They prepared Li₁₋ₓMₓFePO₄ samples by the solid-state reaction, with the dopant (M = Mg²⁺, Al³⁺, Ti⁴⁺, Zr⁴⁺, Nb⁵⁺ or W⁶⁺) being added as a metal alkoxide. It suggested that, using supervalent cations to replace the Li-site, lead to the co-existence of Fe²⁺/Fe³⁺ mixed valent phases. LiFePO₄ was charged and discharged in structure between p-type phase and n-type phase according to the variation of Fe²⁺/Fe³⁺ proportion. Li₀.90M₀.01FePO₄ showed electrical conductivity at room temperature that was a factor of ~10⁸ greater than undoped LiFePO₄, and absolute values >10⁻³ S cm⁻¹ over the temperature range of -20°C to +150°C, which was shown in Fig. 4. As shown in Fig. 4, the doped electrode materials exhibited well rate performance, with discharge capacities over 60 mAh g⁻¹ at 21.5 C rate.

However, the mechanism and effect of supervalent cation doping on electronic conductivity reported so far are still in controversy. Herle et al. [49] examined the LiₓZr₀.₀₁FePO₄ (x = 0.87 to 0.99) and found that percolating “nano-networks” of metal-rich phosphides within the grain boundaries of LiFePO₄ crystallites were responsible for the enhanced electronic conductivity. Delacourt et al. [50] were unsuccessful in Nb doping of LiFePO₄, instead, they formed crystalline β-NbOPO₄ and/or an amorphous (Nb, Fe, C, O, P) “cobweb” around LiFePO₄ particles, which was responsible for superior electrochemical activity. The electronic conductivity of pure LiFePO₄ and LiFePO₄/β-NbOPO₄ composites is ~10⁻⁸ S cm⁻¹ while that of Nb- and/or C-containing LiFePO₄ composites increase up to 1.6×10⁻¹ S cm⁻¹. The first principle calculations by Ouyang et al. [51] showed that Li diffusion in olivine LiFePO₄ was one dimensional, thus even though the
Li-site doping could enhance the electronic conductivity, it did not improve the electrochemical performance for LiFePO₄ as cathode material. As the high valence heavy metal ions in the Li sites will block the one-dimensional diffusion pathways, the ionic conductivity is decreased, which is certainly harmful to the battery performance. An atomic-scale simulation by Islam et al. [16] suggested that, low favorable energies were found only for divalent dopants (e.g., Al, Ga, Zr, Ti, Nb, Ta) on either Li or Fe sites. As Mg and Mn), and on energetic grounds, LiFePO₄ was not tolerant to aliovalent doping (e.g., Al, Ga, Zr, Ti, Nb, Ta) on either Li or Fe sites.

Fe site doping

Similar to Li-site doping, Fe-site doping can also improve the electrochemical performance of LiFePO₄ by causing lattice defects [52, 53]. Wang et al. [54] reported Fe-site doped LiFe₀.9M₀.1PO₄ (M = Ni, Co, Mg) cathode materials with good rate performance and cyclic stability by solid-state reactions. The capacities of LiFe₀.9M₀.1PO₄ (M = Ni, Co, Mg) maintained at 81.7, 90.4 and 88.7 mAh g⁻¹ under 10 C rate, respectively, in comparison with 53.7 mAh g⁻¹ and 54.8 mAh g⁻¹ for non-doped and carbon-coated LiFePO₄, respectively. Such a significant improvement in electrochemical performance should be partially related to the enhanced electronic conductivities (from 2.2 × 10⁻⁹ to < 2.5 × 10⁻⁷ S cm⁻¹) and Li⁺ ions mobility in the doped samples. The Cr-doped LiFePO₄/C was synthesized by a mechanochemical process with the employment of planetary ball milling followed by a one-step heat treatment [55]. The LiFe₀.97Cr₀.03PO₄/C showed excellent rate performance, delivering a discharge capacity up to 120 mAh g⁻¹ at 10 C. The synchrotron-based in situ X-ray diffraction (XRD) analysis indicated that Cr doping facilitated the phase transformation between triphylite and heterosite during cycling and thus improved the rate performances of LiFePO₄/C. Sun et al. [56] reported V-doped LiFePO₄/C cathode materials using a carbothermal reduction route. The V-doped LiFePO₄/C showed a high discharge capacity of ~70 mAh g⁻¹ at the rate of 20 C. This was attributed to the optimization of the morphology and the crystal microstructure by V-doping, which facilitates the Li⁺ ion diffusion.

O site doping

Besides cation doping, anion doping is also expected as an effective way to enhance the electronic conductivity of LiFePO₄. Some researches select Cl⁻ and F⁻ as the substitution for O²⁻ anion [57]. Lu et al. [58] reported the F-doped LiFePO₄/C cathode materials were synthesized via a carbothermal reduction route by Sun et al. [59]. The Cl-doped LiFePO₄/C cathode materials presented a high discharge capacity of ~90 mAh g⁻¹ at the rate of 20 C. The results indicated that the optimized electrochemical reaction and Li⁺ diffusion in the bulk of LiFePO₄ due to Cl-doping. The improved Li⁺ diffusion capability was attributed to the microstructure modification of LiFePO₄ via Cl-doping.
Preparation of nanosized materials

Carbon coating and elements doping are efficient ways to increase the electronic conductivity of LiFePO$_4$ electrode materials [60-62]. However, both carbon coating and doping do not solve the problem of the low intrinsic ionic conductivity of LiFePO$_4$ which could be addressed by downsizing the particles. Obviously, decreasing the particle size, which leads to a decrease in solid state transport length and increase in surface reactivity, has been the main method to solve above problem [17]. In addition, Lee et al. [63] studied the lithiation/delithiation mechanism for the general case of nanoparticles with a heterogeneous particle size distribution (Fig. 6). They proved that ionic transport occurs between nano and bulk particles in a cell at equilibrium, due to their electrochemical potential difference that originates from their different thermodynamic properties and surface energies. Based on the careful analysis of the results reported by different research groups, Gaberscek et al. [64] showed the relationship between the average particle size and the electrochemical performance of LiFePO$_4$-based electrodes. They pointed out that the electrical resistance of electrode materials depended solely on the mean particle size, as shown in the Fig. 7(a). Meanwhile, the discharge capacity of LiFePO$_4$-based electrodes dropped approximately linearly with average particle size, regardless of the presence/absence of a native carbon coating, which was shown in Fig. 7(b).

Fig. 6 The relationship between thermodynamics and particle size: (a) Nano-LiFePO$_4$; (b) Bulk-LiFePO$_4$ [63].

Fig. 7 The relationship between average particle diameter and electrode resistance per unit mass (a); discharge capacity (b) [64].

Delacourt et al. [65] prepared carbon-free LiFePO$_4$ crystalline powders by a direct precipitation method. The particle size distribution is very narrow, centered on about 140 nm. A soft thermal treatment, typically at 500°C for 3 h under slight reducing conditions (N$_2$/H$_2$ gas flow) was shown to be necessary to obtain satisfactory electrochemical Li$^+$ deinsertion/insertion properties. This thermal treatment does not lead to grain growth or sintering of the particles, and does not alter the surface of the particles. The powders exhibited excellent electrochemical performances of about 147 mAh g$^{-1}$ at a rate of 5 C. Gibot et al. [66] reported a single phase carbon-free LiFePO$_4$ nanoparticles by a low-temperature precipitation process. They reported the feasibility to drive the well-established two-phase room-temperature insertion process in LiFePO$_4$ electrodes into a single-phase one by modifying the material’s particle size and ion ordering. Electrodes made of LiFePO$_4$ nanoparticles (40 nm) exhibited excellent rate capability even at 10 C, with over 89%...
capacity retention of the initial capacity. The rate capability of the hollow cathode was higher than that of the nanowire cathode due to its higher surface area.

Of course, we recognized that the morphology and crystal orientation of LiFePO$_4$ related to the ionic kinetics is also significantly affecting its electrochemical performance in the nanosized electrode materials [68, 69]. Wang’s group [70] synthesized 3D hierarchical LiFePO$_4$ particles networked with electronically conducting multi-walled carbon nanotubes (MWCNT) including particle-like nanoparticles, shuttle-like nanoparticles and disk-like nanoparticles by a hydrothermal approach. The particle morphology, crystal orientation, and electrochemical reactivity of the prepared LiFePO$_4$/MWCNT particles could be tailored by varying the P source. Among the as-prepared

![Fig. 8 (a-b) SEM image and HRTEM image combined with the Fourier transform of the selected area showing the orientation of the crystallite of the 40 nm nanosized LiFePO$_4$; (c) Charge/discharge galvanostatic curves at 0.1 C and 1 C for a Li/carbon-free 40 nm LiFePO$_4$ cell cycled between 2.5 and 4 V, together with its capacity retention over 60 cycles [66].](image)

![Fig. 9 Electron microscopy images of the hollow sphere secondary structure of nanoparticles [72].](image)
LiFePO$_4$ materials, the disk-like crystal showed the most excellent performance, with the capacity reaching 121.5 mAh g$^{-1}$ at 30 C. Saravanan et al. [71] reported LiFePO$_4$ nanoplates with a uniform amorphous carbon coating of 5 nm surface by the solvothermal method. The thickness of the nanoplates along the b-axis was found to be 30-40 nm. The LiFePO$_4$/C nanoplates delivered the initial discharge capacity of about 165 mAh g$^{-1}$ at 0.1 C and about 50 mAh g$^{-1}$ at 30 C. Lee et al. reported on the evolution of a hollow sphere secondary structure of spherical nanoparticles by a solubilization-reprecipitation mechanism based on the difference of solubility products ($K_{sp}$) of two different precipitates [72]. Carbon-coated nanoparticles of olivine structure LiFePO$_4$ served as the primary nano-blocks to build the secondary nano-architecture (Fig. 9). The size of the secondary particles was about 300 nm, which was developed in a shape of hollow sphere with its shell consisting of the primary particles (about 25 nm). The carbon layer wrapping primary particles was clearly shown with the thickness of 3 to 5 nm. By controlling the morphology of the electrode materials, the hollow LiFePO$_4$ spheres showed good rate performances. The high rates charging were achieved 133 mAh g$^{-1}$ at 10 C and 100 mAh g$^{-1}$ at 50 C.

Decreasing the particle size to increase the electrode-electrolyte interface is the most effective method to enhance electrochemical performances of LiFePO$_4$, particularly at high rate charge-discharge. Unfortunately, because of the surface lattice relaxation and self-aggregation, nano-sized LiFePO$_4$ usually exhibit low capacitance retention and low tap density or volumetric energy density. Meanwhile, there are also some problems existed in large-scale production, separation and admixing with carbon black [9].

Preparation of porous materials

In order to introduce fast ionic permeation and high electronic conductivity into the Li-ion battery materials, new concepts of electrode structuring are needed [73]. Recently, the porous LiFePO$_4$ material has attracted comprehensive researches. In a porous material, the pore-to-pore distance determines the solid-state diffusion of Li$^{+}$. Apparently, this distance has a similar value as the average diameter of nano-particles in particular materials [74]. While, porous LiFePO$_4$ particles provide good contact with electrolyte and, in principle, are easier to bind than isolated nano-sized LiFePO$_4$ particles [75]. Meanwhile, such porous structure is more useful if the pores are decorated with an electronic conductor, especially with a thin carbon film [76]. Solid electron-conducting carbon will be homogeneously distributed within the final composite materials [77].

Dominko et al. [78] prepared microsized porous LiFePO$_4$/C particles by sol-gel techniques, using Fe(III) citrate as a precursor. The particles internal porosity in the range of 4-200 nm was controlled by appropriate selection of several synthesis parameters. Within this sol-gel technique the increase in heating rate lead to a more interlaced pore system, a smaller mesoporous volume, and a larger number of surface apertures, although the micropore volume did not change significantly. These features resulted in a better electrochemical rate performance of 120 mAh g$^{-1}$ at 5 C rate. Doherty et al. [79] used a novel method to prepare nanostructured hierarchically porous LiFePO$_4$ electrode materials. A meso/macroporous carbon monolith with bimodal porosity was nanocasted from a hard silica template, which was used to provide a conductive framework for LiFePO$_4$ and increase the electrode/electrolyte interface. The surface area of the sample detected by Brunauer-Emmet-Teller (BET) was 200 m$^2$ g$^{-1}$ with a pore volume of 0.3 cm$^3$ g$^{-1}$. This type of structure was potentially ideal as electrode materials to improve the rate capability of the batteries. The as-prepared sample displayed a capacity of 100 mAh g$^{-1}$ at discharge rate of 5 C. Drummond et al. [80] reported a hierarchically porous LiFePO$_4$ electrode materials via a colloidal crystal templates technique. Beads of polymethylmethacrylate (PMMA) were synthesized with diameters of 100, 140, and 270 nm and used to form colloidal crystal templates to produce LiFePO$_4$, which featured pores spanning from 10 to 100 nm (Fig. 10). The materials with the largest pores, around 100 nm diameters, presented the highest discharge capacities of 160 mAh g$^{-1}$ at 0.1 C and 115 mAh g$^{-1}$ at 5 C. Sinha et al. [81] achieved a mesoporous LiFePO$_4$/C composite with dual porosity by a solution-based polymer templating technique. Pluronic acid was used as the templating agent in the presence of a cosurfactant in an emulsion medium. The LiFePO$_4$/C composite prepared at 700°C contains dual porosity with pore-size distributions spread around 4 and 50 nm, which exhibited a high rate capability and stable capacity retention upon cycling. It delivered 60 mAh g$^{-1}$ reversible capacities even at a current rate of 14.7 C.

Template-free techniques have also been developed to prepare porous LiFePO$_4$ cathode materials. Yu et al. [82] prepared porous micro-spherical aggregates of LiFePO$_4$/C nanocomposites via a sol-gel-spray drying method without employing any surfactants or templates. The as-obtained LiFePO$_4$ porous microspheres had an average pore size of 45 nm and gave large specific surface area (20.2 m$^2$ g$^{-1}$). The particles could be easy to bring into contact with electrolyte, facilitate the electron and lithium ion diffusion. The as-obtained sample delivered a large reversible discharge capacity of 138 mAh g$^{-1}$ at 0.1 C and a good rate capacity of 54 mAh g$^{-1}$ at 10 C (Fig. 11). Qian et al. [83] suggested
that the ideal structure of LiFePO₄ with both high volumetric energy density and high rate capability should be a microsphere composed of nanocrystallites tightly compacted to form three-dimensional electronic and ionic channels. They prepared nanoembossed mesoporous LiFePO₄ microspheres by a template-free hydrothermal process. The microspheres showed a uniform size distribution of ~3 µm and were composed of many densely aggregated ~100 nm nanoparticles and interconnected nanochannels. This mesoporous structure allowed better irrigation of electrolyte, and therefore provided a huge electrochemically available surface for enhancing the rate capability of the lithium insertion/deinsertion reaction. The discharge capability of LiFePO₄ microspheres reached 115 mAh g⁻¹ at a high rate of 10 C. Recently, we adopted the supercritical carbon dioxide (scCO₂) to modify the size and morphology of hydrothermally synthesized LiFePO₄ [84]. After the scCO₂ treatment, aggregation was largely reduced, different morphologies were obtained and impurities were almost removed. The effects of the formation of porous LiFePO₄ had also been found after the scCO₂ treatment. Meanwhile, a possible crystal dissolution formation mechanism was proposed from theoretical models [85]. The electrochemical performance of porous LiFePO₄ had been significantly improved. At the

![Fig. 10](image1.png)

(a) TEM image of 140 nm bead-templated LiFePO₄ calcined at 320°C and (b) calcined at 600°C. (c) SEM image of 270 nm bead-templated LiFePO₄ calcined at 700°C [80].

![Fig. 11](image2.png)

(a) Description of process from slurry droplet to porous micro-spherical aggregates of LiFePO₄/C nanocomposites during spray drying and subsequently carbothermal reaction; (b) the cyclic stability of the as-obtained product LFP with various discharge current rates [82].
discharge rate of 5 C, the discharge capacity was 105 mAh g\(^{-1}\) [86].

The porous structure could be depicted as an inverse picture of nanoparticles arrangement, where pores serve as paths for Li-ion supply and the distance between the pores determines the materials kinetics [87]. The porous structure is also the critical factor for affecting high power capability of LiFePO\(_4\), so optimization of the porous structure by controlling synthesis methods and technological conditions is the key step to improve electrochemical properties of LiFePO\(_4\) at high rates [88].

**Preparation of composites**

As a kind of carbon materials, graphene has attracted attention in increasing the electrochemical performance of LiFePO\(_4\) because of its large specific surface area (theoretical value of 2630 m\(^2\) g\(^{-1}\)), flexible structure, superior chemical/thermal stability, and most importantly excellent electric conductivity [89-94]. With the help of graphene, the electrons could be transferred easily between the LiFePO\(_4\) particles and current collectors, reducing the internal resistance and enhancing the power density of the batteries [95, 96].

Zhou et al. [97] described a graphene-modified LiFePO\(_4\) composite for a Li-ion battery cathode material. The composite was prepared with LiFePO\(_4\) nanoparticles and the relatively simple availability of graphene oxide nanosheets using spray-drying and annealing processes. The LiFePO\(_4\) primary nanoparticles embedded in micro-sized spherical secondary particles with diameters of 2-5 µm were wrapped homogeneously and loosely with a graphene 3D network. The carbon film had a thickness of about 2 nm and consisted of 3-5 layers of graphene, which was shown in Fig. 12. Such structure supported the maximum fulfillment of graphene’s functionality, because electrons were easily transferred between the surface of LiFePO\(_4\) nanocrystals and graphene, and moved unobstructed over the nanoparticles to attain a high rate capability. The composite delivered a capacity of 70 mAh g\(^{-1}\) at 60 C discharge rate and showed a capacity decay rate of < 15% when cycled under 10 C charging and 20 C discharging for 1000 times. Su et al. [98] reported a novel LiFePO\(_4\)/graphene/carbon composite by an in situ solvothermal method to synthesize LiFePO\(_4\)/graphene powders as precursors and then followed by a carbon-coating process. The ethanol adopted in the experiment acted as a reducing agent, which was used to avoid the formation of undesirable ferric impurities in the solvothermal [99]. The results indicated that the co-modification of LiFePO\(_4\) with graphene and carbon coating could construct an effective conducting network, which significantly enhanced the electrochemical activity of LiFePO\(_4\)/carbon based composite. The composite with a low content of graphene exhibited a high initial discharge capacity of 163.7 mAh g\(^{-1}\) at 0.1 C and 114 mAh g\(^{-1}\) at 5 C, as well as an excellent cycling stability. Ha et al. [100] mixed chemically activated graphene (CA-graphene) with LiFePO\(_4\) to prepare the composite for lithium ion batteries. CA-graphene in the composite provided abundant porous channels for the diffusion of lithium ions. Moreover, it acted as a conducting network for easy charge transfer and as a divider, preventing the aggregation of LiFePO\(_4\) particles. The CA-graphene/LiFePO\(_4\) composite exhibited remarkably better rate capability and stable cycling

![Fig. 12 (a-f) SEM and TEM images of the LFP/G particles; (g) Comparison of rate capability of LFP/G, LFP/C, and LFP/(G + C) [97].](image-url)
performance compared to the conventional graphene/LiFePO$_4$ composite and bare LiFePO$_4$. The as-obtained sample delivered 73 mAh g$^{-1}$ of discharge capacity at 25 C. Shi and co-workers [101] described an advanced microwave-assisted hydrothermal route for preparation of a highly ordered LiFePO$_4$/C/graphene nano-composite. LiFePO$_4$/C nanoparticles were embedded in the conductive and interconnected graphene networks, and exhibited a discharge capacity of 88 mAh g$^{-1}$ at 10 C.

On the other hand, in order to improve the lithium ion diffusion of the electrode materials, the modified graphene with 3D conducting matrix are developed to grow and anchor on the insulating LiFePO$_4$ materials [102, 103]. Sun et al. [104] successfully prepared a three-dimensional porous self-assembled LiFePO$_4$/graphene (LFP/G) composite using a facile template-free sol-gel approach. Graphene nanosheets were dispersed into the porous hierarchical network homogeneously, which greatly enhanced the efficient use of the active materials, leading to an outstanding electrochemical performance of the hybrid cathodes. The LFP/G composite had a reversible capacity of 65 mAh g$^{-1}$ at 5 C rate. One year later, Sun’s group [105] reported that the unfolded graphene was used as a three dimensional (3D) conducting network for LiFePO$_4$ nano-particle growth (Fig. 13). The use of unfolded graphene improved the dispersion of LiFePO$_4$ and restricted the LiFePO$_4$ particle size at the nanoscale. Meanwhile, it enabled both Li-ion and electrons to migrate and sufficiently utilized the LiFePO$_4$ active materials. This facile designed composite showed both high specific capacity and rate performances. The discharge capacity of the nanocomposite remained stable at relatively high rate (75 mAh g$^{-1}$ at 10 C and 60 mAh g$^{-1}$ at 15 C, respectively).

Carbon nanotubes, with high electrical conductivity, large surface area and high aspect ratio, are also considered as the promising materials to form high electrical conductivity and enhance the ion transport for LiFePO$_4$ [106, 107]. Sun and his colleagues [108] synthesized 3D nitrogen-doped CNTs modified porous LiFePO$_4$ by a sol-gel method without templates or surfactants. Nitrogen doped CNTs possessed many active defects and hydrophilic properties, which brought to intimate contact with active materials. Meanwhile, in nitrogen doped CNTs, nitrogen atom provided electron carriers for the conduction band, which further.
improved the electronic conductivity [109-111]. The as-prepared LiFePO$_4$/nitrogen-doped CNTs exhibited excellent rate performance of 80 mAh g$^{-1}$ at the rate of 5 C. Toprakci et al. [112] reported that the LiFePO$_4$/CNT/C composite nanofibers were synthesized via a combination of electrospinning and sol-gel methods, where polyacrylonitrile (PAN) was used as the electrospinning media and carbon source. Electrospinning was an effective way to minimize the aggregation of LiFePO$_4$ particles and promote the formation of a conducting carbonaceous layer. CNTs were found to be well-dispersed in the carbonaceous matrix and increased the electrochemical performance of the composite nanofibers. The average reversible capacities of the above composites were obtained as 134 mAh g$^{-1}$ and 121 mAh g$^{-1}$ at 1 C and 2 C, respectively. Zhou et al. [113] prepared the highly-conductive 3D nanotube networks combined with interlaced porous LiFePO$_4$ electrodes by an in situ sol-gel technique. This design developed the manifold benefits of CNTs to create a highly-conductive 3D network united with the porous LiFePO$_4$. At high rate of 6 C, the composite material retained a capacity of 110 mAh g$^{-1}$.

From the above papers we can see that the composites electrode materials are believed to be one of the most promising cathode materials for lithium ion batteries.

Others

During the synthesis process of LiFePO$_4$ material, some conductive impurities and amorphous phases may be produced [114]. These metal impurities play an important role in increasing electronic conductivity and evidently improving the electrochemical performance. Xu et al. [115] prepared LiFePO$_4$/C materials by a reformatory solid-coordination method. Fe$_2$P phase arised as an impure phase among the LiFePO$_4$/C materials when they were prepared at relatively high annealing temperature of 725°C. The discharge capacity of the above sample was 10% higher than the pristine LiFePO$_4$. Kang and Ceder [116] created a fast ion-conducting surface phase of Li$_2$P$_2$O$_7$ through controlled off-stoichiometry. The as-prepared LiFePO$_4$ exhibited excellent rate performance of 136 mAh g$^{-1}$ and 60 mAh g$^{-1}$ at 50 C and 400 C, respectively. However, Goodenough et al. doubted that the announced battery was impossible to reach high recharging rate capability for a Li-ion battery of 9 s, although the authors responded to the unsupported claims of ultrafast charging of Li-ion batteries [117, 118]. This debate is not yet clear.

Conclusions

The olivine LiFePO$_4$ has been considered as the most promising cathode materials for EVs and PHEVs applications due to its inherent merits including low toxicity, low material cost, flat voltage profile, long cycle ability and high safety compared to other cathode materials. However, LiFePO$_4$ has severe disadvantages of low intrinsic electronic conductivity of LiFePO$_4$ and small diffusion coefficient of lithium ion, which are the main demerits that make it difficult to be applied in high-rate battery. In this paper, we have reviewed some of the recent progress and advances in improving the rate performance of LiFePO$_4$ from peer-reviewed journal publications. Carbon coating on the LiFePO$_4$ particle surface is one of the most important techniques used to improve its electronic conductivity between particles. Doping with cations and anions can greatly improves the intrinsic electronic conductivity of materials, although the mechanism and effect of doping on electronic conductivity reported are still in controversy. Both carbon coating and doping do not solve the problem of the low intrinsic ionic conductivity of LiFePO$_4$, which could be addressed by downsizing the particles. In order to introduce fast ionic permeation and high electronic conductivity into the Li-ion battery materials, porous structure and the composites electrode materials are depicted to improve the high rate electrochemical properties of LiFePO$_4$. With regard to the large-scale industrial production, a reliable, low-cost, highly effective synthetic method for preparing LiFePO$_4$ cathode materials with high rate performance is still highly desirable. With comprehensive research, we believe that LiFePO$_4$ will be widely used for the Li-ion battery and practical application of EVs.

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Magneto-Impedance Effect of Composite Wires Prepared by Chemical Plating under DC Current

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Abstract: CuBe composite wires of 100 µm in diameter coated with a layer of NiCoP were prepared by a chemical plating method under DC current (CPUDC). The influences of DC current on coating morphology, deposition rate, composition, giant magneto-impedance (GMI) effect and magnetic properties were investigated. It was shown that the circumferential domain structure of coating layer was induced by the DC current going through the wires. A maximum GMI ratio of 870% was obtained in the composite wire prepared under 150 mA and tested at 180 kHz. It is 30 times higher than that of the composite wire plated in the same condition by conventional chemical plating method, indicating that CPUDC is an easy and effective approach to obtain composite wires and its applications will be further extended on magnetic sensors.

Keywords: GMI; Chemical plating; Magnetic properties

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Introduction

Recently, giant magneto-impedence (GMI) effect has been intensively studied for its potential applications in highly sensitive magnetic sensors with high spatial/temporal resolution since it was firstly observed in Co-based amorphous wires in 1992 [1,2]. Experimental and theoretical results confirmed that the origin of the GMI is classical skin effect [4-6]. Although the studies on GMI effect was initially focused in homogeneous materials [1-3], great attention has been paid to the heterogeneous materials such as composite wires and sandwiched films [7,8], since it has great advantages over the homogeneous materials such as [9]: (1) the GMI effect was enhanced obviously, which results from the enhanced skin effect of the coating layer caused by electromagnetic interactions between the conductive and ferromagnetic layers; (2) the MI effect can be observed at much lower frequencies; and (3) realization of miniaturization and practicability for sensors.

Commonly, the composite wires were fabricated by magnetron sputtering [11], electroplating [12-16], chemical plating [17], or MEMS technique [18]. However, the GMI sensitivity of the composite wires is not high since their magnetic structure cannot be well controlled by these methods. It was found that GMI sensitivity could be increased through subsequent processes such as tensile stress annealing treatment [19, 20] and Joule annealing treatment [21].

In this paper, a new technique based on chemical plating was proposed and NiCoP/CuBe composite wires were fabricated. DC current was applied on the wire during the plating process. The influence of pH value of the plating bath and the current magnitude on GMI effect and magnetic structure of the wires were analyzed.

Experimental details

All chemicals used in this work were purchased from
The composite wires were prepared by chemical plating under DC current (CPUDC) along a CuBe wire in diameter of 100 μm. Firstly, the wire was rinsed in hydrochloric acid (6 mol/L HCl) for 5 min, followed by sensitization in sensitizing solution (0.11 mol/L SnCl₂·2H₂O, 0.48 mol/L HCl) for 5 ~ 10 min and activation in activate fluid (2.8 × 10⁻⁴ mol/L PdCl₂, 0.48 mol/L HCl) for 10 min. The plating solution consists of NiSO₄·6H₂O (0.025 mol/L), CoSO₄·7H₂O (0.035 mol/L), Na₃C₆H₅O₇·2H₂O (0.10 mol/L), C₄H₆O₆Na₂·2H₂O (0.15 mol/L), (NH₄)₂SO₄ (0.50 mol/L), NaH₂PO₂·H₂O (0.30 mol/L) and different contents of NaOH. After fully mixing the plating solution, the chemical plating process was carried out by the conventional method and CPUDC method, respectively. The temperature of the plating bath was kept at 363 ± 1 K and the pH value was adjusted in the range of 8.0 ~ 8.8 by adding NaOH dropwise, while the DC current varied from 0 mA to 250 mA.

The morphology and thicknesses of the core and the plated layer under each DC current were determined by the conventional method and CPUDC method, respectively. The maximum applied magnetic field was 100 Oe. During the measurements, the applied external magnetic field was generated by a pair of Helmholtz coils and the maximum value of external magnetic field was 100 Oe. During the measurements, the composite wires were subjected along the longitudinal direction and vertical to geomagnetic field.

The GMI ratio was defined as

$$\Delta Z/Z = \left( \frac{Z(H_{ex}) - Z(H_0)}{Z(H_0)} \right) \times 100\%$$ (1)

where $Z(H_{ex})$ and $Z(H_0)$ are the sample impedance values under a magnetic field of $H_{ex}$ and 0 Oe, respectively. The maximum applied magnetic field was 100 Oe.

Results and discussion

Figure 1 shows the GMI effect curves tested at 400 kHz for the composite wires prepared by conventional chemical plating under different pH values. Initially, the MI ratio increases with $H_{ex}$ to a maximum value, and then decreases with further increase of the field. It means that the easy axis of the coating layer is orientated in circumferential direction [3]. However, the field sensitivity defined as $d(\Delta Z/Z)/dH_{ex}$ is not high, which means that the moment direction deviates from the circumferential direction. When the pH value was increased from 8.0 to 8.8, the maximum MI ratio increases from 8.9% to 24.3%, and then decreased to 17.0%. The pH value of the bath may change the composition and magnetic properties of the coating layer. It is evident that the highest MI ratio was obtained when pH value is 8.4. The optimal pH value is much higher than that of electroplating method [13-16,22]. The pH value was kept at 8.4 in the following CPUDC method.

Figure 2(a) shows the surface morphology of CuBe wire before deposition. The surface is smooth and uniform. Figure 2 shows the surface morphology of composite wires prepared by conventional chemical plating (Fig. 2(b)) and under DC current of 50 mA (Fig. 2(c)) or 250 mA (Fig. 2(d)). It can be seen that the surface of deposited layer is less smooth and uniform. Evidently, there are tiny holes on the surface of deposited layer because of oxidation-reduction reaction. The number of holes increases with the magnitude of the DC current, giving rise to higher roughness at larger current.

Figure 3 shows the relationship of the deposition rate versus the DC current. It can be seen that the deposition rate increases monotonously with the DC current. The essence of chemical deposition process is oxidation-reduction reaction, associated with the reaction accompanied by electron transfer at the surface of the substrate. With a magnetic field induced by the DC current, the solution near substrate was slightly agitated and the motion of free ions was accelerated because of the microstructure magneto hydrodynamics effect (MHD effect) [22]. Hence, the reaction rate increased by the acceleration of ion motion. This behavior reveals that the deposition rate increases with...
the augmentation of the induced magnetic field. Nevertheless, the increased DC current induces higher roughness of the surface during oxidation-reduction reaction, which impedes further augmentation of the deposition rate. Consequently, the magnetic field induced by proper DC current, 100 mA in this work, enhanced the deposition rate significantly due to these two effects.

The composition of the coating layers plated under different DC current was measured by EDX. The current has slight influence on the composition of wires, shown in Fig. 4. Apparently, the variations of the Co, Ni and P percentage in the layers plated under the DC current ranging from 50 mA to 250 mA are all small. The average composition of the coating is Ni_{27}Co_{55}P_{14}.

Figure 5 shows the MI ratio curves tested at 400 kHz for the composite wires plated under different current. It is shown that the MI ratio of the composite wires increases initially and then decreases with the current. A remarkable enhancement of MI ratio occurs at 150 mA. Besides, the field sensitivity of MI curves for the samples with DC current are obviously increased relative to the sample fabricated without current. It reveals that the magnetic domain in these samples are circumferential orientated. Thus, circumferential domain structure in coating layer can be induced by CPUDC method, and the GMI ratio of composite wires prepared using this method improves significantly.
Fig. 5 Field dependence of the GMI ratio of the composite wires prepared by CPUDC method under different DC current.

It is obvious that the maximum GMI ratio increases firstly and then decreases with the increasing of DC current. A maximum GMI ratio of 868% was obtained for the sample deposited under 150 mA. Though the result is a little lower than the ratio of 1100% in electroplated NiFe/Cu composite wire after Joule annealing, CPUDC is one step method [23]. When the DC current is smaller, the induced circumferential structure may increase the GMI ratio. With further increase of the current, the coating roughness and thickness increased. The induced field decreases with the coating thickness layer according to the Ampere law. Consequently, the magnetic moments direction of the magnetic film may orientate from circumferential direction to longitudinal direction [24]. In addition, thicker coating layer results in smaller dynamic driving field, which leads to the weaker magnetization of the magnetic layer. Both the moment deviation and weaker magnetization can result in the significant decrease of the GMI ratio. As for the current of 150 mA, it is the optimal value to get largest GMI ratio.

In previous study [13,22], GMI effect can be enhanced by Joule annealing which induces circumferential magnetic domain. The corresponding annealing current ranges from several hundred milliamperes to several amperes. In this work, CPUDC method could induce circumferential magnetic domain structure during the process of sample preparation. Compared to Joule annealing, this method has simplified the experimental set-up. Meanwhile, the amplitude of the current is smaller.

Figure 6 shows GMI spectra of the samples deposited under different DC current. It can be seen that with frequency increasing, the GMI ratio first increases, undergo a peak, and finally drops down. Each sample has a maximum MI ratio at the critical frequency. With the increase of DC current form 50 mA to 150 mA, the critical frequency decreases from 1.44 MHz to 180 kHz. Further increase of the DC current leads to the increase of critical frequency up to 460 kHz. The critical frequency mainly depended on the softness and thickness of the coating layer [25]. The lowest critical frequency was obtained in the composite wire plated under 150 mA.

Fig. 6 Frequency dependence of the maximum GMI ratio under different DC current.

Figure 7 shows hysteresis loops of the composite wires mentioned above. It can be seen from the loops that the wire prepared by conventional chemical plating method has some circumferential magnetic structure. Whereas the sample prepared by CPUDC method shows that their coating layer has better circumferential magnetic structure when the current amplitude is below 150 mA. Apparently, for composite wire deposited under 150 mA, the coercivity and the energy loss are both smaller.

It is well known that the peak field value in MI curves is the effective anisotropy field of the ferromagnetic layer. Figure 8 shows the dependence of the maximum MI ratio and anisotropy fields acquired from Fig. 5 and 7. It can be seen that the \( H_k \) values have the same variation trend as DC current, though the numerical value itself is not completely identical. It can be also seen that the GMI ratio is not coincident with the \( H_k \) values. The sample plated under 150 mA has the maximum MI ratio. However its \( H_k \) value is not the smallest one. Hence, both of the \( H_k \) value and domain structure are important for GMI effect. This result agrees well with the above discussion from the MI curves.

**Conclusion**

In summary, we have prepared the NiCoP/CuBe composite wires by conventional chemical plating method and CPUDC method. It was found that pH value and DC current had significant effect on GMI effect. The optimal pH value by conventional chemical plating method is 8.4. The GMI ratio was much enhanced using CPUDC method, because of the induced
circumferential domain structure in the coating layer. It was found that GMI ratio reached 870% when the DC current is 150 mA. The established method with DC current is convenient and effective to enhance the MI ratio and could be used to prepare sensing element for magnetic sensors.

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Preparation of Palladium Supported on Ferric Oxide Nano-catalysts for Carbon Monoxide Oxidation in Low Temperature

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Abstract: Catalytic property of Pd/Fe₂O₃ catalysts on carbon monoxide (CO) oxidation at low temperature were investigated in this paper. Both the as-prepared and H₂-pretreated Pd/Fe₂O₃ catalysts show catalytic performances on CO oxidation. The CO was completely converted at 333 K for the as-prepared sample, whereas at 313 K for H₂-pretreated Pd/Fe₂O₃-573 catalyst. The catalytic performance of the Pd/Fe₂O₃ catalyst decreases with increased calcination temperature. This may be due to the increased crystallinity of the support and decreased metal-support interaction. Progressive deactivation of the catalysts during long-time reaction was associated with the formation of carbonates on the catalyst surface that inhibits CO activation or intermediate transformation.

Keywords: Pd/Fe₂O₃; Carbon monoxide; Catalytic oxidation; Low temperature

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Introduction

Carbon monoxide (CO) catalytic oxidation is considered as a very important reaction in environmental applications, for example, vehicle exhausts elimination in semi-closed spaces [1-3]. To date, this reaction was mostly studied on supported noble metal catalysts like Au, Pt and Pd due to their high activities at low temperatures [4-6]. However, high prices and deactivation drawbacks of these metal catalysts limit applications in many fields [5,7-9]. The deactivation was mainly originated from aggregation of active metal, coverage of carbonates and competitive adsorption between CO and moisture [10,11]. In contrast, much lower cost Pd catalyst showed comparable activity and long lifespan for CO oxidation at low temperatures [12-14]. It has a very potential possibility that Pd catalysts might replace Au catalysts for CO oxidation, especially when the catalysts needed to be prepared in large-scale and applied in engineering aspects.

Catalytic performance is found highly dependent on the catalyst preparation methods [15]. Co-precipitation is one of the simplest methods for preparation of homogeneous dispersed catalysts. Some results even showed single-atom dispersion that owning high intrinsic activity [16]. Pd nanoparticles can be synthesized by co-precipitation method with high dispersion, and exhibited excellent activity in CO oxidation [17]. Because of the unique redox behavior and coordinative unsaturated Fe sites, Fe₂O₃ was considered to be an effective support for catalyst preparation [18,19]. It was reported that noble metals/FeOₓ are promising catalysts for CO oxidation [20].

In this paper, Pd/Fe₂O₃ catalysts were prepared by co-precipitation method and their application in CO oxidation at low temperatures was investigated. The advantages of H₂-pretreated catalysts were analyzed, the reaction mechanism was discussed and the reason...
for deactivation was illustrated.

Experimental

PdCl₂ (AR) was available from Heraeus Materials Technology Shanghai Ltd., Fe(NO₃)₃·9H₂O (AR) and Na₂CO₃ (AR) from Sinopharm Chemical Reagent Co., Ltd. (SCRC).

The 2.0 wt% Pd/Fe₂O₃ catalysts were prepared by co-precipitation method. Typically, PdCl₂ and Fe(NO₃)₃ were firstly dissolved in 60 mL de-ionic water and stirred for 30 min. Then, the mixture was slowly dropped into Na₂CO₃ aqueous solution at 338 K under vigorous stirring. The pH of the solution was maintained 8~9. After aged for 2 h, the brown precipitate was filtered and washed by hot water for several times until the chloride ions were undetected by silver nitrate. The finally obtained slurry was dried at 373 K overnight and calcined for 4 h at 573, 673 and 773 K, respectively. The samples were noted as Pd/Fe₂O₃-T (T is the calcination temperature).

The Brunauer-Emmett-Teller (BET) specific surface area of the sample was measured by adsorption-desorption of nitrogen at 77 K using an ASAP 2020 instrument (Micromeritics). Before the measurement, the samples were degassed at 573 K for 3 h. The X-ray power diffraction (XRD) was carried out on a D/MAX-2600PC diffractometer (Rigaku) operated at 40 kV and 100 mA with Ni-filtered Cu Kα (0.15418 nm) radiation source. The patterns were collected from 10° to 70° (2θ) with a step width of 0.02°. Hydrogen temperature programmed reduction (H₂-TPR) was performed with an Auto Chem II chemisorption analyzer (Micromeritics) using a thermal conductive detector (TCD). The sample was pretreated by He (30 mL/min) at 573 K for 1 h to remove surface contaminants. After cooling to 273 K, 10% H₂/Ar (30 mL/min) mixture was introduced and the temperature was raised to 873 K at a rate of 10 K/min. The dispersion of Pd was measured by CO pulse chemisorption at 273 K. The transmission electron microscopy (TEM) images were obtained on a JEM-2100 (JEOL) instrument at an accelerating voltage of 200 kV.

The CO catalytic oxidation test was performed in a continuous-flow fixed-bed reactor (8 mm internal diameter) at atmospheric pressure. 0.5 g catalyst powder was loaded between two layers of quartz wool. Before the test, the as-prepared Pd/Fe₂O₃ catalysts were reduced by 10% H₂/N₂ (100 mL/min) at 353 K for 1 h. After the catalysts were cooled to 273 K under N₂ (90 mL/min), the feed gas containing 100 ppm CO balanced with compressed air was passed through the reactor at 1000 mL/min. The reaction temperature, measured with a thermocouple, was increased from 273 K to 333 K at intervals of 10 K. CO concentration was monitored by an online CO analyzer Model 48i (Thermal Scientific).

The CO conversion was calculated according to the following equation,

\[ X(\%) = \frac{(\text{CO}_{\text{inlet}} - \text{CO}_{\text{outlet}})}{\text{CO}_{\text{inlet}}} \times 100 \]

where X is the CO conversion, CO_{inlet} is the initial CO concentration in the inlet, and CO_{outlet} is the CO concentration in the outlet.

Results and discussion

Characterizations of the as-prepared catalysts

The ICP results of Pd content and BET surface areas of the as-prepared Pd/Fe₂O₃ catalysts are listed in Table 1. The Pd content was in the range of 1.82-1.89 wt%, closing to the theoretical value of 2.0 wt%. The BET specific surface area of the as-prepared Pd/Fe₂O₃-573 catalyst was 180 m²/g, whereas, it was decreased sharply to 79 and 35 m²/g for Pd/Fe₂O₃-673 and Pd/Fe₂O₃-773 catalyst, respectively. These results demonstrated that calcination at high temperature could dramatically decrease the BET specific surface of the as-prepared catalysts. This might be associated with that the number of support pores were decreased or the supports pores were blocked by the entry of some Pd species at higher temperatures [17].

Table 1 The chemical and physical properties of the Pd/Fe₂O₃ catalysts

| Samples           | BET (m²/g) | Pd loading (wt%) | Pd dispersion (%) | Fe₂O₃ size (nm) | Pd size (nm) |
|-------------------|------------|------------------|-------------------|----------------|--------------|
| Pd/Fe₂O₃-573      | 180        | 1.87             | 55                | 9a             | 1.8          |
|                   |            | 5-10b            |                   |                |              |
| Pd/Fe₂O₃-673      | 79         | 1.89             | 51                | 22a            | 2.0          |
|                   |            | 20-25b           |                   |                |              |
| Pd/Fe₂O₃-773      | 35         | 1.82             | 4.7               | 31a            | 2.1          |
|                   |            | 30-40b           |                   |                |              |

Note: *the size of Fe₂O₃ calculated from Scherer formula; ^the size range of Fe₂O₃ judged from the TEM images; “the Pd size was calculated according to d_pdl=1/D_pdl×100%.

Figure 1 presents the XRD patterns of the as-prepared Pd/Fe₂O₃ catalysts. There is no observable PdO diffraction peak for all the catalysts, indicating that PdO is finely dispersed. The PdO nanoparticles size was maintained at about 2 nm in diameter (calculated according to the dispersion of Pd, Table 1) even after calcination at 773 K. While for the Fe₂O₃ support, the main diffraction peaks are all assigned to hexagonal Fe₂O₃ (PDF#33-0064). The support crystalline size was 9 nm for Pd/Fe₂O₃-573 catalyst, and it was
increased to 22 nm for Pd/Fe₂O₃-673 and 31 nm for Pd/Fe₂O₃-773 catalysts with the calcination temperature increasing, which is in accordance with the BET specific surface results.

The sintering of the Fe₂O₃ support is further confirmed by the TEM images shown in Fig. 2. The Pd/Fe₂O₃-573 catalyst had the average Fe₂O₃ crystalline size of ∼10 nm (see Fig. 2(a)). When the calcination temperature was increased to 673 K (Pd/Fe₂O₃-673), the Fe₂O₃ size was increased to ∼20 nm (see Fig. 2(b)), and further increased to ∼30 nm at 773 K (Pd/Fe₂O₃-773) (see Fig. 2(c)). There is no visible PdO nanoparticle, because the 2 nm PdO particle is impossible to be distinguished from the speckle contrast exhibited by the support.

H₂-TPR experiments were carried out on the as-prepared Pd/Fe₂O₃ catalysts, and the profiles are displayed in Figure 3. The temperatures of reduction peaks maxima and the quantitative evaluation of H₂ consumption are given in Table 2. The reduction peaks of PdO species were centered at 316-340 K [14,21]. Among these three catalysts, Pd/Fe₂O₃-573 exhibited the largest H₂ consumption below 400 K (shown in Table 2), which might be associated with the strongest metal-support interaction [22]. In the case of Pd/Fe₂O₃-573 catalyst, the H₂ consumption at 340 K was 355 µmol/gcat, which was much larger than 155 µmol/gcat of theoretical value for PdO to Pd, indicating the co-reduction of PdO and partial surface Fe₂O₃ near the Pd nanoparticles where hydrogen can easily spillover onto the support surface [23]. The reduction peak centered at 450 K (H₂ consumption is 352 µmol/gcat) was due to the further reduction of Fe₂O₃ to Fe₃O₄. It appears that Pd could enhance the Fe₂O₃ support reducibility significantly since the reduction temperature was much lower than the typical one of 633 K for Fe₂O₃ to Fe₃O₄ [24,25]. The reduction behaviors of Pd/Fe₂O₃-673 and Pd/Fe₂O₃-773 catalysts were similar to that of the Pd/Fe₂O₃-573 catalyst. However, the Pd enhancement becomes weaker by considering that the H₂ consumption at low temperature (∼320 K) was decreased and the reduction temperature for Fe₂O₃ to Fe₃O₄ was shifted to higher temperatures.
Catalytic performance of the Pd/Fe₂O₃ catalysts in CO oxidation

Catalytic activity of the Pd/Fe₂O₃ catalysts

Figure 4 shows the catalytic activity in CO oxidation of the as-prepared and H₂-pretreated Pd/Fe₂O₃ catalysts. For the as-prepared catalysts, (see Fig. 4(a)) the T₅₀ (the temperature corresponding to 50% CO conversion) was 287 K for Pd/Fe₂O₃-573, 309 K for Pd/Fe₂O₃-673, and 313 K for Pd/Fe₂O₃-773 catalysts, respectively. A 100% CO conversion was observed on the Pd/Fe₂O₃-573 catalyst at 333 K, whereas, they were corresponded to only 80% and 70% for the Pd/Fe₂O₃-673 and Pd/Fe₂O₃-773 catalysts, respectively. A 100% CO conversion was observed on the as-prepared Pd/Fe₂O₃-773 catalyst at 333 K, whereas, they were corresponded to only 80% and 70% for the H₂-pretreated Pd/Fe₂O₃ catalysts at the same temperature. The results indicated that CO could be oxidized by PdO species without pre-reduction [25]. This might be due to the redox behavior of the highly dispersed PdO nanoparticles: PdO + CO → Pd + CO₂, 2Pd + O₂ → 2PdO.

The H₂ pretreatment promoted the catalytic activity of the Pd/Fe₂O₃ catalysts, and the results are shown in Fig. 4(b). The CO conversion at 273 K was 50~55% for the Pd/Fe₂O₃-773 and Pd/Fe₂O₃-673 catalysts, which was slightly lower than 65% for the Pd/Fe₂O₃-573 catalyst. For all the three catalysts, the CO conversion was about 70% at 283 K, and increased to 100% at 323 K. The much higher performances of the H₂-pretreated Pd/Fe₂O₃ catalysts may be due to the well dispersed PdO nanoparticles and the unique Pd-Fe₂O₃ interaction [26]. It was considered that the well dispersed Pd nanoparticles would weaken C-O and O-O bonds after CO and O₂adsorption, influencing the interaction between the surface and the adsorbents and favoring CO activation [20,27].

The influence of Pd loading content

The influence of amounts of Pd loading on CO oxidation conversion for the as-prepared and H₂-pretreated Pd/Fe₂O₃ catalysts is shown in Fig. 5. It is clearly seen that the CO conversion was all improved when the loaded Pd content was increased. For the as-prepared Pd/Fe₂O₃-573 catalyst, the CO conversion was increased from 68% to 90% when Pd content was increased from 1 wt% to 3 wt%. Similarly, it was increased from 79% to 99% for H₂-pretreated Pd/Fe₂O₃-573 catalyst. This may be explained by the more active sites which were produced as the loaded Pd content increased for CO adsorption, activation and intermediates transformation.

The influence of gas hourly space velocity (GHSV)

The catalytic performances of the as-prepared and H₂-pretreated Pd/Fe₂O₃-573 catalysts under different gas hourly space velocity (GHSV) were performed at 303 K (Fig. 6). For all the catalysts, a higher space...
the decrease extents were different. The CO conversion over the catalyst surface with the increased GHSV. However, accounted on the decreased reactants residence time on the catalyst surface with the increased GHSV (60,000 mL/(gh) to 120,000 mL/(gh)).

Fig. 6 The influences of gas hourly space velocity on CO conversion over the as-prepared and H₂-pretreated Pd/Fe₂O₃ catalysts calcined at 573 K (Reaction conditions: mass of catalyst: 1.0 g; Total flow rate: 1000 mL/min; Feedstock: 100 ppm CO/air; T: 303 K, GHSV=60000 mL/gh).

velocity resulted in a lower CO conversion. This was accounted on the decreased reactants residence time on the catalyst surface with the increased GHSV. However, the decrease extents were different. The CO conversion was decreased from 81% to 72% when the space velocity was increased from 60,000 mL/(gh) to 120,000 mL/(gh) over the as-prepared Pd/Fe₂O₃-573 catalyst. While for the H₂-pretreated catalysts, the CO conversion was only slightly decreased from 99% to 97% with the gas hourly space velocity was increased from 60,000 mL/(gh) to 120,000 mL/(gh). The results suggested that the CO oxidation reaction rate was much faster on the H₂-pretreated catalyst than that on the as-prepared catalyst.

The intrinsic rate of CO conversion

The excellent activity of the Pd/Fe₂O₃ catalysts can be further confirmed from Table 3, where a comparison of the specific rate of the as-prepared and H₂-pretreated Pd/Fe₂O₃ catalysts for CO oxidation with a range of supported Pd and Au catalysts from the literatures has been made. The as-prepared Pd/Fe₂O₃ catalyst showed a relative high specific rate (4.3 × 10⁻² mol/gₚd/h), which was as active as Au/La₂O₃ catalyst (specific rate is 4.0 × 10⁻² mol/gₐu/h). The H₂ pretreatment enhanced the activity further, the specific rate over the H₂-pretreated Pd/Fe₂O₃ catalyst was increased to 10.7 × 10⁻² mol/gₚd/h, which was a little higher than that of the Au/Fe₂O₃ catalyst (9.1 × 10⁻² mol/gₐu/h) prepared by deposition-precipitation method [17,28]. These results showed that the activities of Fe₂O₃-supported Pd catalysts may be comparable to those of supported Au catalysts for CO oxidation.

In order to have an insight into the intrinsic activities of the Pd catalysts, the turn over frequencies (TOFs) were also compared in Table 3. As expected, the TOF of H₂-pretreated Pd/Fe₂O₃-573 catalyst was 0.038 s⁻¹, exhibiting significantly higher activity than that of the as-prepared Pd/Fe₂O₃-573 catalyst (0.012 s⁻¹). The TOF value of H₂-pretreated Pd/Fe₂O₃-573 catalyst was comparable to that of the Au/CeO₂ catalyst (TOF=0.047s⁻¹) [29] and the commercial Au/Fe₂O₃ catalyst (TOF = 0.04 s⁻¹) [30]. The TOF value of H₂-pretreat

| Table 3 Specific rates of CO conversion and TOFs data of catalysts from this work and literatures |
|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Catalysts | Metal loadings (wt%) | Specific rate × 10² (molCO · gₚd/Au⁻¹ · h⁻¹) | TOF × 10² (s⁻¹) | Temperature (K) | References |
| As-prepared Pd/Fe₂O₃-573 | 1.87 | 4.3 | 1.2 | 298 | This work |
| H₂-pretreated Pd/Fe₂O₃-573 | 1.87 | 10.7 | 3.8 | 298 | This work |
| Pd/Fe₂O₃ | 2.1 | 1.4 | 3.7 | 300 | [17] |
| Pd/SiO₂ | 5.0 | NA | 3.1 | 450 | [31] |
| Au/Fe₂O₃ | 4.4 | 9.1 | 4.0 | 300 | [17] |
| Au/La₂O₃ | NA | 4.0 | 1.0 | 298 | [29] |
| Au/CeO₂ | 5.0 | NA | 4.7 | 273 | [30] |

Note: *Co-precipitation; ²Deposition-precipitation; NA: Not available
Pd/Fe$_2$O$_3$-573 catalyst was in great agreement with the same Pd/Fe$_2$O$_3$ catalyst reported in reference [17]. This was assigned to the small size of the synthesized Pd nanoparticles (<3 nm), suggesting much smaller activation energy [31]. It was well known that the size of metal particles plays an important role in CO activation. The TOF results strongly suggested that supported Pd catalysts may be a good alternative to gold in CO oxidation if proper preparation method and support are adopted.

**Stability of the Pd/Fe$_2$O$_3$ catalysts for CO oxidation**

The stability of Pd/Fe$_2$O$_3$ catalysts shown in Fig. 7 was tested at 293 K. The CO conversion was readily decreased from 70% to 65% for the Pd/Fe$_2$O$_3$-573 catalyst after 10 h (Fig. 7(a)). For Pd/Fe$_2$O$_3$-673 catalyst it maintained around 40%, whereas, for Pd/Fe$_2$O$_3$-773 catalyst it decreased from 35% to 25% after 10 h. The stability test further evidenced the highest performance of the as-prepared Pd/Fe$_2$O$_3$-573 catalyst. Because the reaction temperature (293 K) was much lower than the calcination (573 K) and reduction temperature (353 K), it was inferred that no obvious PdO or Fe$_2$O$_3$ sintering was occurred during the reaction course. Hence the deactivation of the as-prepared Pd/Fe$_2$O$_3$ catalysts might be originated from the gradually deposition of soft carbonate or carbonyl species on the catalyst surface.

Figure 7(b) shows the stability of CO conversion over the H$_2$-pretreated Pd/Fe$_2$O$_3$ catalysts. The initial CO conversion was about 90%, and the CO conversion was decreased with the time on stream increasing over the three catalysts. After 10 h, CO conversion was decreased to 80%, 70% and 40% over the Pd/Fe$_2$O$_3$-573, Pd/Fe$_2$O$_3$-673 and Pd/Fe$_2$O$_3$-773 catalysts, respectively. The results demonstrated that Pd/Fe$_2$O$_3$-573 catalyst is the most efficient for CO oxidation. It might be associated with the smallest size of Pd (1.8 nm) and the strongest metal-support interaction (Fig. 3) over the Pd/Fe$_2$O$_3$-573 catalyst. Although the Pd sizes over the Pd/Fe$_2$O$_3$-673 and Pd/Fe$_2$O$_3$-773 catalysts were close (2.0 nm and 2.1 nm, respectively), the metal-support interaction was not as strong as that over the Pd/Fe$_2$O$_3$-573 catalyst. Similar to the as-prepared catalysts, the deactivation of the H$_2$-pretreated catalysts could also be contributed to the gradually deposition of carbonates on the surface of catalyst, which hindered the activation of CO and blocked the transformation of intermediates, as discussed later.

**Characterizations of the used catalysts**

**XRD patterns**

In order to clarify the causes of deactivation of the catalysts, characterizations of the used catalysts were carried on. Figure 8 gives the XRD patterns of the used as-prepared and H$_2$-pretreated Pd/Fe$_2$O$_3$ catalysts. The XRD patterns of the used as-prepared Pd/Fe$_2$O$_3$ catalysts (Fig. 8(a)) showed the exact same profiles with the fresh ones. The Fe$_2$O$_3$ diffraction peaks were present and their crystalline sizes kept constant. The diffraction peak of PdO species was still not detected. These observations confirmed that the sintering of PdO and Fe$_2$O$_3$ species were not occurred. In contrast, obvious differences were observed over the used H$_2$-pretreated Pd/Fe$_2$O$_3$ catalysts (Fig. 8(b)). The diffraction peaks of Fe$_2$O$_3$ species were much weaker and the diffraction peaks of Fe$_2$O$_4$ species were appeared. This indicated that the hydrogen pretreatment reduced most of the Fe$_2$O$_3$ to Fe$_3$O$_4$. Pd species were not detected in these used samples, indicating that they were highly dispersed or below the limitation of XRD apparatus. Hence Pd/Fe$_3$O$_4$ catalysts were formed after the hydrogen pretreatment. It has been reported that Fe$_3$O$_4$ contained surface hydroxyl group and was helpful for oxygen activation [17]. So the catalytic performance of the H$_2$-pretreated catalysts was much higher than that.

**Fig. 7** CO conversion of the Pd/Fe$_2$O$_3$ catalysts as a function of time at 293 K (Reaction conditions: mass of catalyst: 0.5 g; Total flow rate: 1000 mL/min; Feedstock: 100 ppm CO/air; T: 293 K; GHSV=120,000 mL/gh).
FTIR analysis of the H₂-pretreated Pd/Fe₂O₃ catalysts

Figure 9 presents the FTIR analysis of the H₂-pretreated Pd/Fe₂O₃ catalysts to identify the carboxyl species on the catalyst surface. In the carbonate-like species range (1000-1700 cm⁻¹) [32], the peak at 1415 cm⁻¹ was related to the unidentate carbonate species [33], and 1539 cm⁻¹ was detected for the carboxylate species [13]. The band observed at 1630 cm⁻¹ was assigned to the bidentate carbonates [9,34]. In the carbonyl region (1800-2250 cm⁻¹), CO adsorption and activation was observed. 1977 cm⁻¹ was due to CO bridged adsorption on Pd⁰ and 2162 cm⁻¹ was related to the CO interacting with partially oxidized Pd center [13]. The IR spectroscopy clearly demonstrated that the carbonate species were formed after the stability tests and gave an insight on the activation of CO. It was suggested that CO was adsorbed on the Pd⁰ and activated on the partially oxidized Pd (because of the presence of oxygen in the feed). The intermediates (carbonates or carbonyl species) were transformed to CO₂ in the Pd-Fe₂O₃ interface. However, due to the much less adsorption and activation of CO, the catalytic performance of the as-prepared catalysts was not as good as that of the H₂-pretreated catalysts. In addition, the carbonates on the surface would further cover the surface of the active sites and block the mobility and transformation of the intermediates, resulting in the deactivation with the time on stream [35].

Conclusions

Pd/Fe₂O₃ nano-catalysts were synthesized by co-precipitation method and were investigated for CO oxidation in this study. The results revealed that both the as-prepared and H₂-pretreated catalysts showed high performance for CO catalytic oxidation at low temperatures. T₅₀ was 293 K and 273 K over the as-prepared and the H₂-pretreated catalysts, respectively. CO can fully be converted at temperature as low as 313 K over the H₂-pretreated catalysts. During the long time stability test, CO conversion was above 80% over the H₂-pretreated Pd/Fe₂O₃-573 catalyst, while 60% conversion was maintained over the as-prepared Pd/Fe₂O₃-573 catalyst. The higher calcination temperature produced a lower performance, which was associated with the different crystalline size and metal-support interaction of the catalyst. The much higher performance of the H₂-pretreated catalysts was attributed to the Fe₃O₄ formation and surface OH group. The former was helpful to the O activation, and the latter was reacted with CO to form reactive adsorbed intermediates. The deactivation caused of the catalyst was assigned to the carbonates formation on the surface that hindered the CO activation and intermediates transformation.

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Doping Induced Tailoring in the Morphology, Band-Gap and Ferromagnetic Properties of Biocompatible ZnO Nanowires, Nanorods and Nanoparticles

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Abstract: The modification of nanostructured materials is of great interest due to controllable and unusual inherent properties in such materials. Single phase Fe doped ZnO nanostructures have been fabricated through simple, versatile and quick low temperature solution route with reproducible results. The amount of Fe dopant is found to play a significant role for the growth of crystal dimension. The effect of changes in the morphology can be obviously observed in the structural and micro-structural investigations, which may be due to a driving force induced by dipole-dipole interaction. The band gap of ZnO nanostructures is highly shifted towards the visible range with increase of Fe contents, while ferromagnetic properties have been significantly improved. The prepared nanostructures have been found to be nontoxic to SH-SY5Y Cells. The present study clearly indicates that the Fe doping provides an effective way of tailoring the crystal dimension, optical band-gap and ferromagnetic properties of ZnO nanostructure-materials with nontoxic nature, which make them potential for visible light activated photocatalyst to overcome environmental pollution, fabricate spintronics devices and biosafe drug delivery agent.

Keywords: ZnO; Fe doping; Dipole-dipole interaction; Band-gap tailoring; Ferromagnetism; Cytotoxicity

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Introduction

ZnO is an important group of II–VI semiconductor with the characteristics of wide direct band gap (3.37 eV), large exciton binding energy (60 meV), inexpensive and environmentally safe material [1,2]. Due to these remarkable characteristics, ZnO nanomaterials have attracted a lot of research interest in the field of science and technology [3,4]. Among ZnO nanomaterials family, the one dimensional (1D) ZnO nanostructures (such as nanowires, nanorods, nanofibers and nanotubes etc) are of special interest because of their high surface area and compatibility with the functional nanodevices. Due to these significant properties, the 1D ZnO nanostructures has found large number of applications in many devices such as nano lasers, single nanowire field effect transistor, UV blockers and detectors, power generators and gas sensors [5-9]. For all these devices, the controlled nanoscale morphological characteristics are highly desired.

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In these days, ZnO based photocatalyst is considered to be an excellent substitute of TiO$_2$ to overcome the current global environmental pollution problem due to its good stability and non-toxic nature [10]. However, the large band gap of ZnO lies in the UV range, which allows for only $\sim$6% of sunlight to be useful for the activation of the catalyst. Therefore, a visible light activated catalyst is highly desired that can take advantage of a larger fraction of the solar spectrum and would be much more effective in environmental cleanup [11]. It has been found that the optical band gap energy of ZnO nanostructures can be effectively tailored via doping of different transitional metals (TMs) [12]. In addition, currently a lot of experimental and theoretical research is also concentrated on TM doped ZnO dilute magnetic semiconductors (DMSs) because of their room temperature ferromagnetic behavior [13]. ZnO nanostructures with tailored optical and magnetic properties may have useful applications in future spintronics devices [13]. In order to look above functionality with morphological modification, optical improvements and room temperature ferromagnetism with high $T_c$, Fe is supposed to be a potential candidate for doping in ZnO.

In addition, the inorganic nanostructures have an important role in biomedical sector because of their significant photocatalytic and antibacterial characteristics [14]. Among these, ZnO nanostructures are of special attention because of their cost effectiveness and established applications in health care products [15]. ZnO could also be used for drug delivery but toxicity concern is there. Bulk ZnO is considered as safe material by FDA (US Food and Drug Administration) but when reduced to the nanoscale, ZnO can develop new actions of toxicity [16].

In this work, Fe doped ZnO nanostructures including nanoparticles, nanorods and nanowires based on the soft chemistry synthetic approach have been prepared at room temperature. A series of Fe doped ZnO samples with varying Fe contents have been systematically studied. The band gap of ZnO has been dramatically reduced with the increase in Fe doping level. The morphology of doped samples shows an interesting change from 1D to zero dimension (0D). The resulting Fe doped ZnO nanostructures possess both tuned optical and magnetic properties, which will enable them for designed industrial applications. Furthermore, the cytotoxicity of Fe doped ZnO nanostructures has been studied and found to be nontoxic for SH-SY5Y Cells.

Experimental

Fe doped ZnO nanostructures have been prepared using wet chemical method as in our previous reported work [17,18]. Different analytical grade chemicals have been used for the fabrication of ultrafine nanostructures. In a typical synthesis process, 0.5 M NaOH solution prepared in ethanol as precipitating agent has been added drop by drop into molar solution of 0.05 M Zn(NO$_3$)$_2$·6H$_2$O with different stoichiometric ratio of FeCl$_3$·6H$_2$O at normal laboratory temperature for 1 h.

$$
\text{Zn(NO}_3\text{)}_2 + \text{NaOH} \rightarrow \text{Zn(NO}_3\text{)}_2(\text{OH}) + \text{NaNO}_3 \\
\text{Zn(NO}_3\text{)}_2(\text{OH}) + \text{NaOH} \rightarrow \text{ZnO} + \text{NaNO}_3 + \text{H}_2\text{O}
$$

After one hour of vigorous magnetic stirring, the solution has been put into an Autoclave (Teflon vessel) and heated at 120°C for 15 h. The precipitates have been collected, washed and then centrifuged. Finally, these washed precipitates have been dried in oven at 110°C. Different characterization techniques have been employed as were used in our previous reported work [17,18].

The SH-SY5Y cells of human being have been used as target which are commercial available at ATTC, USA. The cells have been cultured at 37°C in DMEM medium for 48 h with in humidified environment. The colloidal solution of the synthesized nanostructures with different Fe doping level has been used against these cells. The cells cultured without the presence of these nanostructures have been used as control for comparison.

Results and discussion

Morphology and microstructure

The morphology and microstructure of these prepared crystalline samples have been carefully investigated using electron microscopy techniques. Figure 1(a), (b), (c) and (d) demonstrate the TEM, HRTEM and SAED images of Fe doped ZnO with different compositions $x= 0.5$, $1$, $2$ and $5$% of Fe dopant, respectively. It has been interestingly found that the prepared doped samples undergo a significant morphological changes induced by the amount of Fe dopant concentrations into ZnO structure. The pure ZnO sample portrays the nanowires of length 5 µm and their growth direction is preferably oriented along c-axis. Figure 1(a) shows the morphology of Fe$_{0.5}$Zn$_{0.5}$O sample, which exhibits nanowires of average length $3 \mu m$ with $40 \text{ nm}$ of diameter. The microstructure study with HRTEM of grown nanowires shows single phase structure with the interspacing between planes of $0.22 \text{ nm}$ and length of c-axis $0.5204 \text{ nm}$, which reveals that the growth direction of these nanowires is preferably oriented along (0001) as shown in Fig. 1(a). The sample with the nominal composition of $x= 1$% has a morphology of nanorods within the average length of $900 \text{ nm}$ and a diameter of $90 \text{ nm}$ as shown in Fig. 1(b). The microstructural HRTEM study of these as prepared nanorods shows that the c-axis lattice constant value is little reduced and the spacing between planes is also changed.
However, the absence of secondary phases can be ruled out from Fig. 1(b). With the increase of Fe doping concentration up to 2%, there are two kinds of mixed morphology consisting of nanorods and nanoparticles as shown in Fig. 1(c). The major part of morphology is nanorods, whose micro-structural investigation in high resolution shows that the growth along c-axis planes is highly influenced and the micro-structure has mixed morphology overlook. In order to confirm the structure formation, SAED has been carried out for this sample and is depicted in the Fig. 1(c). All resolved fringes pattern of diffraction shows the single phase wurtzite structure formation. When the concentration of Fe dopant is increased up to 5%, the morphology is dramatically changed from 1D to nanoparticles as shown in Fig. 1(d). The average size of these nanoparticles lies in the range of 12 nm. The HRTEM and SAED investigations of these prepared nanoparticles demon-
strate that they are in ZnO wurtzite single phase and all selected area diffraction fringes can be indexed to hexagonal wurtzite structure as shown in Fig. 1(d). In order to make the picture of morphology change more clear, it has been noted that with the introduction of Fe into ZnO lattice, the growth along c-axis is affected and the length of nanowires and nanorods is decreased, while diameter increased, which gives the evidences of some force to hinder the growth of crystal along c-axis. There is overall a schematic change in the morphology with the variation of Fe doping concentration as depicted in diagram 1.

The growth mechanism of nanocrystal structure can be explained on the basis of the polar surfaces of ZnO. The hexagonal wurtzite structure of ZnO has a series of a number of alternating planes which are made of tetrahedral coordinated $O^{2-}$ and $Zn^{2+}$ ions, piling up along the $c$-axis [19]. The ions create positively charged $(0001)$-Zn and negatively charged $(0001)$-O polar surfaces as shown in the inset of Fig. 1(d) [20]. The incorporation of Fe$^{3+}$ into ZnO matrix can produce planar defects along (0001) plane which may reduce the surface energy and result in the quick anisotropic growth along different direction instead of c-axis without affecting the intrinsic polarity of nanostructures. The change of morphology from nanowires to nanorods and then nanoparticles may be due to the reason that polar surfaces tend to minimize their surface area. The electrostatic energy may be reduced by interfacing of (0001)-Zn plane with (0001)-O plane. This interfacing will balance the local polar charges and leads to reduce surface area. In brief, the change in the morphology as a function of doping concentration may be due to the increase of charge carriers of Fe$^{3+}$ to replace Zn$^{2+}$ sites into lattice, the positive charge on c-axis growth plane increases and there is driving force produced by dipole-dipole electrostatics interaction, which hinders the growth along one direction [21].

Figure 2 demonstrates the EDS spectra of Fe doped ZnO nanostructures. The spectra of all samples show...
an obvious presence of Fe dopants and its variation in the concentration into nanostructures. The signals of carbon (C) and copper (Cu) come from the sample grid used for TEM and HRTEM investigations. The statistical analyses over dozen of individual nanowires, nanorods and nanoparticles show that Fe atoms are doped uniformly in the range of $x = 0.5 \sim 5\%$ into nanostructures, which are almost consistent with nominal compositions used at the time of chemical reaction during the synthesis process.

Crystal structure and oxidation state

The XRD patterns of Fe$_x$Zn$_{1-x}$O ($x = 0.5\%, 1\%, 2\%$ & $5\%$) nanostructures are shown in Fig. 3(a). All the diffraction peaks can be well matched to standard wurtzite structure of ZnO, which confirms single phase crystallinity of the prepared nanostructures. The close view of diffraction patterns in Fig. 3(b) demonstrates two obvious changes as a function of Fe dopant concentration. Firstly, the main diffraction peaks are slightly shifted towards lower angles, which are the results of successful doping [19] due to the small variations in the lattice parameters induced by dopant concentrations. Secondly, it can also be seen in Fig. 3(b) that the width of all peaks is increased with the variation of Fe concentration, which is due to preferred growth of crystal direction and changing in the grain size as different morphologies observed in the above electron microscopic investigations.

In addition, it is interesting to note that the intensity ratio of (002) polar plane to (100) non-polar plane ($I_{(002)}/I_{(100)}$) is remarkably enhanced with the morphological changes (having the following order Nanowires < Nanorods & Nanoparticles) as shown in Fig. 3(b) and given in Table 1. A high ratio of $I_{(002)}/I_{(100)}$ with Fe doping shows a large fraction of polar planes, which clearly demonstrates that the polarization plays an important role for the growth direction [22]. The absence of any extra peak further rules out the formation of secondary phases and in-corroborates well with the HRTEM and SAED results for single phase crystallinity.

XPS is a surface chemical analysis technique that can be used to study the oxidation state and the concentration of elements present in the material. XPS spectra of Fe dopant for all samples have been recorded and typical spectra for $x = 0.5$ and $5\%$ are displayed in Fig. 4 (a & b). All samples exhibit same spectrum pattern with error of $\pm 0.2$ eV, in which Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ peaks are positioned at 724.9 and 710.5 eV, respectively. The peaks positions are different from metallic Fe peak (Fe$_{1+}$Zn$_{1-x}$O).

| $x$ (%) | Morphology | Lattice Parameters | $I_{(002)}/I_{(100)}$ | Band-gap (nm) | Magnetic Parameters |
|--------|-----------|--------------------|-----------------------|---------------|---------------------|
|        |           | $a=b$ (Å) | $c$ (Å) | $V$ (Å$^3$) |                   | $M_s$ (emu/g) | $H_c$ (Oe) |
| 0      | Nanowires | 3.2509  | 5.2069  | 55.03 | 0.79 | 380 | — | — |
| 0.5    | Nanowires | 3.2464  | 5.2044  | 54.85 | 0.91 | 388 | 0.02 | 9 |
| 1      | Nanorods | 3.2439  | 5.2028  | 54.75 | 1.09 | 392 | 0.07 | 11 |
| 2      | Nanorods + Nanoparticles | 3.2420  | 5.2012  | 54.67 | 1.12 | 407 | 0.20 | 139 |
| 5      | Nanoparticles | 3.2401  | 5.1985  | 54.58 | 1.02 | 443 | 1.5 | 261 |

Table 1 The Rietveld refinement calculations of lattice parameters.

![Fig. 3](a) Full and (b) Extended XRD patterns of Fe$_x$Zn$_{1-x}$O Nanostructures.
The existence of satellite lines (S₁ and S₂) suggests that the Fe is incorporated into the ZnO and is in Fe³⁺ valence state for all samples [25]. The concentration of Fe dopants in ZnO is in well agreement with EDS measurements and nominal compositions.

Photoluminescence and ferromagnetic properties

In order to see the Fe doping induced effects on the optical properties of ZnO, the PL spectra have been carried out and are shown in the Fig. 5. The pure ZnO has two emission peaks in UV (380 nm) and visible luminescence (VL) (524 nm) regions of the spectrum. The peak in UV is attributed to near band edge (NBE) transition due to interaction of exciton-exciton through collision process, while in VL usually called green emission band is assigned to the defects (such as singly ionized oxygen vacancy and Zn interstitial defects) [26,27]. The results for Fe doping demonstrate that the NBE and VL are strongly influenced from the amount of Fe doping as shown in Fig. 5 and given in Table 1. It has been interestingly found that NBE of ZnO shows a red shift of about 8, 12, 27 and 63 nm
in the band gap from that of pure ZnO nanowires for 0.5%, 1%, 2% and 5%, respectively. The shift in the UV peak positions illustrates that the Fe doping can significantly tailor the electronic structure and band-gap of ZnO nanostructures. The red shift observed in the band gap of Fe doped ZnO nanoparticles is highest up to recent reported and makes this material potential for the proposed visible light (solar) photocatalyst to overcome the environmental pollution. The red-shift in the band gap of Fe doped ZnO nanoparticles is highest up to recent reported and makes this material potential for the proposed visible light (solar) photocatalyst to overcome the environmental pollution. The red-shift in the band gap of Fe doped ZnO nanoparticles is highest up to recent reported and makes this material potential for the proposed visible light (solar) photocatalyst to overcome the environmental pollution.

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Figure 6 shows the M-H curves of 0.5%, 1%, 2% and 5% Fe-doped ZnO at room-temperature. The samples with low compositions of 0.5% and 1% exhibit both ferromagnetic and paramagnetic behaviors; while for 2% and 5% samples, there are obvious hysteresis loops. It is noteworthy that the magnetic moment \( (M_s) \), remanence \( (M_r) \) and coercivity \( (H_c) \) are significantly increased with Fe doping concentration in ZnO nanostructures as shown in Fig. 6 and given in Table 1.

The exact origin of room temperature ferromagnetism (FM) in TM doped ZnO is not yet very clear and there are many conflicting reports about it. At this moment, the origin of the FM has usually been explained by several hypotheses: double exchange, superexchange, direct exchange, carrier mediated exchange interactions, role of anisotropy, oxygen vacancy, bound magnetic polaron overlapping and long-range exchange interactions (RKKY) etc [30-33]. In this mechanism,

![Fe\textsubscript{2}Zn\textsubscript{1-x}O \( x=0.5\% \)](M=0.02 \text{ emu/g}
H\textsubscript{c}=9 Oe)

![Fe\textsubscript{2}Zn\textsubscript{1-x}O \( x=1\% \)](M=0.07 \text{ emu/g}
H\textsubscript{c}=11 Oe)

![Fe\textsubscript{2}Zn\textsubscript{1-x}O \( x=2\% \)](M=0.24 \text{ emu/g}
H\textsubscript{c}=139 Oe)

![Fe\textsubscript{2}Zn\textsubscript{1-x}O \( x=5\% \)](M=1.5 \text{ emu/g}
H\textsubscript{c}=261 Oe)

Fig. 6 Field dependent magnetization of Fe doped ZnO Nanostructures.
role of defects (such as oxygen vacancy and zinc interstitial) is mostly considered to be an important for the observed FM in TM doped ZnO [34]. As it is clear from the above morphology and PL results that sp-d exchange interactions and presence of defects are increased with increasing Fe concentration, which may be responsible for the origin of observed FM in Fe doped ZnO nanostructures. Moreover, it has been reported that grain boundaries and grain sizes also play a significant role in the ferromagnetic properties of TM doped ZnO [35]. The ferromagnetic behavior of Fe doped ZnO is believed to be more prominent, if it is comprised of nano-grains [36]. Furthermore, it has been reported that Fe doped ZnO samples exhibit ferromagnetic behavior only if containing certain minimum amount of grain boundaries. The amount of grain boundaries is strongly dependent on Fe concentration in the host matrix [36]. Hence, the ferromagnetic behavior of the prepared nanostructures may also be due to smaller grain sizes of the samples and presence of grain boundaries.

**Effect of Fe doping on ZnO nanostructures cytotoxicity and ROS production**

The biocompatibility of the prepared nanostructures has been examined on the human cell line (SH-SY5Y cells). The cells have been cultured in Dulbecco’s Modification of Eagle’s Medium (DMEM) with 10% Fetal Bovine Serum (FBS). These cells have been treated with ZnO nanostructures doped with different Fe concentrations (0.5, 1, 2, 3, 5%) and incubated for 24 hours at 37°C. The effects on the cells have been studied. In order to determine the influence of the synthesized nanostructures on cell viability; CCK-8 analysis has been performed along with phase contrast microscopy to quantify the total number of cells with and without prepared nanostructures. It is depicted in Fig. 7(a) that the prepared nanostructures have no significant effect on the viability of the tested cells. From Fig. 7(b), it is clear that 0.5% Fe doped ZnO nanostructures has no effect on the SH-SY5Y cell viability. With the higher concentration of Fe dopant, the viability of SH-SY5Y cells is slightly affected by ZnO nanostructures, but all the prepared nanostructures may be thought as non toxic towards SH-SY5Y due to very low proportion of damage.

The toxicity of the prepared nanostructures has been further examined by reactive oxygen species (ROS) generation analysis. ROS generation is considered as the main mechanism through which nanomaterials cause damage to the healthy cells. It is generated on the surfaces of the nanomaterials because of the electronic properties of the material. Furthermore, ROS can be generated by the obstructed electronic transport in the mitochondrial inner membrane [37]. The elevated generation of ROS can lead to damage cell membrane and
cell which causes cell death [37]. ROS generation has been investigated by Flow cytometry. The cell permeable DCFH-DA dye has been used to know about the oxidative stress in cells [37]. Figure 8 depicts that a negligible amount of ROS produced in SH-SY5Y cells treated with ZnO nanostructures doped with different Fe concentrations (0.5, 1, 2 and 5%).

Conclusions

In conclusion, Fe is successfully doped up to 5% into ZnO lattice using reproducible low-temperature simple, quick and versatile synthesis approach. The investigations reveal that the doping concentration plays a very important role to tune the growth direction of nanocrystal, band gap transitions and FM of nanomaterials. The results appear interesting in the light of the proposed possibilities for the shift of ZnO band gap to represent an alternative of TiO$_2$ for solar light activated photocatalyst, magneto optical and solar cells devices for the innovative technological applications. It is concluded that Fe doping in ZnO does not change very much the cell viability and ROS production. It is also revealed that Fe doped ZnO is biosafe and biocompatible material for SH-SY5Y Cells.

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Pt-Containing Ag$_2$S-Noble Metal Nanocomposites as Highly Active Electrocatalysts for the Oxidation of Formic Acid

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Abstract: Nanocomposites with synergistic effect are of great interest for their enhanced properties in a given application. Herein, we reported the high catalytic activity of Pt-containing Ag$_2$S-noble metal nanocomposites in formic acid oxidation, which is a key reaction in direct formic acid fuel cell. The electrochemical measurements including voltammograms and chronoamperograms are used to characterize the catalytic property of Pt-containing nanocomposites for the oxidation of formic acid. In view of the limited literatures on using nanocomposites consisting of semiconductor and noble metals for catalyzing the reactions of polymer electrolyte membrane-based fuel cells, this study provides a helpful exploration for expanding the application of semiconductor-noble metal nanocomposites.

Keywords: Nanocomposites; Synergistic effect; Formic acid oxidation; Direct formic acid fuel cell

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Introduction

Platinum (Pt) nanoparticles are active electrocatalysts to facilitate both anodic and cathodic reactions in polymer electrolyte membrane fuel cells (PEMFCs) [1-3]. However, in methanol or formic acid-fed PEMFCs, the Pt catalysts usually suffer from the poisoning at the anode by carbon monoxide (CO), which is an intermediate product of the fuels [4-7]. Over the past few decades, a number of strategies including the reduction of particle size, taking control of particle shape and structure, and alloying with transitional metals [3,8-12], have been successfully used to enhance the Pt electrocatalytic activity and resistance to deactivation.

Our recent work demonstrated that the integration of Pt with a suitable semiconductor might be an effective way to improve the catalytic property of Pt for PEMFC reactions [13,14]. For example, in the Ag$_2$S-noble metal nanomaterials reports recently, the Pt-containing nanocomposites were found to display excellent catalytic activity for methanol oxidation, due to electron donation from the semiconductor domains to the ultrafine Pt crystallites [13]. In addition, in core-shell structured CdSe-Pt nanocomposites were obtained by reducing platinum precursors by sodium citrate in the presence of previously formed CdSe nanocrystals, and the compressive strain effect imposed from the CdSe core on the deposited Pt shell results in an appropriate downshift of the d band center of Pt catalysts, which leads to the enhancement of the core-shell structured nanocomposites for catalyzing the oxygen reduction and methanol oxidation in direct methanol fuel cells [14].

Herein, we reported our experimental extensions on
the formic acid oxidation reaction (FAOR) using Pt-containing Ag$_2$S-noble metal nanocomposites as electrocatalysts. Oxidation of Formic acid is a key reaction of direct formic acid fuel cell (DFAFC) [15,16], in which the low crossover rate of formic acid through the Nafion membrane allows higher fuel concentrations to be used than in the case of direct methanol fuel cell (DMFC) [17]. In view of the quite limited literatures on using nanocomposites consisting of semiconductor and noble metals for PEMFC reactions, this study might be a salutary exploration for expanding the application of semiconductor-metal nanocomposites.

**Experimental sections**

**Materials**

The reagents, if not indicated specifically, were from Sigma-Aldrich; ethanol, and toluene were from Beijing Chemical Works; bis (p-sulfonatophenyl) phenylphospho-line dihydrate dipotassium salt (BSPP) was from Strem Chemicals; and Vulcan XC-72 carbon powders were from Cabot. All glassware and Teflon-coated magnetic stirring bars were cleaned with aqua regia, followed by copious rinsing with de-ionized water before drying in an oven.

**Synthesis of Ag$_2$S nanocrystals and Ag$_2$S-noble metal nanocomposites**

The syntheses of Ag$_2$S nanocrystals and Ag$_2$S-noble metal nanocomposites followed a protocol reported previously with modifications [13]. In a typical synthesis of a hydrosol of monoclinic Ag$_2$S nanocrystals, 600 mg of BSPP was added to 300 mL of aqueous AgNO$_3$ solution (1 mM). The mixture was stirred for 1 h, followed by the prompt addition of 10 mL of aqueous Na$_2$S solution (50 mM). A brownish hydrosol was obtained after stirring the reaction mixture at room temperature for 4 h, indicating the formation of Ag$_2$S nanocrystals.

A more simplified protocol was used to prepare Ag$_2$S-Pt and Ag$_2$S-Au-Pt nanocomposites. In brief, 60 mL of the Ag$_2$S hydrosol was refluxed at 110°C for 3 min in a 100-mL three-necked flask equipped with a condenser and a Teflon-coated magnetic stirring bar. Next, 3 mL of aqueous sodium citrate solution (100 mM) was added. The resulting mixture was refluxed for 1 min at 110°C, and then 1.2 mL of aqueous H$_2$PtCl$_6$ solution (50 mM) or a mixture of 1.2 mL of aqueous HAuCl$_4$ solution (50 mM) and 1.2 mL of aqueous solution of H$_2$PtCl$_6$ (50 mM) were added swiftly. The reaction mixture was continuously refluxed for 2 h at 110°C to form a hydrosol of Ag$_2$S-Pt or Ag$_2$S-Au-Pt nanocomposite.

Ag$_2$S-Au nanocomposites and pure Pt nanoparticles with analogous size to the Pt domain in the Pt-containing nanocomposites were also prepared for comparison. For Ag$_2$S-Au, 60 mL of the Ag$_2$S hydrosol was refluxed at 105°C for 3 min, followed by the addition of 3 mL of aqueous sodium citrate solution (100 mM). The resulting mixture was refluxed for 1 min at 105°C, and then 1.2 mL of aqueous H$_2$PtCl$_6$ solution (50 mM) was added swiftly. The reaction mixture was continuously refluxed for 30 min at 105°C to form a hydrosol of Ag$_2$S-Au nanocomposite. The tiny Pt nanoparticles were prepared using an ethanol mediated phase transfer protocol [18]. In a typical experiment, 50 mL of 1 mM of aqueous H$_2$PtCl$_6$ solution was mixed with 50 mL of ethanol containing 1 mL of dodecylamine. After 3 min of stirring, 50 mL of toluene was added, and stirring was continued for more than 1 minute. The Pt precursors in toluene were separated from the aqueous phase, and mixed with 3 mL of aqueous NaNBH$_4$ solution (100 mM). The mixture was agitated for several minutes to form Pt organosol in toluene.

After preparation, the Ag$_2$S-noble metal nanocomposites (Ag$_2$S-Au, Ag$_2$S-Pt, and Ag$_2$S-Au-Pt) were also transferred in toluene using the ethanol mediated phase transfer method for the standardization of the particle surface, which is important for further electrochemical comparison. After the phase transfer treatment, the Ag$_2$S-noble metal nanocomposites and the monometallic Pt nanoparticles would have the same stabilizer molecules (dodecylamine) adsorbed on their surfaces. In addition, the phase transfer of nanocomposites from aqueous phase to a non-polar organic medium was conducted since we experimentally found that the loading efficiency of the particles on XC-72C carbon powders from the organic medium (~99%) was much higher than that from the aqueous phase (~37%). Typically, the Ag$_2$S-metal hydrosol was mixed with an equal volume of ethanolic solution of dodecylamine (90 mM). After 5 min of stirring, an equal volume of toluene was added and stirred for 3 minutes. Phase transfer of the Ag$_2$S-metal nanocomposite from water to toluene would then occur quickly and completely, leaving a clear colorless solution in the aqueous phase.

**Particle characterizations**

Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 electron microscope operated at 200 kV with the software package for automated electron tomography. A drop of the nanoparticle solution was first dispensed onto a 3-mm carbon-coated copper grid. Excessive solution was removed by an absorbent paper, and the sample was dried under vacuum at room temperature. An EDX analyzer attached to the TEM was used to analyze the components in samples. XPS analyses were conducted on an ESCALAB MKII spectrometer (VG Scientific) using Al-K$_\alpha$ radiation (1486.71 eV). Samples for XPS were concentrated...
from the toluene solution of Pt nanoparticle or Ag$_2$S-metal nanocomposite to 0.5 mL using flowing Ar. 10 mL of ethanol was then added to precipitate the particles, which were then recovered by centrifugation, and washed with ethanol several times, and dried at room temperature in vacuum.

**Electrochemical measurements**

Electrochemical measurements were carried out in a standard three-electrode cell connected to a Bio-logic VMP3 (with EC-lab software version 9.56) potentiostat. A leak-free Ag/AgCl (saturated with KCl) electrode was used as the reference electrode. The counter electrode was a platinum mesh (1 × 1 cm$^2$) attached to a platinum wire.

For the loading of the Pt-containing nanocomposites on Vulcan XC-72 carbon support, a calculated amount of carbon powder was added to the toluene solution of nanocomposites. After stirring the mixture for 24 h, the nanocomposites/C (20 wt% Pt on carbon support) was collected by centrifugation, and washed thrice with methanol, and then dried at room temperature in vacuum.

The working electrode was a thin layer of Nafion-impregnated catalyst cast on a vitreous carbon disk. This electrode was prepared by ultrasonically dispersing 10 mg of the nanocomposites/C in 10 mL of aqueous solution containing 4 mL of ethanol and 0.1 mL of Nafton. A calculated volume of the ink was dispensed into the toluene solution of 10 mg of the nanocomposites/C in 10 mL of aqueous solution containing 4 mL of ethanol and 0.1 mL of Nafton. A calculated volume of the ink was dispensed onto the 5 mm glassy carbon disk electrode to produce a nominal catalyst loading of 20 µg cm$^{-2}$ (Pt basis). The carbon electrode was then dried in a stream of warm air at 70°C for 1 h.

The catalyst performance in room-temperature formic acid oxidation reaction (FAOR) was measured by cyclic voltammetry. For these measurements, the potential window of 0 V to 1 V was scanned at 20 mV s$^{-1}$ until a stable response was obtained, before the voltammograms were recorded. The electrolyte was formic acid (1 M) mixed in perchloric acid (0.1 M).

**Results and discussion**

**Nanocomposites of Ag$_2$S and noble metals (Au, Pt)**

The as-prepared Ag$_2$S nanocrystals, which were used as seeds for the subsequent deposition of different metals, were shown by the TEM image in Fig. 1(a). The nanocrystals were spherical, nearly monodispersed, and had an average size of 8.4 nm. The high-resolution TEM (HRTEM) image (Fig. 1(b)) illustrated the lattice planes in these nanocrystals, confirming that these Ag$_2$S particles were of high crystallinity.

As schematically shown in Fig. 2(a) and 2(b), the reduction of metal precursors (Au and Pt) in the presence of preformed Ag$_2$S nanocrystals resulted in the heterogeneous deposition of noble metals on the surface of Ag$_2$S. The obtained nanocomposites were illustrated in Fig. 3(a) and 3(c). The deposition of noble metals on the Ag$_2$S nanocrystals was clearly identified via brightness contrast, and confirmed by the energy-dispersive X-ray (EDX) analyses (Fig. 3(b) and 3(d)). In addition, Fig. 3(a) and 3(c) illustrated that gold was deposited only at a single site on each Ag$_2$S nanocrystal, whereas the nucleation and growth of Pt occurred at multiple sites on each Ag$_2$S nanocrystal.
analysis (Fig. 3(f)). Fig. 3(g) and 3(h) showed the TEM image and EDX analysis of the pure Pt nanoparticles derived from an ethanol mediated transfer method, which had analogous size (1.4 nm) to the Pt domains in the nanocomposites.

**Electrochemical measurements of Pt-containing nanocomposites for oxidation of formic acid**

The Ag$_2$S-noble metal nanocomposites (Ag$_2$S-Au, Ag$_2$S-Pt, and Ag$_2$S-Au-Pt) and pure Pt nanoparticles were examined for their electrocatalytic activities for the formic acid oxidation reaction (FAOR) at room temperature. The voltammograms of formic acid oxidation in Fig. 4(a) were obtained in the potential window of 0-1 V at a scan rate of 20 mV s$^{-1}$. The current densities in the voltammograms were normalized with the geometric area of the glassy carbon electrode. The peak current densities of these catalysts associated with formic acid oxidation in the forward and reverse scans were 70.2 mA cm$^{-2}$ and 193.1 mA cm$^{-2}$ for Pt,
167.7 mA cm\(^{-2}\) and 300.4 mA cm\(^{-2}\) for Ag\(_2\)S-Pt, 225.3 mA cm\(^{-2}\) and 427.6 mA cm\(^{-2}\) for Ag\(_2\)S-Au-Pt, respectively. The Ag\(_2\)S-Au nanocomposites did not display catalytic activity for FAOR. The comparison in current densities indicated that the Ag\(_2\)S-Au-Pt nanocomposites had higher activity for formic acid oxidation than that of Ag\(_2\)S-Pt nanocomposites and pure Pt nanoparticles.

The Ag\(_2\)S-Au-Pt nanocomposites had higher activity for formic acid oxidation than that of Ag\(_2\)S-Pt nanocomposites and pure Pt nanoparticles.

![Graph](image)

**Fig. 4** Cyclic voltammograms of pure Pt nanoparticles and Pt-containing nanocomposites in argon-purged HClO\(_4\) (0.1 M) with 1 M formic acid (a); and chronoamperograms of pure Pt nanoparticles and Pt-containing nanocomposites at 0.4 V vs. Ag/AgCl at room temperature in argon-purged HClO\(_4\) (0.1 M) with 1 M formic acid (b).

Analogous to the superior catalytic activity of the Pt-containing nanocomposites for methanol oxidation [13], the enhanced catalytic activity of the Ag\(_2\)S-Au-Pt nanocomposites for FAOR could also be attributed to the electronic coupling between the different domains in the nanocomposites. The XPS Pt 4f spectra of the Pt-containing nanocomposites (Ag\(_2\)S-Pt, Ag\(_2\)S-Au-Pt) and pure Pt nanoparticles were analyzed. As shown in Fig. 5, the Pt 4f spectra can be deconvoluted into two pairs of doublets, in which the more intense doublet (at 70.0 eV and 73.3 eV for pure Pt, 69.5 eV and 72.8 eV for Ag\(_2\)S-Pt, 69.1 eV and 72.4 eV for Ag\(_2\)S-Au-Pt) corresponded to Pt zero valent metal, while the second and weaker doublet, with binding energies of ∼1.4 eV higher than those of Pt metal, could be assigned to Pt\(^{2+}\) as in PtO and Pt(OH)\(_2\) [19]. Compared with the Pt 4f\(_{7/2}\) and 4f\(_{5/2}\) binding energies of pure Pt nanoparticles, an appreciable shift to lower values was observed in the Ag\(_2\)S-Pt and Ag\(_2\)S-Au-Pt nanocomposites, suggesting that electrons were transferred to Pt from other domains of the nanocomposites. The comparison of the Pt 4f XPS spectra of Ag\(_2\)S-Pt and Ag\(_2\)S-Au-Pt nanocomposites further revealed that the presence of the Au domain could promote this electron-donating effect. This electron-donating effect to Pt domains might be induced by intra-particle charge transfer. Analogous charge transfer has been observed in the core-shell Au@PbS system, whereby the electrons transfer from PbS shell to the inner Au core resulted in the n-type to p-type change in hydrazine-treated PbS [20]. The electron flow from Au and Ag\(_2\)S to the neighboring Pt domains due to the alignment of energy levels was believed to result in a substantial increase in the electron density around the Pt sites, which weakens the chemisorption of CO (a FAOR intermediate product and catalyst inhibitor) and hence promotes the FAOR. The long-term performance of pure Pt and Pt-containing Ag\(_2\)S-metal nanocomposites in formic acid oxidation was illustrated in the chronoaamperograms of Fig. 4(b). The slower rate of decay for the Pt-containing nanocomposites indicated their superior CO tolerance to the pure Pt catalysts.

**Fig. 5** 4f XPS spectra of Pt in pure Pt nanoparticles (a); Ag\(_2\)S-Pt (b); and Ag\(_2\)S-Au-Pt nanocomposites (c).

### Conclusions

In summary, we have demonstrated an aqueous strategy for the synthesis of Pt-containing Ag\(_2\)S-noble metal nanocomposites, which involved the preparation of Ag\(_2\)S nanocrystals in aqueous phase, followed by the reaction or co-reduction of Au and Pt metal precur-
sors with sodium citrate in aqueous phase. The Pt-containing nanocomposites displayed highly enhanced activity for catalyzing the formic acid oxidation reaction at room temperature due to the strong electronic coupling effect between the different domains in the nanocomposites. By optimizing the domain sizes for the nanocomposite system through varying the ratio of metal precursor to semiconductor seeds in the synthesis, further enhancement in FAOR activity could be expected.

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Magnetic Fe₃O₄-Reduced Graphene Oxide Nanocomposites-Based Electrochemical Biosensing

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Abstract: An electrochemical biosensing platform was developed based on glucose oxidase (GOx)/Fe₃O₄-reduced graphene oxide (Fe₃O₄-RGO) nanosheets loaded on the magnetic glassy carbon electrode (MGCE). With the advantages of the magnetism, conductivity and biocompatibility of the Fe₃O₄-RGO nanosheets, the nanocomposites could be facilely adhered to the electrode surface by magnetically controllable assembling and beneficial to achieve the direct redox reactions and electrocatalytic behaviors of GOx immobilized into the nanocomposites. The biosensor exhibited good electrocatalytic activity, high sensitivity and stability. The current response is linear over glucose concentration ranging from 0.05 to 1.5 mM with a low detection limit of 0.15 µM. Meanwhile, validation of the applicability of the biosensor was carried out by determining glucose in serum samples. The proposed protocol is simple, inexpensive and convenient, which shows great potential in biosensing application.

Keywords: Fe₃O₄-reduced graphene oxide (Fe₃O₄-RGO); Nanocomposites; Magnetically controllable assembling; Direct electron transfer; Biosensor

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Introduction

Diabetes mellitus is a worldwide public health problem, which resulted from either a deficiency or tolerance in insulin [1]. Glucose biosensors are becoming an indispensable means for the diagnosis and therapy of diabetes mellitus [2]. Amperometric enzyme electrodes based on glucose oxidase (GOx) have been extensively used for the detection of the blood glucose concentration due to the high catalytic activity for the oxidation of glucose to gluconolactone [3]. Nevertheless, the direct electron communication between redox proteins and electrode surfaces is difficult because the redox center in biomolecules is usually buried in the large three-dimensional structure of enzyme molecules [4,5]. Various materials have been studied to promote electron transfer of redox enzymes onto the surface of electrodes [6-9].

Magnetic nanomaterials have received much attention because of the unusual structural, excellent adsorption, catalytic properties and inherent electrical conductivity [10-14]. Graphene, a two-dimensional (2D) sheet of carbon atoms arranged in a honeycombed network, has received tremendous attention because of its high electrical conductivity, large surface area per volume, excellent electrocatalytic properties, all of which lead to their excellent performance as electrochemical biosensing platforms [15]. Furthermore, decoration with inorganic materials, such as metal or semiconductor nanoparticles (NPs) onto the reduced graphene oxide (RGO) sheets could form interesting 2D nanocomposite structures [16]. Fe₃O₄ magnetic NPs have been widely used in biomagnetics fields due to their magnetic properties, low toxicity, high adsorption ability and good biocompatibility [17-19]. Graphene sheets as
2D substrates can effectively prevent the agglomeration of Fe₃O₄ NPs and enable a good dispersion of these magnetic NPs [20]. In addition, Fe₃O₄-RGO nanocomposites may offer feasible biocompatible microenvironment, which preserves the biological and electrochemical activities of the immobilized biomolecules. Because of these fascinating properties, Fe₃O₄-RGO is promising as a potential magnetically controllable material for biosensor.

In this paper, magnetic Fe₃O₄-RGO nanosheets were prepared by a facile solvothermal method and characterized by transmission electron microscopy (TEM), atomic force microscopic (AFM) and X-ray diffraction spectra (XRD). Due to the inherent magnetic property and biocompatibility, the nanosheets could be served as a suitable substrate for the immobilization of GOx enzyme molecules and adhered to the magnetic electrode surface without any additional adhesive reagent. Thus the Fe₃O₄-RGO nanocomposites-based electrochemical biosensing systems were constructed by magnetically controllable assembling (Scheme 1). The direct electron transfer (DET) between the immobilized redox proteins and electrode was studied. Meanwhile, the developed biosensor showed good sensitivity, reproducibility and stability. The results indicated that magnetic Fe₃O₄-RGO based magnetically controllable protocol could reduce the analytes diffusion limitation, and well maintain the activity of enzyme. Therefore, this work provides a new avenue to broaden the applications of Fe₃O₄-RGO in electrochemical biosensors.

![Scheme 1 Schematic illustration of Fe₃O₄-reduced graphene oxide nanocomposites-based electrochemical biosensors via magnetically controllable assembling.](image)

**Experimental**

**Reagents and materials**

Graphite powder with 98% purity was purchased from Aladdin. Glucose oxidase (GOx, 100 U/mg) was purchased from Sangon Biotech. The D-(+)-Glucose from Aladdin. Glucose oxidase (GOx, 100 U/mg) was obtained from Sinopharm Chemical Reagent Co., Ltd. FeCl₃·6H₂O, FeCl₂·4H₂O, diethylene glycol (DEG), diethanolamine (DEA), sodium hydroxide, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Glucose stock solutions (0.1 M) were prepared and allowed to mutarotate overnight at room temperature before use. Phosphate buffer solution (PBS, 0.1 M) was prepared from 0.1 M NaH₂PO₄ and Na₂HPO₄ in doubly distilled water and the pH was adjusted to 6.0. All other reagents used were of analytical grade, and all aqueous solutions were prepared with doubly distilled water.

**Apparatus and measurements**

JEOL 2100 transition electronic microscopy was used for transmission electron microscopy (TEM) analysis. Atomic force microscope (AFM) measurement was carried out on a MultiMode Nanoscope from digital instruments (Bruker AXS GmbH). X-ray diffraction patterns were collected on a Bragg-Brentano diffractometer (Rigaku D/Max-2000) with monochromatic Cu Ko radiation (λ = 1.5418 Å) of a graphite curve monochromator. UV-vis absorption spectra were recorded by a Multiskan spectrum with wavelength range of 200-1000 nm. Magnetic property was carried out at room temperature using a vibrating sample magnetometer (Lake Shore, VSM736).

All electrochemical measurements were performed on a CHI660B electrochemical workstation (Chenhua Instruments, Shanghai, China). Electrochemical experiments were performed with a conventional three-electrode system comprising of a bare or Fe₃O₄-RGO-modified MGCE as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode.

**Synthesis of Fe₃O₄-RGO nanocomposites**

Graphite oxide (GO) was prepared from natural graphite by the modified Hummer’s method [21,22]. The superparamagnetic Fe₃O₄-RGO nanosheets were prepared via solvothermal method with some modification of those reported literatures [23,24]. In brief, a solution of FeCl₂·4H₂O (5 mmol) was mixed with FeCl₃·6H₂O solution (10 mmol) and dissolved in 10 mL of hot DEG at 90°C in an oil bath. After 30 min of stirring, 2.5 mL of DEA was added to the above solution. Meanwhile, NaOH (10 mmol) and DEG (20 mL) were mixed to produce a stock solution. The resulting solution was dropped into the hot iron solution under vigorous stirring for another 10 min. Subsequently, the homogeneous GO (15 mg) dispersion was mixed with DEG solution (10 mL) followed by 30 min of vigorous stirring. The mixture was then transferred to a Teflon-lined autoclave and maintained at 180°C for 8 h. After centrifugation, the products were washed with ethanol and distilled water in turn until neutralization and dried under vacuum at room temperature finally.
Fabrication of GOx/Fe₃O₄-RGO/MGCE

The magnetic glassy carbon electrode (MGCE) was first polished to a mirror with 0.3 and 0.05 μm alumina slurry, and sonicated in ethanol and water successively. The electrodes were successively sonicated in 1:1 (v/v) nitric acid, acetic acid and ethanol, and then allowed to dry under a stream of nitrogen. For the preparation of GOx/Fe₃O₄-RGO modified electrode, MGCE was immersed in 0.2 mL as-prepared Fe₃O₄-RGO suspension (2 mg mL⁻¹) at room temperature. Fe₃O₄-RGO sheets were firmly attached to the electrode surface by a simple magnetically controllable adsorption. After washing with water, the obtained Fe₃O₄-RGO/MGCE was dipped into GOx solution (3 mg mL⁻¹ at pH 6.0) at 4℃ overnight for protein immobilization. The resulting electrodes were washed with water and stored at 4℃ when not in use.

Results and discussion

Characterization of Fe₃O₄-RGO nanocomposites

Transmission electron microscopy (TEM) was employed to characterize the dispersity and particle size of the prepared samples. Figure 1(a) presents representative TEM image of graphene nanosheets, clearly illustrating the flake-like shapes and a crumpled structure. These monolayer sheets possess large surface areas, and particles can be anchored on both sides of these sheets [20]. As shown in Fig. 1(b), Fe₃O₄ MNPs have been located on the RGO nanosheets. Furthermore, the anchored Fe₃O₄ metal NPs distributed uniformly on these graphene sheets without obvious aggregations.

Atomic force microscopic (AFM) images were recorded with a Nanoscope IIIa scanning probe microscope using a tapping mode. The sample used for AFM measurements was prepared by casting the suspension of GO or Fe₃O₄-RGO on the surface of a mica sheet and allowed to be evaporated. Typical AFM images of GO and Fe₃O₄-RGO nanosheets are presented in Fig. 2. The cross-sectional analysis indicates the mean thickness of GO (Fig. 2(a)) monolayer is ca. 1.0 nm, which is corresponding to previous report [25]. And the thickness of Fe₃O₄-RGO sheets (Fig. 2(b)) was determined to be ca. 18.0 nm, indicating the successful loading of Fe₃O₄ nanoparticles on the nanosheets.

The interconnected two-dimensional (2D) substrates could be served as a platform for enzyme immobilization through non-covalent adsorption and covalent binding [26]. Zeta potential measurements showed that after the surface modification with Fe₃O₄ nanoparticles, the Zeta potential value of GO dramatically changed from -43.7 mV to +31.5 mV. It may be due to the adsorption and complexing of DEA, thereby the surfaces of the as-prepared Fe₃O₄ nanoparticles are terminated with many NH₂ groups, which provide the surface of the magnetic nanosheets with positive charges [23] and benefit for further bioconjugates. Thus GOx molecules could easily be adsorbed on the Fe₃O₄-RGO, which are mainly dominated by the electrostatic interaction between positively charged Fe₃O₄-RGO nanocomposites and negatively charged enzyme molecules. In addition, other kinds of interaction such as hydrophobic attraction and hydrogen bonding might also be functioned in the adsorption process [27].

Representative X-ray diffraction (XRD) patterns of the prepared samples are depicted in Fig. 3(A). As shown in curve a, the characteristic diffraction peaks at 18° (111), 30° (220), 36° (311), 43° (400), 54° (422) and 57° (511) are consistent with the standard XRD data of the crystalline planes of face-centered cubic (fcc) Fe₃O₄ according to the standard spectrum of Fe₃O₄ (JCPDS, No. 65-3107). Besides these peaks, an additional peak at 26.0° corresponding to the RGO can be observed in curve b [28]. This indicated the coexistence of Fe₃O₄ and RGO in the hybrid. As shown in Fig. 3(B), the magnetic hysteresis loop of the Fe₃O₄-RGO hybrid is measured at room temperature with an applied magnetic field sweeping from -5000 to +5000 Oe, exhibiting superparamagnetic property of the magnetic nanocomposite [29].

Fig. 1 TEM images of (a) GO and (b) Fe₃O₄-RGO nanosheets.
UV-vis absorption spectra have been carried out to study the effects of Fe₃O₄-RGO on the microstructures of immobilized GOx. Figure 4(A) shows UV-vis absorption spectra of Fe₃O₄-RGO, GOx and the mixture of GOx and Fe₃O₄-RGO, respectively. As shown in Fig. 4(A), in the case of pure GOx an intense band appeared at 275 nm and two well defined peaks of light absorption at 375 nm and 452 nm (Fig. 4(A), curve a) could be distinguished [30]. The UV-vis spectra of the Fe₃O₄-RGO indicate no absorption peak appearing in the range of 250-500 nm (Fig. 4(A), curve b). After bioconjugation of GOx with Fe₃O₄-RGO (Fig. 4(A), curve c), there is nearly no change in the absorption band, similar to that of native GOx. The results indicated
that GOx entrapped in the nanocomposites has an unchanged secondary structure and retains its biological activity.

Electrochemical impedance spectroscopy (EIS) is a highly effective tool to measure the change of interface properties of the modified electrode surface during the fabrication process [31]. Figure 4(B) illustrates the typical Nyquist plots of the bare MGCE, Fe₃O₄-RGO/MGCE and GOx/Fe₃O₄-RGO/MGCE in the presence of 1.0 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] and 0.1 M KCl for (a) bare MGCE; (b) Fe₃O₄-RGO modified MGCE; (c) Fe₃O₄-RGO-GOx modified MGCE. AC amplitude: 5 mV; frequency range: 0.1 Hz to 100 kHz. Inset: equivalent circuit used to model impedance data.

**Direct electrochemistry of GOx/Fe₃O₄-RGO/MGCE**

Figure 5(A) exhibits the cyclic voltammograms (CVs) in nitrogen-saturated 0.1 M PBS (pH 6.0) at the scan rate of 100 mV/s. (B) Cyclic voltammograms of GOx/Fe₃O₄-RGO/MGCE in 0.1 M nitrogen-saturated PBS (pH 6.0) at various scan rates (from inner to outer): 20, 10, 20, 40, 80, 100, and 400 mV s⁻¹. Inset: plots of peak currents (ip) vs. scan rates.
of the MGCE, Fe₃O₄-RGO/MGCE and GOx/Fe₃O₄-RGO/MGCE in 0.1 M nitrogen-saturated PBS (pH 6.0) at a scan rate of 100 mV/s. It is found that there are no any redox peaks at the MGCE (Fig. 5(A), curve a) and Fe₃O₄-RGO/MGCE (Fig. 5(A), curve b), which indicates that Fe₃O₄-RGO is not electroactive in the potential range from −0.6 V to −0.2 V. Conversely, a pair of well-defined and nearly reversible redox waves could be observed at RGO/Fe₃O₄-GOX/MGCE. Its formal potential $E^0$ (defined as the average of the anodic and cathodic peak potential) is calculated to be −0.44 V, which is close to those previously reported for immobilized GOx [32,33]. This observation confirms the facile direct electron transfer from the redox site of GOx (FAD) to the electrode. This result suggests that Fe₃O₄-RGO nanocomposites could provide a favorable microenvironment to facilitate the electron exchange between GOx and underlying electrode.

The effect of scan rates on the response of immobilized GOx is shown in Fig. 5(B). The anodic peak potential shifted to a more positive direction and the cathodic peak potential moved negatively with the increasing scan rate. However, formal potential of FAD/FADH₂ redox couple is nearly not changed. The linear dependence of $I_{pa}$ and $I_{pc}$ on scan rate is given in the inset of Fig. 5(B). The redox peak currents are directly proportional to the scan rate in the range of 10–400 mV s⁻¹, indicating a typical surface-controlled electrode process. According to the model of Laviron [34], the electron transfer rate constant ($k_s$) value is estimated to be 3.4 s⁻¹. This value is larger than those obtained for GOx immobilized on PMB₀Sio₂(nano)/GCE (2.44 s⁻¹) [35] and GOx/BCNTs/MGCE (1.56 s⁻¹) [33], suggesting that the Fe₃O₄-RGO nanocomposites can greatly promote the electron exchange between active site of GOx and the electrode.

The pH-dependent response of the Fe₃O₄-RGO/GOx nanocomposite modified MGCE was also evaluated. As shown in Fig. 6(A), stable and well-defined reversible redox peaks are observed in the various pH solutions. Elevation of the solution pH from 4.5 to 8.0 leads to negative shift in both reduction and oxidation peak potentials. The slope of formal potential is estimated to be −58.4 mV/pH (Fig. 6(B)), which is close to the theoretical value of −58.5 mV/pH [36]. The results indicate that two-proton coupled with two-electron accompanies the electron transfer of GOx (FAD) to electrodes.

**Electrocatalytical behavior of the Fe₃O₄-RGO-GOX/MGCE**

Figure 7(A) shows cyclic voltammograms of GOx/Fe₃O₄-RGO/MGCE in N₂-saturated solution (Fig. 7(A), curve a), air-saturated solution without (Fig. 7(A), curve b) and with (Fig. 7(A), curve c) 1.0 mM glucose. A pair of redox peaks is observed in both N₂-saturated and air-saturated 0.1 M PBS (pH 6.0) solution. Under N₂-saturated condition, there appears a pair of well-defined and reversible redox peaks (Fig. 7(A), curve a). However, in the presence of dissolved oxygen (Fig. 7(A), curve b), original oxidation peak decreases and reduction peak increases. The results indicate that GOx immobilized on Fe₃O₄-RGO/MGCE can catalyze the reduction of dissolved oxygen. This electrocatalytic process toward the reduction of dissolved oxygen may be expressed as follows: [35,37]

$$\text{GOx(FAD)} + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{GOx(FADH}_2)$$  
$$\text{GOx(FADH}_2) + \text{O}_2 \rightarrow \text{GOx(FAD)} + \text{H}_2\text{O}_2$$  

When glucose was added into air-saturated PBS, the reduction peak current at the GOx/Fe₃O₄-RGO/MGCE decreased (Fig. 7(A), curve c). It can be explained that glucose as the substrate of GOx can result in an enzyme-catalyzed reaction (Eq. (3)) and decrease the amount of the oxidized form (FAD) of GOx on the electrode surface.

$$\text{Glucose} + \text{GOx(FAD)} \rightarrow \text{gluconolactone} + \text{GOx(FADH}_2)$$
is dependent on the concentration of glucose. Therefore, the results of amperometric responses are in correspondence with those of the above CV measurements. The developed biosensor shows a steady state amperometric response towards glucose in the range of 0.05-1.5 mM with a detection limit of 0.15 µM (S/N = 3 and inset in Fig. 7(B)). The sensitivity of the enzyme electrode was calculated to be about 9.04 µA mM⁻¹ cm⁻², which was higher than those reported at a GOx/TiO₂-SWCNT/ITO-based glucose biosensor (5.32 µA mM⁻¹ cm⁻²) [38] and GOx/titania sol/gel film (7.2µA mM⁻¹ cm⁻²) [39]. Furthermore, according to the electrochemical version of the Lineweaver-Burk plot [40], the apparent Michaelis-Menten constant (Kₘₐₛₚ) for the GOx/Fe₃O₄-RGO/MGCE is estimated to be 0.34 mM, which is smaller than that of GOx on nitrogen-doped carbon nanotubes of 2.2 mM [41]. The smaller Kₘₐₛₚ value indicates that the immobilized GOx possesses high enzymatic activity and the biosensor exhibits a high affinity for glucose.

Furthermore, the stability and real sample analysis of the biosensor were investigated. The GOx-Fe₃O₄-RGO/MGCE could retain the direct electrochemistry of the immobilized GOx at constant current values upon the continuous cyclic voltammograms sweep over several hundred cycles. No obvious decrease in the current response to glucose was observed after one month storage in the refrigerator at 4°C. Human serum samples were assayed to testify the practical use of the proposed biosensor. The recovery experiments were carried out in diluted human serum samples, using a standard addition method. As presented in Table 1, the recovery of the biosensor is between 95% and 105%. The results indicate that the biosensor is effective and sensitive for the determination of glucose in real samples.

| Sample | Added (nM) | Found (mM) | Recovery (%) |
|--------|------------|------------|--------------|
| 1      | 0.15       | 0.17       | 96.66        |
| 2      | 0.80       | 0.82       | 102.50       |
| 3      | 1.00       | 0.98       | 98.07        |

Table 1 Determination of glucose concentration in human serum samples using the GOx-Fe₃O₄/reduced graphene oxide/MGCE

Conclusions

To summarize, we constructed a magnetic Fe₃O₄-reduced graphene oxide nanocomposites-based on electrochemical biosensing system for glucose determination. Owing to their excellent magnetic property and biocompatibility, Fe₃O₄-RGO nanocomposites could be used as suitable matrix for the immobilization of GOx enzyme and conveniently loaded on the surface of magnetic glass carbon electrodes by magnetically con-
trollable assembling. The direct electron transfer of GOx assembled on Fe₃O₄-RGO nanosheets could be achieved, indicating that nanocomposites provide a favorable microenvironment to facilitate the electron exchange between enzyme and electrode. The developed biosensor exhibited good electrocatalytic activity toward glucose, and could be effectively applied for glucose measurements in real samples.

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The torsional characteristics of single walled carbon nanotube (SWCNT) with water interactions are studied in this work using molecular dynamics simulation method. The torsional properties of carbon nanotubes (CNTs) in a hydrodynamic environment such as water are critical for its key role in determining the lifetime and stability of CNT based nano-fluidic devices. The effect of chirality, defects and the density of water encapsulation is studied by subjecting the SWCNT to torsion. The findings show that the torsional strength of SWCNT decreases due to interaction of water molecules and presence of defects in the SWCNT. Additionally, for the case of water molecules encapsulated inside SWCNT, the torsional response depends on the density of packing of water molecules. Our findings and conclusions obtained from this paper is expected to further compliment the potential applications of CNTs as promising candidates for applications in nano-biological and nano-fluidic devices.

Keywords: Carbon nanotube; Water interaction; Torsion; Water encapsulation; Nano-fluid; Molecular dynamics

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Introduction

Research in carbon nanotubes (CNTs) has gained enormous interest in nanotechnology and materials science due to its remarkable physical and mechanical properties [1,2]. CNTs possess a unique combination of high strength and ultra-light weight which makes it a promising application in nanoelectromechanical systems (NEMS) such as springs [3], and oscillators [4]. These applications require a critical understanding of the torsional properties of CNTs. In addition, CNTs have also demonstrated the potential to be used in the field of nano-drug delivery systems [5,6], and nano-fluidic devices [7,8]. Hence, understanding the torsional elastic properties of CNTs in a hydrodynamic environment is important to optimize the performance of CNTs for its use in NEMS and nano-level biological devices.

Many studies have been aimed to investigate the torsional elastic properties of CNTs by means of experimental or theoretical based approaches [9-12]. Lu and Hu [13] proposed a novel and improved finite element 3D model based on molecular mechanics approach to study the elastic properties of CNTs under tension and torsion. Using this model, they investigated the effects of diameter and helicity on the Young’s modulus and shear modulus of SWCNTs. Wang et al [10] deployed Molecular dynamics (MD) simulation technique to determine the mechanical properties of CNTs under torsion. They found that the shear modulus of CNT increases with increasing the radius of CNT. Zhang et al [12] studied the effect of various types of defects and temperature on the torsional responses of
defective SWCNT. The studies showed that the torsional strength is strongly dependent on the chirality, type of defects, and temperature. Faria et al. [14] studied the elastic behavior of chiral SWCNTs namely the (6, 3) CNT, under combined tension-twisting. They conducted MD simulation studies on the SWCNT subjected to three forms of mechanical loading, viz. pure tension, pure torsion and combined tension-torsion. It was found that the elastic modulus of the SWCNT under pure tension and torsion were much higher than that of the combined tension-torsion. Jeong et al. [15] studied the torsional responses of carbon nanotubes filled with SWCNTs, fullerenes and gases. Their investigations revealed that the torsional responses of SWCNTs will be distinct which depends on the density and nature of the filling material. In addition, the torsional characteristics of CNTs filled with metals such as copper [16] and silicon atoms [17] have also been studied in the literature.

It can be seen from the above mentioned literature studies that the torsional properties of the CNTs have been well studied and investigated in freeform and those filled with gases and metal atoms. However, it should be noted that the torsional strength of CNTs in hydrodynamic environment (with water) is still yet to be investigated. It is widely recognized that CNTs operating in hydrodynamics environment (such as nano-fluidic devices) will experience distinct loading conditions due to interaction of the surrounding water molecules. Hence, the main objective of our work is to investigate the torsional characteristics of free form and water submerged SWCNT. Furthermore, the influence of geometrical characteristics such as the chirality and the effect of defects on the torsional response of a CNT in water medium present an important and crucial design input for fabricating CNT based nano-fluidics and NEMS devices. The elastic properties of SWCNTs under various forms of water interaction have been comprehensively studied and the results are presented in this paper.

**Computational model**

The numerical simulations described in this work were carried out by using the classical molecular dynamics simulation method using LAMMPS software [18] where force field equations are used to describe the inter-atomic interactions. These inter-atomic interactions can be divided into the interaction between the carbon atoms of SWCNT, the interaction between the water molecules and the carbon atoms of SWCNT and the interaction between the water molecules. The inter-atomic interactions of carbon atoms in SWCNT are described using the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential [19]. The AIREBO potential is able to accurately describe the properties of solid-state and molecular carbon nanostructures [20,21] while maintaining the accuracies of the ab initio and semi-empirical methods in simulating large systems [22]. The torsional interaction due to dihedral angles in the system is also implemented in addition to the long range interactions in the AIREBO potential. The AIREBO function is defined mathematically as [19],

$$ E_{\text{AIREBO}} = E_{\text{REBO}} + E_{\text{LJ}} + E_{\text{TORS}} $$

(1)

where the $E_{\text{REBO}}$ represents the interaction energy defined by the Brenner’s second generation REBO potential [23]. The torsional interaction is represented by $E_{\text{TORS}}$ and $E_{\text{LJ}}$ describes the long range Lennard-Jones (LJ) (12-6) interaction between the carbon atoms.

The non-bonded interactions between the SWCNTs and the water molecule is typically modeled using a LJ potential function [24,25], which accurately describes the short-range electron repulsion and long-range electron attraction between the CNT and water molecules. The LJ potential is tuned using the parameters obtained from Ref. [26,27] to accurately describe the experimentally observed water-graphene contact angle. The non-bonded interactions between the carbon atoms and the water molecule is given by [26],

$$ E_{\text{non-bond}} = \sum_{i,j} 4\varepsilon \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] $$

(2)

where $\varepsilon_{CO} = 0.392$ kJ/mol and $\sigma_{CO} = 0.319$ nm are the LJ parameters between carbon to oxygen atoms [26]. Similarly, $\varepsilon_{CH} = 0.243$ kJ/mol and $\sigma_{CH} = 0.282$ nm are the LJ parameters between carbon to hydrogen atoms [27].

The interaction between the water molecules is described using the flexible fixed-point charge (FPC) water model [28]. The FPC water model is capable of accurately reproducing the properties of water for different ranges of pressure, temperature, integration time steps and system sizes. The FPC water model is described as [28],

$$ E_{\text{FPC}} = E_{\text{bond}} + E_{\text{bend}} + E_{\text{vdW}} + E_{\text{cls}} $$

(3)

where $E_{\text{bond}}$ and $E_{\text{bend}}$ are intra-molecular potential functions that represent the bond strength energy and bending energy in a water molecule respectively. The terms $E_{\text{cls}}$ and $E_{\text{vdW}}$ denote the electrostatic potential and van der Waals potential between water molecules respectively. The complete details of this potential function are described in the work by Zhang et al. [28].

**Calculation of torsional force and torque on SWCNT**

The torsional force is calculated by summation of inter-atomic forces between carbon atoms at the ends
of the SWCNT. The inter-atomic force, $\vec{F}_{ij}$, between atoms $i$ and $j$ is obtained by the gradient of potential energy described mathematically as [18],

$$\vec{F}_{ij} = -\left(\frac{dE(r_{ij})}{dr_{ij}}\right)$$  \hspace{1cm} (4)

where $r_{ij}$ is the distance between the atoms $i$ and $j$ and $E(r_{ij})$ is the potential between the atoms $i$ and $j$.

The torque, $T$, of SWCNT is then calculated by the product of torsional force $F$ and the radius $R$ of the SWCNT [12].

**Simulation details**

The work described in this paper is divided into two parts. The first part of the paper will focus on the torsional elastic characteristics of uncapped (open ended) SWCNTs submerged in water. The elastic properties of the capped SWCNTs encapsulated with varying densities of water molecules are discussed in following. Figure 1 describes the method of torsional loading condition applied in SWCNT considered in our study. To investigate the effect of geometry on the torsional properties of SWCNT, we considered armchair and zigzag SWCNTs of varying aspect ratios. Furthermore, the effect of defect density and distribution on the torsional properties is also investigated in this paper. In order to accomplish this, firstly we constructed a single vacancy defect approximately at the center of the SWCNT. This vacancy defect is then expanded in the radial or axial direction to form a bigger defect as illustrated in Fig. 2. This method of defect reconstruction allows us to study the role of defect distribution on the torsional properties of SWCNT [29,30].

The computational procedure described herein is similar to our previous work on the tensile loading characteristics of SWCNTs in water [30]. A simulation box of dimension $40 \AA \times 40 \AA \times 150 \AA$ is deployed in this work to simulate the interaction of CNT with the water molecules and PBCs are applied on all three directions of the system. Each time step in the MD simulation has a unit of 1 fs. At the beginning of the simulation, we equilibrate the system to release the residual stresses by achieving thermal equilibrium in an NVT ensemble. The simulations are carried out by maintaining a constant system temperature of 300 K and the density of water molecules is at $0.997 \text{ g/cm}^3$ (approx. $1 \text{ g/cm}^3$). The temperature stability of the system is achieved by employing Nose-Hoover thermostat [31,32]. Following this, the torsional loading is applied on the SWCNT as defined in Fig. 1. Equal number of atoms is fixed on the either ends of SWCNT and the number of fixed atoms at each end of SWCNTs for different geometries is listed in Table 1. The method of torsional rotation applied in our simulation is shown in Fig. 1, where the atoms at one end of the SWCNT are rigidly fixed (enclosed inside red rectangle) and the atoms at the other end (enclosed inside black rectangle) are subjected to constant incremental torsional rotation of 0.006 radians. After each rotation, the remaining atoms (those that are not fixed) are subjected to equilibration for

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**Fig. 1** The procedure of torsional loading of the SWCNT in our study. The end atoms enclosed within the red rectangle are fixed rigidly. The atoms enclosed inside the black rectangle is subjected to clockwise rotational displacement (twist speed = 0.0062 rad/ps, i.e. strain rate = 0.001 ps$^{-1}$) to affect torsion.

**Fig. 2** An illustration of vacancy defect construction in a perfect SWCNT lattice is employed in our study. A single vacancy defect is constructed at the center and the defect is expanded along the (a) axial or (b) radial direction. Only the front part of the SWCNT is shown.
1000 time steps (1 ps) such that the atoms attain the favorable minimum energy positions. The twist speed applied to the movable fixed end of carbon atoms in SWCNT in our MD simulation is 0.006 rad/ps. The end atoms are subsequently again twisted to a new position after calculation of the trajectories of atoms based on Verlet algorithm [33]. The remaining atoms are relaxed in an NVT ensemble and the procedure is repeated until failure occurs.

The snapshot of the equilibrated system consisting of a (10, 0) SWCNT in a simulation box filled with water molecules of density 0.9 g/cm$^3$ is depicted in Fig. 3(a).

We note from this figure that the narrow diameter of (10, 0) SWCNT allows for a single-file arrangement of water molecules inside the SWCNT, which is in agreement with results reported in Ref. [34]. The radial distribution function (RDF) of water molecules from the center of the (10, 0) SWCNT given by $g(R_d)$, where $R_d$ is the radial distance from the center of the SWCNT is shown in Fig. 3(b). It can be observed from this figure that the first peak occurs at radial distance less than 0.05 nm which indicates a region near the center of the SWCNT. This means that it is more likely to find a water molecule at the center than any other region inside the SWCNT. The radial distribution then drops down to zero and remains at this value until radial distances exceed 0.69 nm. This is due to the van der Waal’s interaction between the water molecules and the carbon atoms of SWCNT as described by Eqn. (2). A second characteristic peak is observed outside the surface of SWCNT which is in qualitative agreement with the previous simulated results described in Ref. [35]. At larger distances from the surface of the CNT, the radial distribution function fluctuates around the value of 1 due to weak interaction between the water molecules and the carbon atom. Overall, the resulting post-equilibrated structure of SWCNT submerged in simulation box of water molecules helps us to confirm the accuracy of the simulation.

### Results and discussion

#### Validation of the simulation model

The elastic properties of a free form SWCNT under torsional loading is discussed in this section. In order to validate the computational model employed in the current study, we subjected the same SWCNT model (a (10, 10) SWCNT of length 100 Å) as used in Ref. [15] simulated using the AIREBO potential function under NVT ensemble as described in section 3. The torsional elastic response of the (10, 10) SWCNT is depicted in Fig. 4. The torque (measured as the product of torsional force and the radius of the SWCNT) increases linearly with strain until about it reaches a specific torsional strain $\gamma = 0.07$. After this point, we note that the nature of the curve deviates markedly from its linear behavior. This change in curve is caused due to the elastic to plastic transition of the SWCNT under torsion, which is in good agreement with results reported in earlier research [12]. It should further be noted from this figure that the observed maximum torque of 14.698 nN/nm at torsional strain of $\gamma = 0.078$ is in excellent agreement with the values reported in Ref. [15].
Effect of surrounding water molecules

This section focuses on the effect of surrounding water molecules on the torsional properties of SWCNT. This is accomplished by submerging a (10, 10) SWCNT in a simulation box filled with water molecules of density 0.9 g/cm$^3$. Three lengths of the SWCNT are considered here, viz. $L = 50 \, \text{Å}$, $75 \, \text{Å}$ and $100 \, \text{Å}$. These lengths correspond to aspect ratios $(L/D)$ of 3.69, 5.53 and 7.37 respectively. It should be noted that we maintain the same aspect ratio for different SWCNTs considered in our study which will be described in the subsequent sections. Figure 5 shows the torsional characteristics of the free form and water submerged (10, 10) SWCNT. It can be noted from this figure that the maximum torque decreases while the torsional angle increases with the aspect ratio of the SWCNT, which is similar to results reported previously Ref. [15,16]. This is because SWCNTs with small aspect ratio are stocky and would require larger torque while SWCNTs with large aspect ratio are slender and can be twisted easily to large angles. Furthermore, this dependence is in agreement with the continuum elastic definition of torque $(T)$ given by Ref. [15],

$$T = K \theta / L$$  \hspace{1cm} (5)

where $K$ is the torsional stiffness, $\theta$ is the torsional angle and $L$ is the length of the tube.

It can be noted from Fig. 5 that the effect of interacting water molecules decreases the torsional performance of the SWCNT. This can be explained as follows. The plot of the strain energy of the free form and water submerged SWCNT plotted against strain is illustrated in Fig. 6. It can be seen from this figure that the strain energy of water submerged SWCNT is higher than that of the free form SWCNT at smaller strain levels. The interaction of water molecules surrounding the SWCNT increases the strain on the SWCNT surface which reduces the torsional performance of the SWCNT. Additionally, we can also see from this figure that the presence of water molecules surrounding the SWCNT decreases the threshold strain energy required to induce elasticity to plastic transition in the SWCNT due to torsional twisting.

It is also worthwhile to note from Fig. 6 that at the onset of plastic deformation, there is a change in the quadratic behavior of the strain energy curve of free form and water submerged SWCNT with torsional strain. Thereafter, the strain energy of free form and water submerged SWCNT fluctuates slowly with increasing torsional angle in the plastic stage. This gradual change of the strain energy after plastic transition is different to the drastic drop in strain energy for the case of SWCNTs under tensile [30] or compressive loading [20,36]. This phenomenon as explained in Ref. [12] is due to the reason that the elastic to plastic transition
Fig. 7 Snapshots of torsional deformation of water submerged (10,10) SWCNT of aspect ratio, $L/D = 7.37$ when it is twisted by (a) 0°, (b) 30°, (c) 60°, and (d) 90°. The water molecules are not shown in this figure for clarity.

in an SWCNT under torsion results in a small structural change compared to that of the tensile or compressive loading. The variation in the strain energy fluctuations of free form and water submerged SWCNT in the plastic stage may be attributed to the difference in loading conditions on SWCNT caused due to absence and presence of water molecules respectively. The snapshots of the torsional deformation of water submerged SWCNTs are shown in Fig. 7. In this figure, only the carbon atoms comprising the SWCNT are shown and the water molecules surrounding the SWCNT have been made invisible for the ease of analysis. It can be seen from this figure that the SWCNT maintains its stable structure when no torsional twisting is applied at the end atoms of the SWCNT. When the end atoms of the SWCNT are subjected to the torsion of 30°, the resulting structure shows small changes compared to that of the initial SWCNT before torsion. Higher torsional angles result in screw twisted configurations of the SWCNT.

The radial distribution of water molecules surrounding a (10, 0) SWCNT submerged in the simulation box consisting of water molecules is shown in Fig. 8. It can be noted from this figure that the first peak occurs at small radial distances of SWCNT not exceeding 0.05 nm. This means that the water molecules inside SWCNT are more concentrated near the center of the SWCNT. We also see that the radial distribution of the first peak decreases while increasing the angle of twist. This is because twisting of SWCNT results in squeezing of water molecules from the interior of the SWCNT to outer space in simulation box. This could also be a possibility as to why we can see an increase in the second characteristic peak of water molecules outside

Fig. 8 RDF of water molecules during torsional loading of a (10, 0) SWCNT submerged in simulation box consisting of water molecules for different angles of twisting displaced vertically for clarity. The torsional loading of SWCNT results in wall contraction of the SWCNT.
Fig. 9 Torsional characteristics of armchair and zigzag SWCNTs submerged in water at temperature $T = 300$ K.

the wall of SWCNT. Similarly, as angle of twist increases, the occurrence of second characteristic peak also decreases. This is because the contraction of the SWCNT due to twisting increases van der Waal’s distance between carbon and water molecules that will further push the water molecules towards the wall of the SWCNT.

**Effect of SWCNT geometry**

In this section we investigate the effect of SWCNT geometry on the torsional properties of SWCNT submerged in water. The effect of chirality is analyzed by investigating the torsional characteristics of armchair and zigzag SWCNT. The effect of size is analyzed by varying the aspect ratio of the considered SWCNTs. We employed $(10, 10)$, $(5, 5)$, $(18, 0)$ and $(10, 0)$ SWCNTs of three aspect ratios, viz. 3.69, 5.53 and 7.37. The SWCNTs are then submerged in a simulation box filled with water molecules of density $0.997 \text{ g/cm}^3$ (approx. 1 g/cm$^3$) and subjected to torsion. The variation in the torsional characteristics of the armchair and zigzag water submerged SWCNTs are shown in Fig. 9. We note from this figure that regardless of chirality, the torque decreases with reducing diameter of the SWCNT. This is due to the reason that reducing the diameter of SWCNT decreases its cross sectional area which ultimately lowers down the maximum torque of the SWCNT. Figure 9 also shows that the armchair water submerged SWCNTs can withstand slightly higher torque compared to that of zigzag SWCNTs. This observation is in quantitative agreement with the study on torsional properties of free form of SWCNTs reported by Zhang et al. [12]. It can be noted from Fig. 10 that the application of torsional loading in SWCNTs induces radial wall contraction of the SWCNT. The wall contraction of an armchair SWCNT is comparatively lower than that of zigzag SWCNT. The bonds in armchair SWCNT are arranged parallel to the radial circumference of SWCNT which could result in better resistance to the torsional deformation.

**Effect of location and number of defects on SWCNT**

The effect of location and number of defects on elastic properties of water submerged SWCNT is discussed in this section. For this purpose we considered $(5, 5)$ and $(10, 10)$ SWCNTs of aspect ratio 7.37 under torsional loading as shown in Fig. 1. The mechanical characteristics of the water submerged SWCNTs with different defect density are shown in Fig. 11. The presence of defects strongly impact the torsional properties of water submerged SWCNTs which is consistent with the observations on free form SWCNTs [12]. Additionally, it can be seen that the dependence of torque on the presence of vacancy defects is more sensitive to the diameter of SWCNT. For instance, the percentage drop in maximum torque for a $(5, 5)$ SWCNT due to the presence of 3 vacancy defects in axial direction is about 41%. This drop is significantly much higher than that of a $(10, 10)$ SWCNT with similar vacancy configuration that experience a drop of about 16%. This is because the $(5, 5)$ SWCNT has a smaller diameter and the defect region occupies a much larger portion when compared to that of the $(10, 10)$ SWCNT with a bigger diameter.

We also investigated the effect of defect location on the torsional response of water submerged SWCNTs. By varying the defects along the axial or radial direction of SWCNT (Fig. 2), the dependence of defect distribution on the torsional response can be studied. We note from Fig. 11 that the defects placed along the radial direction of SWCNT has a significant impact on the torsional response of SWCNT compared to the axial defects. Defects along the radial direction are arranged parallel to the loading direction, which will aid in breaking and shear of SWCNTs more easily in contrast to that of the axial defects that are perpendicular
to the torsional loading direction. This is an important factor that needs to be considered while designing SWCNT based fluid delivery systems. Adequate care must be taken to ensure that the radial defects are kept to the minimum to ensure greater stability of SWCNT based nano-fluidic devices.

Analysis of SWCNT torsion with continuum mechanics theory

The torsional stiffness \( K \) of the SWCNTs in our study is computed in MD simulation method by obtaining the variation of strain energy \( E \) with the torsional angle \( \theta \). The torsional stiffness is then defined by the following equation \([11,15]\)

\[
K = L \frac{d^2E}{d\theta^2}
\]

where \( L \) is the length of the SWCNT.

The torsional stiffness of the free form and water submerged \((10, 10)\) and \((5, 5)\) SWCNTs of aspect ratio \( L/D = 7.37 \) is computed using Eq. (7). The results are then plotted against the respective radius of the \((10, 10)\) and \((5, 5)\) SWCNTs and is presented in Fig. 12. It can be noted from this figure that the torsional stiffness varies marginally due to the presence of surrounding water molecules. This observation is consistent with the results reported in earlier studies of Ref. \([16,17]\) for the case of SWCNTs interacting with various gases and metals. For the case of freeform SWCNTs, the torsional stiffness of \((10, 10)\) SWCNT has increased by 670% compared to that of \((5, 5)\) SWCNT. Similar percentage variations can also be observed for the case of \((10, 10)\) and \((5, 5)\) SWCNTs that are submerged in water.

The computed torsional modulus of various free form and water submerged SWCNTs of aspect ratio 7.37 under torsion is depicted in Table 2. It can be observed

![Fig. 11 Variation of mechanical properties of \((10, 10)\) and \((5, 5)\) SWCNTs of aspect ratio \( L/D = 7.37 \) with increasing the vacancy defect concentration along the axial and circumferential direction.](image1)

![Fig. 12 Torsional stiffness of free form \((K_{FF})\) and water submerged \((K_{WS})\) SWCNTs depicted for various radius of SWCNTs considered in our study.](image2)
that the interaction due to surrounding water molecules decreases the torsional modulus of SWCNTs. It is important to note that the trend of torsional modulus variation for armchair and zigzag SWCNTs is agree well with the earlier results obtained by MD simulation studies [10,12,15]. However, the computed torsional modulus is lesser than the values predicted using continuum theory [39] and experiment [9]. The corresponding shear modulus values obtained in these literature studies is given in Table 3.

Table 2  Torsional modulus of freeform and water submerged SWCNTs

| Geometry | Free form SWCNT (TPa) | Water submerged SWCNT (TPa) | Percentage variation (%) |
|----------|-----------------------|----------------------------|--------------------------|
| (10,10)  | 0.378                 | 0.351                      | 7.1                      |
| (5,5)    | 0.335                 | 0.304                      | 9.2                      |
| (18,0)   | 0.367                 | 0.338                      | 7.9                      |
| (10,0)   | 0.329                 | 0.302                      | 8.2                      |

Table 3  A summary of torsional modulus of SWCNTs reported in literature

| Authors             | Employed technique | Torsional modulus (TPa) |
|---------------------|--------------------|-------------------------|
| Zhang et al. [12]   | MD simulation      | 0.381                   |
| Jeong et al. [15]   | MD simulation      | 0.338                   |
| Wang et al. [10]    | MD simulation      | 0.36 ~ 0.48             |
| Lu and Zhang [39]   | Nanoscale continuum theory | 0.41 ~ 0.54         |
| Hall et al. [9]     | Experimental method | 0.41 ± 0.36             |
| Present authors     | MD simulation      | 0.329 ~ 0.378           |

Elastic properties of capped SWCNT

The torsional properties of capped SWCNTs encapsulated with water molecules is discussed in this section. For this purpose, we chose a (10, 10) capped SWCNT with aspect ratio of 7.37 encapsulated with water molecules of three different densities ($\rho$) viz. empty ($\rho = 0$ g/cm$^3$), half-filled ($\rho = 0.49$ g/cm$^3$) and fully-filled ($\rho = 0.98$ g/cm$^3$) SWCNT. The torsional properties of such water encapsulated SWCNTs were then investigated in free form and water submerged states. The torsional response of the free form capped SWCNTs with water molecules of different encapsulation densities is shown in Fig. 13. We note from this figure that the torsional characteristics of half-filled SWCNTs are almost similar to that of an empty SWCNT. The interaction force exerted by water molecules on the half-filled capped SWCNT is depicted in Fig. 14. It can be seen from this plot that the water molecules exert an average of 1.18 nN/nm, which is insignificant to cause any variation in the torsional response of half-filled SWCNT. Additionally, for the case of a fully-filled SWCNT, the torsional response shows a marked difference compared to that of the empty and half-filled SWCNTs. It can be noted from Fig. 13 that prior to torsion, the fully-filled SWCNT can withstand more torque compared to that of the empty and half-filled SWCNT. This observation is consistent with the earlier reports of the torsional response of SWCNTs filled with SWCNTs [15], gases [17] and metals [16]. It is worth noting that when torsional strain is about 0.06, there is a sudden drop in torque of a fully-filled SWCNT in contrast to that of the empty and half-filled SWCNTs. This can be explained by analyzing the snap shot of the torsional deformation of fully-filled SWCNTs as depicted in Fig. 15. The torsional twisting of SWCNT
results in contraction of tube walls in the radial direction of the SWCNT (as shown in Fig. 10). This contraction result is in compression of water molecules. Because we cannot compress the water molecules further, therefore the water molecules have nowhere to escape, but to break open the walls of SWCNT which results in sudden drop in the torsional response of the fully-filled SWCNT. Additionally, the release of encapsulated water molecules from the fully-filled SWCNT due to torsional loading can prove to be a useful mechanism for nano-level fluidic devices aimed at targeted drug-delivery.

It is also useful to investigate the torsional response of water-encapsulated capped SWCNTs submerged in water. The variation in the torsional response of the water submerged capped SWCNTs are compared with that of the free form SWCNTs as shown in Fig. 16. Figure 16 indicates that the effect of surrounding water molecules reduces the torsional properties of water encapsulated SWCNTs. Based on our foregoing discussion, presence of surrounding water molecules increases the strain of the capped SWCNT which affects the torsional resistance of capped SWCNT. Hence, it can be concluded from this study that dense packing of water molecules can result in breaking and fracture of capped SWCNTs. Furthermore, the interaction of water molecules outside the capped SWCNT can affect the overall torsional response of capped SWCNTs irrespective of the filling concentrations.

**Conclusions**

In this paper, the torsional characteristics of water submerged SWCNT has been studied using MD simulation method. The understanding of torsional properties of SWCNT in hydrodynamics environment is crucial for optimizing the performance of nano-fluidic based NEMS devices. The studies show that the torsional characteristics of SWCNTs reduce due to the interaction of surrounding water molecules. The results also indicate that the torsional properties of SWCNTs with defects are more sensitive to the defect distribution and diameter of the SWCNT. Furthermore, for the case of capped SWCNTs, dense filling of water molecules in an
SWCNT will result in breaking and fracture of SWCNT under torsion resulting in release of encapsulated water molecules. This mechanism could be useful in the design of SWCNT based nano-drug delivery devices. The results obtained from our studies will provide valuable insights for the application of CNTs for nano-level processes involving water molecules such as nano-fluidic devices, NEMS, and drug delivery devices.

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Controlling the Cassie-to-Wenzel Transition: an Easy Route towards the Realization of Tridimensional Arrays of Biological Objects

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Abstract: In this paper we provide evidence that the Cassie-to-Wenzel transition, despite its detrimental effects on the wetting properties of superhydrophobic surfaces, can be exploited as an effective micro-fabrication strategy to obtain highly ordered arrays of biological objects. To this purpose we fabricated a patterned surface wetted in the Cassie state, where we deposited a droplet containing genomic DNA. We observed that, when the droplet wets the surface in the Cassie state, an array of DNA filaments pinned on the top edges between pillars is formed. Conversely, when the Cassie-to-Wenzel transition occurs, DNA can be pinned at different height between pillars. These results open the way to the realization of tridimensional arrays of biological objects.

Keywords: Superhydrophobic patterned surfaces; Cassie-to-Wenzel transition; DNA arrays

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Introduction

In the last decades a large effort has been devoted to the realization of microstructured superhydrophobic surfaces, exhibiting both high contact angles (larger than 140°-150°) and low roll-off angles [1-4]. Thanks to their wetting properties, these surfaces are of increasing interest in a variety of fields including self-cleaning and antifouling surfaces, film coating, MEMS/BioMEMS and microfluidics [5-8].

Two wetting regimes are possible for a water droplet deposited on these surfaces: the Cassie-Baxter state (often referred as suspended state) and the Wenzel state (often referred as impaled state).

In the Cassie-Baxter state, the droplet bridges between surface features with trapped air underneath. This wetting regime competes with the Wenzel state, where the liquid wets entirely the surface and no air is trapped.

However, a transition between the Cassie-Baxter state and the Wenzel state can easily occur for several reasons, including droplet evaporation [9-12].

For most of the technological application this transition is highly detrimental and needs to be prevented. The Cassie state indeed minimizes the water adhesion, the contact angles hysteresis (the difference between advancing and receding contact angles) and the water roll-off angle [13-15].

These characteristics are key factors in the realization of self-cleaning surfaces. Hence, in many practical applications the Cassie state is preferred over the Wenzel state.
As a consequence, many studies have been performed to shed light on the mechanism behind this transition with the aim to realize a suspended state as stable as possible [16].

To this purpose, Papadopoulos and co-workers recently imaged the implement dynamics of a drop deposited on a pillar array by confocal microscopy, detailing the Cassie-to-Wenzel transition while it is occurring. Under evaporation condition, they demonstrated the drop rim recedes via stepwise depinning from the edge of the pillars. Once the pressure becomes too high, the drop slowly impales the texture. As soon as the rim touches the substrate, a complete wetting occurs in the millisecond timescale [17].

However, since most of the research effort has been devoted to preserve a stable Cassie state, the possible technological applications of the Cassie-to-Wenzel transition are largely unexplored.

In this paper we provide evidence that this transition – despite its detrimental effect on the surface wetting properties - can provide an effective micro-fabrication strategy to obtain highly ordered tridimensional arrays of biological objects using a bottom-up approach. Toward this end, we fabricated a patterned superhydrophobic surface, where we deposited a droplet containing genomic DNA. We observed that, when the droplet wets the surface in the Cassie state, an array of DNA filaments pinned on the top edges between adjacent pillars is formed. Conversely when the Cassie-to-Wenzel transition occurs, DNA bundles can stick at different height between pillars.

Materials and methods

Fabrication of superhydrophobic surfaces

Two Different pillar geometries have been tested, namely square-shaped pillars and saw-shaped pillars. The former was fabricated on silicon substrate by electron beam lithography (Vistec EPBG-5HR acceleration voltage: 100keV) and Inductive Coupled Plasma (ICP) Si etching. A 1.2 µm thick layer of Shipley UVIII electronic resist was spun on the silicon surface, exposed with a dose of 25 µC/cm² and developed. A thin Cr film (30 nm) was then deposited and lifted off to define the device pattern: an array of pillars (5 µm side; 14 µm pitch). The device pattern was transferred on the substrate by a two-steps ICP Si etching (First step: protection, pressure: 100 mTorr, Ar:30 sccm, C4F8:187 sccm, ICP: 600 Watt, t: 2s; Second step: etching, pressure: 100mTorr, Ar:100 sccm, SF6: 90 sccm, Cathode bias: 70V, ICP: 500 Watt, t:10s). As for the saw-shaped pillars array, a 400 nm thick layer PMMA 950K 9% was spun on a Si wafer, exposed with a dose of 700 µC/cm² and developed. A 30 nm thick Cr film was then deposited by e-gun assisted evaporator and lifted off. The device pattern was transferred on the substrate by the same ICP etching procedure. After cleaning in Piranha solution (H2SO4/H2O2=3:1), both microstructured Si wafers were silanized with 10% trimethylchlorosilane in toluene to impart the superhydrophobic behavior. This fabrication step is fully discussed in reference [18].

DNA isolation

DNA isolation was performed according to standard phenol/chloroform protocol. To 1 mL blood sample (EDTA, heparin, citrate), 0.8 mL 1X SSC buffer was added and mixed. Sample was centrifuged for 1 minute at 12,000 rpm and the supernatant discarded. Then 1 mL of 1X SSC buffer was added. The sample was vortexed and centrifuged for 1 minute, and then the supernatant was removed. 375 µL of 0.2M NaOAc was added to pellet and vortexed briefly. Then 25 µL of 10% SDS and 5 µL of protease K (20 mg/ml in H2O) (Sigma P-0390) were vortexed briefly and incubated for 4 hours at 55°C. 120 µL phenol/chloroform/isoamyl alcohol were added and vortexed for 30 seconds. The sample was centrifuged for 2 minutes at 12,000 rpm in a microcentrifuge tube. The aqueous layer was removed and transferred to a new 1.5 mL microcentrifuge tube, and 1 mL of cold 100% ethanol was mixed and incubated for 15 minutes at −20°C. Then the samples were centrifuged for 2 minutes at 12,000 rpm in a microcentrifuge. The supernatant was decanted and drained. 180 µL 10:1 of TE buffer were added to the sample, and then the sample was vortexed and incubated at 55°C for 10 minutes.

20 µL of sodium acetate (2M) were added and mixed to the sample. Then 500 µL of cold 100% ethanol was added and centrifuged for 1 minute at 12,000 rpm in a microcentrifuge. The supernatant was decanted and the pellet was rinsed with 1 mL of 80% ethanol. After 1 minute centrifugation at 12,000 rpm in a microcentrifuge, the supernatant was decanted and the pellet dried. The pellet was resuspended by adding 200 µL of 10:1 TE buffer. After incubation overnight at 55°C, the sample was vortexed periodically to dissolve the genomic DNA. The DNA concentration was assayed by spectrophotometer (260 nm) and was 150 ng/mL.

Results and discussion

Figure 1 shows two SEM micrographs of stretched DNA bundles obtained by the deposition of 5 µL genomic DNA solution on a superhydrophobic surface previously wetted in the Cassie state. After the droplet deposition, the patterned surface was tilted by 10° and the droplet was allowed to completely evaporate before measuring.
Two superhydrophobic surfaces with different pillar geometries were used: a square shaped geometry containing small protrusions as shown in Fig. 1(a) and a saw-shaped geometry in Fig. 1(b). In both cases, DNA filaments are suspended above pillars and precisely pinned to the pillars’ asperities.

Figure 2(a) shows a SEM micrograph of an ordered array of DNA bundles stretched on a superhydrophobic surface with saw-shaped pillars. Two different regions can be clearly distinguished: on the left, three perfectly aligned and suspended DNA bundles can be recognized. The mechanism behind the deposition of aligned and suspended filaments of biological objects is fully detailed in reference [19-22]. Briefly, under evaporation conditions, the retracting drop edge at the three phase contact line stretches the DNA filaments along the de-wetting direction. While receding, the droplet forms capillaries which precisely pin to the pillar protrusions allowing us to control the bundles position and orientation with a high level of accuracy. During this process the drop wets the surface in the Cassie state and therefore the stretched DNA bundles are pinned exclusively on the top of the pillars.

On the right part of the figure, a large DNA deposit can be observed. As demonstrated in reference 9 and 24, the presence of this deposit indicates the occurrence of a Cassie-to-Wenzel transition. The solute indeed remained not only at the top of the pillars but also at the bottom, proving that the drop sank inside the texture.

Figure 2(b) shows a SEM micrograph of the whole DNA deposit. The deposit has a circular shape with a radius of few hundreds of microns.

In Fig. 2(c) an enlarged details of the outer rim of the deposit are shown. Two stretched DNA bundles suspended above the solute deposit are highlighted by red arrows.

The presence of these filaments can be explained by taking into account the peculiar Cassie-to-Wenzel transition dynamics.

As the drop volume reduces, the drop contact line slides inward, with a consequent decrease in the rim diameter. During its motion, the contact line stretches DNA bundles above pillars (this step is schematically represented in Fig. 3(a) and Fig. 3(b)). However, as soon as the Cassie-to-Wenzel transition occurs, it is accompanied by a decrease of the apparent contact angle by a few degrees. Therefore, in order to conserve the drop volume, the contact line jumps back.
outward with a consequent increase in the rim diameter (Fig. 3(c)). Then the contact line remains pinned during further evaporation causing the solute deposition also in the region where, immediately before the transition, DNA filaments have been stretched above pillars (Fig. 3(d)). The above described wetting dynamics fully explains the coexistence in the same sample region of suspended DNA filaments and the DNA deposit observed in Fig. 2(c).

Before the Cassie-to-Wenzel transition

![Schematic view of the Cassie-to-Wenzel transition leading to the DNA deposit formation.](image)

After the Cassie-to-Wenzel transition

![DNA deposit](image)

Fig. 3  (Panel a) Schematic view of the Cassie-to-Wenzel transition leading to the DNA deposit formation. Under evaporation conditions, when the drop is in the Cassie state, the drop contact line slides inward, with a consequent decrease in the rim diameter ($d_0 > d_1$). The rim motion stretches DNA bundles above pillars (panel a and b). After the transition the drop rim jumps back outward with a consequent increase in the rim diameter ($d_2 > d_1$) (Panel c). The contact line remains pinned during further evaporation causing the solute deposition (Panel c and d).

In Fig. 4 two large ordered arrays of stretched DNA bundles are shown. These arrays are obtained before (panel a) and after (panel b) the occurrence of the Cassie-to-Wenzel transition. In the latter case the SEM micrograph has been acquired inside the DNA deposit. It is worth stressing here that DNA deposits are generally not homogenous. Therefore both ordered regions (as shown in Fig. 4(b)) and disordered regions (as in Fig. 2(a) and 2(c)) can be found. This phenomenon is still not fully understood and therefore it needs further in-depth studies. However, in this case, we can estimate a yield for the ordered state of about 15%. Before the transition, DNA bundles are suspended above pillars and precisely pinned to the pillar protrusions. The suspended DNA bundles are monodisperse in sizes, showing a diameter distribution ranging between 20 nm and 30 nm [19].

After the transition, DNA bundles are not suspended above pillars anymore (Fig. 2(c)) in Fig. 4(b). Conversely, they stick to the lower part of the pillars. An enlarged detail of the sticking point is shown in Fig. 5(a), where two DNA bundles are stuck at about 6 microns and 9 microns from the pillar base. As can be clearly observed in Fig. 5(b), after the transition, bundles are larger than those in Fig. 4(a), showing a diameter of few hundreds of nanometres. This is probably due to the fact that DNA concentration in solution increases as the drop volume reduces.

![SEM micrograph of two large ordered arrays of stretched DNA bundles. These arrays are obtained before (Panel a) and after (Panel b) the occurrence of the Cassie-to-Wenzel transition. The scale bar corresponds to a length of 5 µm. The ordered array shown in panel b has been acquired in the square-shaped region highlighted in Fig. 2(b).](image)

It can be noted that DNA bundles in Fig. 4(b) and Fig. 5(a) are not deposited at the pillar base. This fact indicates that the portion of the drop responsible of the bundles formation was in a metastable Cassie state [24]. In this state Laplace pressure is insufficient to
overcome the energy barrier required to completely wet the surface, but it is high enough to wet a portion of the pillars wall. This consideration suggests that DNA bundles can be deposited at different height by controlling Laplace pressure as schematically represented in Fig. 5.

![Fig. 5](image_url)

**Fig. 5** (Panel a) SEM micrograph of the sticking point of two DNA bundles. (Panel b) SEM micrograph of a single DNA bundle obtained after the occurrence of the Cassie-to-Wenzel transition. Bundle diameter is 230 nm. (Bottom) Schematic view of the role of the Laplace pressure in the formation of the DNA bundles. The scale bar corresponds to a length of 1 µm.

In particular several models have been proposed to calculate the drop penetration depth between pillars. Jung and Bhushan proposed a very simple model for an ordered array of circular pillars. According to their model, the maximum droop δ of the droplet can be calculated by the formula \( \delta = (\sqrt{2P - D})^2/(8R) \), where \( R \) is the radius of the drop, \( D \) is the pillar diameter and \( P \) is the array pitch [25].

This equation suggests that several parameters can be varied to control the drop penetration depth and therefore the DNA sticking point. In particular, Laplace pressure can be tuned by varying the initial drop volume according to its radius \( R \). Moreover, further design parameters that can be varied are the pillar sizes (such as the pillar diameter) and the array pitch \( P \). The control of these parameters can be easily achieved thanks to the standard lithographic techniques, and can provide a fine tuning of the sticking point of the DNA bundles.

Our findings suggest that a tridimensional ordered array of DNA molecules can be obtained by the deposition of several droplet on the same substrate by varying the droplet initial position and volume, and the latter controlling the Laplace pressure.

The precise control of the DNA position demonstrated here can be exploited for the development of novel micro-devices with potential application in a wide range of genetic studies. The fabrication of large ordered DNA arrays has been proposed as a promising strategy to perform highly automated analysis in the next-generation DNA chips [26]. Moreover thanks to its high aspect ratio, DNA is also an attractive candidate for the realization of highly aligned 1D nanostructure, showing the potential to address many challenges in electronics [27-29]. To this purpose, the precise controlling over the DNA positioning in the three directions of the space could help the integration of functional DNA filament into devices, since the integration process usually starts from the fabrication of metallic electrodes followed by the alignment of DNA above the electrodes.

Beside DNA applications, the ability to precisely position biological objects in a defined portion of space, could have a positive impact on the study of blood proteins, such as ferritin and low density lipoproteins, which are often available in very limited quantity [30-35]. Furthermore, this system could be particularly important as a scaffold for the growth of controlled networks of biological molecules [36-38].

**Conclusions**

In this paper we demonstrate the possibility to realize highly ordered arrays of stretched DNA bundles by using superhydrophobic patterned surfaces initially wetted in the Cassie-Baxter state. To this purpose we fabricated two superhydrophobic pillar surfaces with different pillar geometries. In both cases, the pillars were decorated with small features resembling tips. These structures allowed us to obtain a fine control over the DNA bundles position in the plane parallel to the device surface.

Moreover we investigated the possibility to exploit the Cassie-to-Wenzel transition in order to control also the DNA sticking point in the third direction of the space. In particular we found that, when the superhy-
drophobic surfaces are wet in the Cassie state, the DNA bundles stick exclusively above pillars. However, under evaporation conditions, a transition between the Cassie state and a Wenzel state occurs as a consequence of an increase in the Laplace pressure which, in its turn, is due to a decrease in the drop radius. After the transition, a large ordered array of DNA bundles can be found. However, DNA bundles do not stick on the pillar top surface; they stick on the lower part of the pillars instead.

These results open the way to realization of tridimensional self-assembled arrays of DNA bundles showing the potential to address challenges in several fields including DNA electronics and the development of novel DNA chips for genetic analysis.

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Unique Characteristics of Vertical Carbon Nanotube Field-effect Transistors on Silicon

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Abstract: A vertical carbon nanotube field-effect transistor (CNTFET) based on silicon (Si) substrate has been proposed and simulated using a semi-classical theory. A single-walled carbon nanotube (SWNT) and an n-type Si nanowire in series construct the channel of the transistor. The CNTFET presents ambipolar characteristics at positive drain voltage ($V_d$) and n-type characteristics at negative $V_d$. The current is significantly influenced by the doping level of n-Si and the SWNT band gap. The n-branch current of the ambipolar characteristics increases with increasing doping level of the n-Si while the p-branch current decreases. The SWNT band gap has the same influence on the p-branch current at a positive $V_d$ and n-type characteristics at negative $V_d$. The lower the SWNT band gap, the higher the current. However, it has no impact on the n-branch current in the ambipolar characteristics. Thick oxide is found to significantly degrade the current and the subthreshold slope of the CNTFETs.

Keywords: Carbon Nanotube; Field-effect Transistors; Semi-classical Simulation

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Introduction

The rapid development of information technology requires a smaller MOSFET (Metal-Oxide-Semiconductor Field-Effect Transistor), the main building block in microelectronics. The shrinkage of the MOSFET must follow the Dennard’s scaling theory [1], i.e., the vertical dimensions must be scaled down with the lateral dimensions to avoid the so-called short channel effect. This means the channel thickness must be scaled down together with the channel length. However, this shrinkage will stop when it meets the physics limit. It has been reported that the bulk silicon MOSFET will not perform reliably at sub-10 nm gate length [2]. New material or new transistor structure must be developed at the end of scaling road map. Single-walled carbon nanotubes (SWNTs) have been considered to be one of the most promising materials for silicon due to their excellent electrical properties and ultrathin body [3, 4]. The sub-2 nm diameter of the SWCNT makes it easier to satisfy the body thickness requirement for a 5 nm node FET while it is impossible for Si technology [2, 5]. Recently-developed CNTFETs with single SWCNT and sub-10 nm channel length have shown much better performance than the best competing silicon devices [6] in switching behavior and the normalized current density at a low operating voltage of 0.5 V. More importantly, the output characteristics have shown clear device saturation behavior at a drain voltage less than 0.4 V, much lower than the 0.64 V predicted by the ITRS Roadmap for 5 nm node transistors [7], showing the power benefit of CNTFETs compared to silicon transistors.

Despite the promising progress in the performance of the CNTFETs, the fabrication of short channel CNT-
FETs still rely on some high cost and low throughput techniques, for example, electron beam lithography. To solve this problem, we have developed vertical carbon nanotube field-effect transistors (CNTFETs) recently [8, 9]. The unique feature of this kind of CNTFETs is that the source and drain of the transistors are vertically stacked with a dielectric sandwiched in between. This configuration makes it easier to fabricate short channel CNTFETs because the channel length is precisely the thickness of the dielectric layer between the source and drain. Short channel length in the range from several nanometers to sub-micrometers can be fabricated without using those complicated techniques. Another advantage of this structure is that it can improve the integration density since the vertical transistors occupy less space than their planar counterpart [10]. Furthermore, it offers an approach to integrate carbon nanotubes to silicon if the vertical CNTFETs are fabricated on silicon. This fabrication does not need to change the silicon technology. By using SiN$_x$ to isolate the Si source and metal drain contact, we have successfully fabricated vertical CNTFETs on Si [9], as schematically shown in Fig. 1(a). The channel length and channel width are 600 nm and 2 µm, respectively. The mobility of our CNTFETs is better than other group’s results which are extracted from planar CNTFETs fabricated using similar CNT solution [11, 12]. Interestingly, the vertical CNTFETs have shown some characteristics significantly different from those CNTFETs fabricated with metal source and drain. The transfer characteristics of the vertical CNTFETs on Si can be either ambipolar or unipolar (n-type or p-type) depending on the sign of the drain voltages [9]. The n-type/p-type characteristics are defined by the Si doping type. We have simulated these phenomena using a semi-classical model in our former paper [9]. The calculation results are well consistent with the experimental observations. However, the variations of Si doping level and carbon nanotube band gap have not been taken into consideration. In this paper, we will present the influence of different alignment of Si Fermi level and different carbon nanotube band gap, and the impact of the oxide thickness on the performance of the CNTFETs in detail. It is very useful for designing a perfect vertical CNTFET on Si.

1 Methods

The performances of the vertical CNTFETs on Si are simulated using a semi-classical method [13-17]. The configuration of the CNTFET is schematically illustrated in Fig. 1(b). Source and drain are vertically stacked, isolated by SiN$_x$. Since the gate overlapped with part of the silicon contact in experiment, as shown in Fig. 1(a), the conductance of this part is also modified by the gate voltage. We therefore propose that the channel is composed of a SWNT and a Si nanowire in the calculation. Two metal contacts are used as source and drain of the CNTFET. A grounded right gate electrode (not shown here) is used for the calculations. It is 190 nm away from the HfO$_2$ gate dielectric layer.

As we know, CNTFETs work as Schottky barrier (SB) transistors [18]. The current is controlled by thermal assisted tunneling through the SBs at the contact. It has been reported that the contact resistance is larger than the channel resistance for ultra-scaled CNTFETs [5]. This means that the contact plays a more important role than scattering in the channel for the CNTFETs with a short channel. Therefore, we suppose the carrier transport in SWNT and the Si channel is ballistic for the simplicity of calculation. This assumption may cause that the calculation result is somewhat higher than that of the actual transistors. The current is given by the Landauer-Büttiker formula.

$$I = \frac{4e}{h} \int [F(E) - F(E + eV_d)]T(E)dE, \quad (1)$$

where $V_d$ is the drain voltage, $F(E)$ is the Fermi function and $T(E)$ is the energy-dependent transmission through the SB between the SWNT/Si and electrodes. $T(E)$ can be estimated using the Wentzel-Kramers-
Brillouin (WKB) approximation

\[ T(E) = \exp \left[ -2 \int_{z_1}^{z_2} k(z)dz \right] , \tag{2} \]

with the wave number

\[ k(z) = \frac{2}{3aV_0} \left( \left( \frac{E_g}{2} \right)^2 - [E + eV(z)]^2 \right)^{1/2} . \tag{3} \]

where \( a = 0.144 \) nm, \( E_g = 0.4 \sim 0.8 \) eV, and \( V_0 = 2.5 \) eV are the C-C bond length, the SWNT band gap and the tight-binding parameter, respectively. \( V(z) \) is the electrostatic potential along the channel and is obtained by numerically solving the Laplace equation. The integration is performed between the two classical turning points, \( z_1 \) and \( z_2 \) [13]. The temperature considered here is 300 K. The Fermi level, \( E_F \), of the source and drain contacts is assumed at the middle of the SWNT band gap. It locates 0.1\~0.3 eV below the conduction band of n-Si for a Si band gap of 1.1 eV.

2 Results and Discussion

We first consider the influence of Si Fermi level (or doping level) on the transfer characteristics of the CNTFETs. For the Si Fermi level locating 0.2 eV below the conduction band (\( \Delta E_{cf} = E_c - E_f = 0.2 \) eV), the calculated results are shown in Fig. 2. It presents ambipolar characteristics for \( V_d \geq 0.5 \) V and n-type characteristics for \( V_d \leq 0.25 \) V. These characteristics are the same as that for the CNTFETs with Si Fermi level locating 0.3 eV below the conduction band (\( \Delta E_{cf} = 0.3 \) eV) [9]. The reasons for these characteristics have been discussed in detail in reference 9.

Here, we focus on the differences between them. We find that both the n-branch current (at \( V_g > 0 \) V) and p-branch current (at \( V_g < 0 \) V) change with \( \Delta E_{cf} \). The minimum current points corresponding to different positive \( V_d \) also shift apparently. These can be seen much clearly in Fig. 3 which shows the transfer characteristics of the CNTFETs for three different \( \Delta E_{cf} \) at \( V_d = 0.75 \) V. The blue, red and black curves represent \( \Delta E_{cf} = 0.1 \) eV, 0.2 eV and 0.3 eV, respectively.

First, the n-branch current increases with decreasing \( \Delta E_{cf} \) and the p-branch current decreases with decreasing \( \Delta E_{cf} \). The minimum current for \( \Delta E_{cf} = 0.2 \) eV is significantly higher than those for the other two cases. These phenomena can be understood using a band diagram, as shown in Fig. 4.

![Fig. 3 Calculated transfer characteristics of the CNTFETs with different Si doping level at \( V_d = 0.75 \) V. The black, red and blue curves are for \( E_c - E_f = 0.3, 0.2 \) and 0.1 eV, respectively. The band gap of the SWNT is 0.6 eV.](image-url)

At a positive \( V_d \), the band of the SWNT at the drain side bends downwards. The center channel band shifts upwards under a negative \( V_g \), leading to a thin SB between SWNT and the drain. If it is thin enough, holes can be injected from the drain to channel, and be collected by the source, contributing to the p-branch current of the ambipolar characteristics. Since the Si band...
gap (1.1 eV) is fixed, the valence band for $\Delta E_{cf} = 0.2$ eV is much lower than that for $\Delta E_{cf} = 0.3$ eV, as shown in Fig. 4. This builds a larger barrier for holes. At the same positive $V_d$, the lower valence band blocks more holes injected from the drain. As a result, the hole current decreases with decreasing $\Delta E_{cf}$, as shown in Fig. 3.

The n-branch current in the ambipolar characteristics is contributed by source electrons at a positive $V_d$. The center channel band shifts downwards when a positive gate voltage is applied. As the increases of the gate voltage, the SB between the source and the Si becomes transparent, allowing electron injection from the source to channel. These electrons are collected by the drain, forming n-branch current. The current depends on the shape of the SB which is defined by the alignment of the Si Fermi level and the gate voltage. At the same gate voltage, the alignment of the Fermi level plays a key role in controlling the current. A smaller $\Delta E_{cf}$ means the Fermi level is much closer to the conduction band, and both the electron density and the transmission probability through the SB are higher. Therefore, the electron current increases with decreasing $\Delta E_{cf}$, as shown in Fig. 3.

The minimum current happens at the point where the n-branch current and the p-branch current meet together. Therefore, the position of this point depends on the relative height of the two branch currents. Since the p-branch current increases with increasing $\Delta E_{cf}$ and the n-branch current decreases with increasing $\Delta E_{cf}$, the p-branch current for $\Delta E_{cf} = 0.1$ eV is much lower than its n-branch counterpart, and hence the minimum current point is close to the p-branch part. The situation for $\Delta E_{cf} = 0.3$ eV is in contrast to that for $\Delta E_{cf} = 0.1$ eV, the minimum current point is thus on the opposite direction of the former one. The n-branch current and p-branch current for $\Delta E_{cf} = 0.2$ eV are almost symmetric with $V_g$, leading to a minimum current point closing to $V_g = 0$ V, and the minimum current is apparently higher than those for the other two cases.

The band gap of carbon nanotubes has important influence on the characteristics of the planar CNTFETs [19]. It is useful to know the performance of our vertical CNTFETs with different band gap. Given $\Delta E_{cf} = 0.3$ eV for Si, the transfer characteristics of the CNTFETs with different band gap are shown in Fig. 5. For the ambipolar characteristics at positive drain voltage, for example, $V_d = 1$ V, the n-branch current keeps unchanged for three different SWNT band energies, as shown in Fig. 5(a). This is because the n-branch current are contributed by the electron injection from the source, and the current depends on the SB between the source and Si. This SB does not change with the variation of the SWNT band gap. Therefore, the n-branch current are the same for the three different SWNT band gaps.

In contrast, the p-branch current in Fig.5(a) increases with decreasing SWNT band gap. The reason is that the p-branch current is contributed by hole injection from the drain when the SWNT band bends downwards at the drain for positive $V_d$. The current is controlled by the SB between the SWNT and the drain. It becomes transparent for holes when a small enough $V_g$ is applied. As the decrease of $E_g$, the distance between the sharp SB and the Fermi level of the SWNT decreases and both of the transmission probability and the hole density increase, leading to an increased hole current.

At a negative $V_d$, the SWNT band bends upwards at the drain. The electrons can be injected from the drain to the channel and form n-type current of the CNTFETs. The current depends on the shape of the SB between SWNT and the drain which define the transmission probability of the electron. This current also increases with decreasing $E_g$ of the SWNT, as shown in Fig. 5(b). The reason is the same as that for the influence of small $\Delta E_{cf}$ on the n-branch current at a positive $V_d$, but the SB between SWNT and the drain instead of that between the source and Si is considered.

![Fig. 5 Calculated transfer characteristics of the CNTFETs with different SWNT band gaps for $V_d = 1$ V (a) and $V_d = -0.75$ V (b). The blue, red, and black curves are for $E_g = 0.4, 0.6$ and 0.8 eV, respectively.](image-url)
here. As the decrease of the band gap, the Fermi level of the SWNT becomes much closer to the sharp point of the SB, resulting in a higher electron current.

We now turn to the impact of the oxide thickness on the performance of the transistors. One of the most important influences of oxide thickness is on the inverse sub-threshold slope of the CNTFETs. It is a measure of the switching speed of a transistor. The inverse sub-threshold slope is calculated using

\[ S = \frac{dV_g}{d(\log I_d)}. \]  

It increases almost linearly from 130 to 290 mV/dec if the oxide thickness is increased from 5 nm to 25 nm, as shown in Fig. 6.

\[ \text{Fig. 6} \quad \text{Inverse sub-threshold slope as a function of the oxide thickness. The Fermi level of Si locates 0.3 eV below the conduction band. The band gap of Si and SWNT are 1.1 eV and 0.6 eV, respectively.} \]

In addition to the inverse sub-threshold slope becoming worse, the drain current also degrades significantly with increasing of the oxide thickness. Since the CNTFETs are Schottky barrier transistors, the electric field distribution in the vicinity of the contact plays a critical role in the transistor performance. This electric field distribution is significantly affected by the oxide thickness if \( V_g \) and \( V_d \) are fixed. Figure 7 shows the \( I_d \) as a function of square root of the oxide thickness at \( V_d = 1 \) V and \( V_g = -1 \) V. It can be seen clearly that \( I_d \) decreases linearly with increasing square root of the oxide thickness. The current degrades more than one order of magnitude when \( t_{ox} \) increases from 5 nm to 25 nm.

\[ \text{Fig. 7} \quad \text{Drain current as a function of square root of the oxide thickness for the CNTFETs at } V_d = 1 \text{ V and } V_g = -1 \text{ V.} \]

3 Conclusion

The performance of a vertical CNTFETs on n-Si was investigated using a semi-classical model. The interesting characteristics of the transistors are that can be ambipolar or unipolar depending on the sign of drain voltage. The CNTFETs show ambipolar characteristics at positive drain voltage and n-type characteristics after reversing the sign of drain voltage. The ambipolar characteristics are affected by both the Si doping level and the carbon nanotube band gap while the n-type characteristics is mainly controlled by the carbon nanotube band gap. The n-branch current for the ambipolar characteristics can be increased by increasing the Si doping level while the p-branch current can be improved by decreasing the Si doping level or decreasing the carbon nanotube band gap. In addition, the current decreases linearly with increasing square root of gate oxide thickness. It can differ by one order of magnitude if the gate oxide thickness is increased from 5 nm to 25 nm. The turn-on performance quantified by sub-threshold slope simultaneously becomes much worse. This study showed the significant basic future for designing the vertical CNTFETs on Si.

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