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Multiple stacking of InGaAs/GaAs (731) nanostructures

Y. Z. Xie, V. P. Kunets, Z. M. Wang*, V. Dorogan, Y. I. Mazur, J. Wu and G. J. Salamo

We studied the multilayering effects of InGaAs quantum dots (QDs) on GaAs(731), a surface lying inside of the stereographic triangle. The surfaces after stacking 16 InGaAs layers were characterized with highly non-uniformity of QD spatial distribution. The bunched step regions driven by strain accumulation are decorated by QDs, therefore GaAs(731) becomes a good candidate substrate for the growth of QD clusters. The unique optical properties of the QD clusters are revealed by photoluminescence measurements. By adjusting the coverage of InGaAs, a bamboo-like nanostructured surface was observed and the quantum dots aligned up in clusters to separate the “bamboo” into sections.

Keywords: Quantum dots; MBE; High index surfaces; Nanostructures; Atomic force microscopy

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The morphological evolution during InGaAs deposition on GaAs high index surfaces has been a subject of numerous experimental efforts for better understanding of growth physics and potential applications of the resulted nanostructures [1-8]. Most of the researches chose a surface index located between two low index planes out of the three, (100), (110), and (111). In other words, the popular choice was a surface index on the sides of the stereographic triangle defined by the three low index planes [3]. For example, GaAs(311), one of the most popular choice, locates between the (100) and (111) planes. Both quantum wires and quantum dots (QDs) were observed during the InGaAs growth on GaAs(311) [1, 2, 6, 8].

Especially during the processes of stacking multiple layers of InGaAs/GaAs(311) QDs, two-dimensional or one-dimensional arrays of QDs were achieved [8]. In the letter, we study the multilayering effects of InGaAs nanostructures on GaAs(731), a surface index lying within the stereographic triangle. The (731) plane became particularly interesting after the dominating facets of InAs/GaAs(100) QDs were identified to this index [9]. Massive amount of investigations have been performed to reveal the growth behavior of InGaAs on GaAs(100) due to the importance of the resulted QDs for optoelectronic applications [10-12].

Experiments were carried out in a solid source Molecular Beam Epitaxy (MBE) 32P Riber system. The adopted GaAs(731) substrates were of n-type and epitaxial ready. After oxide desorption, a GaAs buffer layer of 500 nm was grown at the substrate temperature of 580°C. The GaAs growth rate was one monolayer per second (ML/s) under a constant As beam equivalent pressure (BEP) of 1×10⁻⁵ Torr. Sixteen layers of 7 ML In₀.₄Ga₀.₆As nanostructures were subsequently deposited, partitioned by GaAs spacer in different thicknesses, 120 ML, 70 ML, and 50 ML, respectively. The growth of In₀.₄Ga₀.₆As layer was performed at 540°C and As BEP of 4.4×10⁻⁶ Torr. After the growth of first 5 MLs of GaAs spacer, the growth temperature was rapidly increased up to 580°C and As BEP was turned back to 1×10⁻⁵ Torr. One more sample, grown in addition to the above series, had the GaAs spacer of 70 ML but the In₀.₄Ga₀.₆As coverage of 5.7 ML. Following the growths, samples were quenched to room temperature and then taken out of the MBE chambers for Atomic Force Microscopy (AFM) studies under ambient atmosphere. For optical properties of the samples, the photoluminescence (PL) measurements were performed at 10 K in a closed-cycle helium cryostat. The 532 nm line from a Nd:YAG (yttrium aluminum garnet) laser was used for continuous-wave (CW) PL excitation. The laser spot diameter

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was of ~20 m and the optical excitation power was in the range of $10^{-6}$ to $10^2$ mW. The PL signal from the sample was dispersed by a 0.5 m single-grating monochromator and detected by a liquid nitrogen (LN)-cooled InGaAs photodiode detector array.

Figure 1(a) shows an AFM image of the surface nanostructures after stacking 16 layers of 7 ML In$_{0.4}$Ga$_{0.6}$As spaced by 120 ML GaAs interlayer. The surface is characterized as QD decorated steps and large terraces free of QDs. While (731) was observed as the dominating facets bounding InAs/GaAs(100) QDs, the GaAs(731) surface itself is unstable. GaAs(1 1 5 2), just 2.28° away from GaAs(731), has lower surface energy according to theoretical calculation and was observed to be a stable surface by scanning tunneling microscopy (STM) [13]. Therefore, GaAs(731) is better described as a vicinal GaAs(1 1 5 2) surface, with straight steps along [-113] and ragged steps along [1-32]. The large terraces that are free of QDs shown in Fig. 1(a) resulted from the strain-driven step bunching. It is well documented that QDs prefer to stepped regions for nucleation and growth, especially ragged steps due to its active reaction. The observation in Fig. 1(a) demonstrates that GaAs(731) is a substrate candidate for the growth of InGaAs QD clusters. The corresponding PL spectrum from this sample is shown in Fig. 2. The strong and sharp peak about 1.38 eV can be assigned to the InGaAs wetting layer (WL) covering the whole surface. The assignment is consistent with the high peak energy and large terraces without QDs. Different from usual QDs reported where the PL peak from WL is weak, the carriers excited in InGaAs/GaAs(731) WL cannot find nearby QDs to relax and therefore recombine in WL giving rise to a strong signal. The relatively weak peak around 1.25 eV is expected from the clustered QDs.

By reducing the GaAs spacer thickness from 120 ML to 70 ML, more strain could transmit from the underneath InGaAs layer to the subsequent layers. As a result of the strain-driven mechanism, Fig. 1(b) reveals that the InGaAs QDs grow bigger in size and the free-of-QDs terraces disappear. Consistently, the WL peak disappears from its associated PL spectrum in Fig. 2 and the QD peak around 1.25 eV becomes dominant. Please notice, this peak is from 15 buried layers of QDs. The luminescence from the exposed layer of surface QDs is usually not notable, as in the PL spectrum form the sample with 120 ML spacer. However, the PL contribution from surface QDs can be enhanced as the spacer becomes thinner, as the consequence of carrier tunneling from the buried QDs to the surface. In line with the literature [6], the new developed PL peak around 1.0 eV is assigned to the layer of surface QDs.

With further reducing the GaAs spacer to 50 ML, more strain is accumulated to the surface and the QDs further ripen and even elongate along [-113], as revealed in Fig. 1(c). Due to the thinner spacer, more carriers are able to tunnel from buried layers to the surface. The PL peak from surface QDs becomes stronger, and eventually dominates the spectrum as shown in Fig. 2.

As noticed, the amount of accumulated strain is the key in determining the nanostructure configuration in Fig. 1 and the optical properties in Fig. 2. Specially, the sample with less accumulated strain shown in Fig. 1(a) demonstrated the potential of GaAs(731) for growing QD clusters. Therefore, to pursue better QD clusters, we introduce a new sample with less InGaAs coverage, 5.7 ML, in order to significantly reduce the
total strain. The result is shown in Fig. 3. Comparing Fig. 3(a) to Fig. 1(b), two samples with the same spacer thickness of 70 ML, we are able to rebuild the QD clusters by reducing the accumulated strain. The surface is characterized by steps plus terraces again and QD clusters decorate the ragged steps. Remarkably, the QDs in clusters are aligned as short chains. The visual appearance of the resulted surface morphology resembles itself as a jungle of bamboo. The bunched steps along [-113] visualize the individual bamboo sticks and aligned QD clusters separate each stick into sections. Very interesting, the QD clusters are nearly equally distributed along [-113]. Its periodicity is better resolved in the two-dimensional image of the autocorrelation functions calculated from the AFM image [14]. Figure 3(c) shows a line profile along [-113] through the center of Fig. 3(b). The separation between satellite peaks reveals that the periodicity is about 565 nm. The separations between “bamboos” are not uniform but still resolved from Fig. 3(b), around 1.08 μm.

In conclusion, we stacked multilayer of InGaAs nanostructures on GaAs(731), and studied the effect by varying GaAs spacer thickness and InGaAs coverage. The resulted surface morphologies and optical properties are sensitive to the accumulated strain. GaAs(731) is demonstrated as a good candidate for growing QD clusters. The possibility of QD ordering inside clusters is revealed by AFM for low coverage of InGaAs. Our report indicates the need to study InGaAs growth on GaAs surfaces lying inside the stereographic triangle, thus achieve a comprehensive picture of strain-driven growth and pursuing novel QD configurations.

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One-dimensional GaN nanomaterials transformed from one-dimensional Ga$_2$O$_3$ and Ga nanomaterials

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One-dimensional (1D) GaN nanomaterials exhibiting various morphologies and atomic structures were prepared via ammoniation of either Ga$_2$O$_3$ nanoribbons, Ga$_2$O$_3$ nanorods or Ga nanowires filled into carbon nanotubes (CNTs). The 1D GaN nanomaterials transformed from Ga$_2$O$_3$ nanoribbons consisted of numerous GaN nanoplatelets having the close-packed plane, i.e. (0002)$_{2H}$ or (111)$_{3C}$ parallel to the axes of starting nanoribbons. The 1D GaN nanomaterials converted from Ga$_2$O$_3$ nanorods were polycrystalline rods covered with GaN nanoparticles along the axes. The 1D GaN nanomaterials prepared from Ga nanowires filled into CNTs displayed two dominant morphologies: (i) single crystalline GaN nanocolumns coated by CNTs, and (ii) pure single crystalline GaN nanowires. The cross-sectional shape of GaN nanowires were analyzed through the transmission electron microscopy (TEM) images. Formation mechanism of all-mentioned 1D GaN nanomaterials is then thoroughly discussed.

Keywords: GaN; One-dimensional; Ga$_2$O$_3$; Nanostructures

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GaN is a wide direct-bandgap (3.39 eV at room temperature) semiconductor material and its one-dimensional (1D) structure has a high potential for applications in blue and UV light-emitting and laser diodes as well as in high temperature and high power electronic devices [1,2]. Up to date, the synthetic approaches for 1D GaN nanomaterials have relied on various physical or chemical methods, such as carbon nanotubes (CNTs) [3-5] and anodic alumina membrane [6,7] template-terminated methods, Fe, Co, Ni and Au metal-catalyst vapor-liquid-solid (VLS) growth [8-10], SiO$_2$, Fe$_2$O$_3$, and B$_2$O$_3$ oxide-assisted growth (OAG) [11,12], Precursor-based methods metalorganic chemical vapor deposition (MOCVD) [13], and hydride vapor phase epitaxy (HVPE) [14].

Although the above-mentioned groups are different from each other, all methods are capable of generating 1D GaN nanomaterials with a characteristic single-crystalline structure. Liliental-Weber [15] and Lan [16] have reported preferentially-oriented 1D GaN nanomaterials consisting of small GaN platelets. Furthermore, Zhao [17] and Ogi [18] have studied the influence of starting materials Ga$_2$O$_3$ powders (particles) on growth of GaN nanomaterials. Though the formation mechanism of the GaN nanomaterials has been discussed, the reason behind the oriented growth remains unclear. Our current investigation sheds an additional light on this issue. In addition, the design, synthesis, and characterization of surface-modified nanostructures are of fundamental importance in controlling the mesoscopic properties of new materials and in developing new tools for nanofabrication. So we expect that presently synthesized GaN 1D nanomaterials coated with GaN nanoparticles are capable of bringing new electronic characteristics different from those displaying by their simple mechanical mixtures due to somewhat specific boundary.

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GaN nanoribbons consisting of platelets were fabricated in a conventional furnace with a horizontal quartz tube. Ga and \( \text{Ga}_2\text{O}_3 \) powders were homogeneously mixed in a weight ratio 1:1. The mixture was placed in a BN crucible and covered by a BN plate with drilled mm-size channels. Bundles of CNTs were placed on the BN plate. The synthesis process was performed in two steps. First, the furnace was washed with a \( \text{N}_2 \) gas (3 l/min) over ~2 hours under gradual heating to 900°C. Second, a mixture of \( \text{NH}_3 \) (0.3 l/min) and \( \text{N}_2 \) (1 l/min) was substituted for the original \( \text{N}_2 \) gas flow while the temperature was gradually increased to 970°C over 10 min and then kept constant during 30 min. Then, the whole quartz tube was taken out from the furnace and cooled to the room temperature. We found that the surface of the starting CNTs was covered with a thin layer of yellow-colored material.

Firstly, \( \text{Ga}_2\text{O}_3 \) nanorods and Ga-filled CNTs were synthesized in a vertical radio-frequency furnace by mixture of \( \text{Ga}_2\text{O}_3 \) and pure amorphous active carbon. (see also Refs. [19, 20]) The furnace was heated at 1360°C over 1-2 h. Ga-tipped \( \text{Ga}_2\text{O}_3 \) nanorods were found to be deposited on the outer surface of the C fiber coat where the temperature was estimated to be approximately 1000°C. Meanwhile, Ga-filled CNTs were collected from the inner surface of the outlet pipe of the furnace where the temperature was estimated to be ~800°C. Then, place \( \text{Ga}_2\text{O}_3 \) nanorods and Ga-filled CNTs into the conventional furnace for ammoniation at 970°C (described above), respectively. Finally all the resultant materials were collected and studied by a 300 kV field emission analytical high-resolution transmission electron microscope (HRTEM, JEM-3000 F) equipped with an X-ray energy dispersive spectrometer (EDS).

Figure 1(a) depicts the morphology of the yellow-colored materials synthesized via a reaction Ga and \( \text{Ga}_2\text{O}_3 \) powders with \( \text{NH}_3 \). They have widths of 40-100 nm and lengths of up to 10 \( \mu \text{m} \). The materials were detected to be 1D nanoribbons consisting of numerous nanoplatelets. An energy dispersion spectroscopy (EDS) analysis indicated that the nanoribbons are composed of Ga and N. It is believed that two processes are involved in the growth of the nanoribbons: (i) \( \text{Ga}_2\text{O}_3 \) nanoribbons are crystallized on the surface of CNTs, and, while a \( \text{N}_2 \) gas having impurities of \( \text{O}_2 \) is introduced into the furnace, the chemical reactions proceed as follows:

\[ \text{Ga}_2\text{O}_3+\text{O}_2\rightarrow\text{Ga}_2\text{O}_3 \quad (1.a) \]

where a \( \text{Ga}_2\text{O}_3 \) vapor is generated in line with the reaction described by Han et al [3].

\[ \text{Ga}_2\text{O}_3\rightarrow4\text{Ga} \rightarrow3\text{Ga}_2\text{O} \quad (1.b) \]

The vapor cannot be oxidized further after it reaches the surface of CNTs, because the CNTs serve as a shelter for the \( \text{O}_2 \) impurity in \( \text{N}_2 \) gas; (ii) \( \text{Ga}_2\text{O}_3 \) nanoribbons are transformed into GaN nanoribbons while \( \text{NH}_3 \) is introduced into the furnace; the involved reaction may be written as follows,

\[ \text{Ga}_2\text{O}_3+2\text{NH}_3\rightarrow\text{GaN}+3\text{H}_2\text{O} \quad (2) \]

where GaN platelets may initially nucleate on the side-surface of a \( \text{Ga}_2\text{O}_3 \) nanoribbon and the subsequent growth of GaN platelets propagates along the whole nanoribbon.

To confirm the growth mechanism of the yellow-colored \( \text{Ga}_2\text{O}_3 \) nanoribbons, we carried out additional experiments. Before the second step, we examined a thin layer of the white-colored materials on the surface of CNTs. The materials were determined to be \( \text{Ga}_2\text{O}_3 \) nanoribbons having morphologies depicted in Fig. 1(b). After ammoniation of the \( \text{Ga}_2\text{O}_3 \) nanoribbons at 970°C, we found that the color of the materials was changed from white to yellow. The later materials were

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found to be GaN. There were nanoribbons covered with nano-platelets. A nanoribbon is shown in Fig. 1(c), its axis is parallel to the (0002) plane, as shown in Fig. 1(d), which is the [112\(\overline{0}\)] zone axis diffraction pattern. The similarity between the morphologies in Fig. 1(a) and Fig. 1(c) suggests that the proposed growth mode for the nanoribbons depicted in Fig. 1(a) is correct. The reasonability of the proposed growth mode may require other evidence additive to the fact of similar morphologies of the two kinds of the GaN nanoribbons. Detailed HRTEM investigation may become effective.

Figure 2(a) and (b) are the [11\(\overline{2}\)0] HRTEM images of two platelets on a nanoribbon in Fig. 1(a) and that in Fig. 1(c), respectively. The two images have one characteristic in common - a thicker GaN platelet laying under a thinner GaN platelet with the (0002)\(\text{2H}\) stacking plane. Figure 3(a) and (b), [1\(\overline{1}\)0] HRTEM images of two platelets on a nanoribbon in Fig. 1(a) and that in Fig. 1(c), also showing that a thicker GaN platelet is under a thinner GaN platelet with the (111)\(\text{3C}\) stacking plane. In the four HRTEM images, the close-stacking (0002) and/or (111) planes are parallel to the axis direction of the nanoribbons. The relationship can be explained in terms of the growth mode schematic of GaN nucleation shown in Fig. 4.

When GaN islands nucleate on a certain side surface of a Ga\(_2\)O\(_3\) nanoribbon, their close packing planes stack to the side surface of a certain plane, resulting in the axis parallel to the stacking plane.

Figure 5(a) shows the morphology of Ga-tipped Ga\(_2\)O\(_3\) nanorods, which were found to have a round cross-section under tilting experiments in TEM. After ammoniation, the Ga\(_2\)O\(_3\) nanorods and their spherical tips were transformed to GaN nanorods with spherical GaN tips. Generally the rods were covered by numerous nanoparticles, as shown in Fig. 5(b) and 5(c), respectively. The GaN nanorods were polycrystalline and have no preferred axis direction. These nanorods are different from the GaN nanoribbons converted from Ga\(_2\)O\(_3\) nanoribbons, which have a definite axis direction parallel to the (0002)\(\text{2H}\) and/or (111)\(\text{3C}\) planes. The origin of this phenomenon can be...
explained through a schematic diagram, Fig. 6. During the transformation, randomly-oriented GaN domains nucleate on a round side surface at numerous sites finally resulting in a polycrystalline GaN nanorod.

Figure 7(a) depicts the morphology of a Ga nanowire filled into CNT. After ammoniation, a Ga nanowire can be transformed to GaN nanocolumns coated by CNTs, as shown in Fig. 7(b). Figure 7(c) and d are the EDS spectra taken from the pre- and post-transformed Ga nanowires, respectively. HRTEM study illustrates that each GaN nanocolumn is single crystalline. Figure 7(e) shows a HRTEM image of such single-crystalline GaN nanocolumn coated by C layers.

The formation of GaN nanowires filled in CNTs can be explained as direct ammoniation of Ga nanowires filled in CNTs. However, such explanation may find a better proof if a pure GaN nanorod not covered with a CNT may be found in the ammonia-treated materials. In fact, such material was found, as shown in Fig. 8(a). This rod has an axis perpendicular to the (1100) plane, as displayed in Fig. 8(b) and (c). The most intriguing fact is that new contrast fringes appear in Fig. 8(a). It is believed that the fringes are originated from the thickness difference [21]. According to this, we can conjecture that the cross-section of the rod may have two kinds of possible shapes shown in Fig. 9. The above-presented analysis made us possible to estimate the thickness and the cross-section shape using the observed contrast fringes. It is noted though that a more definite confirmation using a slice method of cross-section is probably needed [22].

To sum up, the presented transformation scheme consists of two steps and relies on conversion of a given 1D material to another 1D material in a given gaseous atmosphere. This approach has been used to synthesize ZnS [23] and GaN nanotubes [24, 25]. It is believed here that the process is an important practical method to synthesize novel 1D material and to fabricate complicated arrays of those with nanoparticles.

We fabricated one-dimensional GaN nanoribbons, nanorods, and nanowires through ammoniation of Ga$_2$O$_3$ nanoribbons, Ga$_2$O$_3$ nanorods and Ga nanowires filled in CNTs, respectively. The GaN nanoribbons consist of numerous GaN nanoplatelets with the close-packed planes, i.e. (0002)$_{2H}$ or (111)$_{3C}$ being in parallel with the axis of nanoribbons. The GaN nanorods obtained from Ga$_2$O$_3$ nanorods are polycrystalline nanorods attaching numerous GaN nanoparticles along their axes. GaN nanowires coated with CNT layers were single-crystalline. The thickness and cross-sectional shape of a pure GaN nanowire may be calculated and conjectured according to the thickness fringes in its transmission electron
microscopy image. Formation mechanisms of 1D GaN nanomaterials are believed to be governed through inhering corresponding 1D characteristics of the starting Ga$_2$O$_3$ and Ga materials, whereas the nucleation during initial transformation stage may result in new nanoparticle formation.

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Semiconducting single-walled carbon nanotubes synthesized by S-doping

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An approach was presented for synthesis of semiconducting single-walled carbon nanotubes (SWNTs) by sulfur (S) doping with the method of graphite arc discharge. Raman spectroscopy, UV-vis-NIR absorption spectroscopy and electronic properties measurements indicated the semiconducting properties of the SWNTs samples. Simulant calculation indicated that S doping could induce conversion of metallic SWNTs into semiconducting ones. This strategy may pave a way for the direct synthesis of pure semiconducting SWNTs.

Keywords: S-doping; Single-wall; Carbon nanotubes; Semiconducting; Arc discharge

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Over the past decades, single-walled carbon nanotubes (SWNTs) used as building blocks of nanoscale electronic devices have attracted great attention due to their quasi one-dimensional structure and unique properties [1-3]. Depending on their diameter and chirality, SWNTs can exhibit either metallic or semiconducting behavior. However, the chirality of nanotubes can not be controlled normally until now [4]. How to obtain purely semiconducting SWNTs (semi-SWNTs) becomes one of the major obstacles to the widespread applications of SWNTs for high performance electronics [5]. Several separation approaches for the enrichment of one certain electronic type of SWNTs have been developed, such as electrical breakdown [6-9], ultracentrifugation [10], selective plasma etching [5], electrophoresis [12] and selective chemical functionalization [6]. But the problem is that the post-treatments processes are tedious beyond controlled and often have the disadvantage of damaging or contaminating SWNTs samples [7,8]. Recently, preferential growth of Semi-SWNTs by chemical vapor deposition (CVD) methods by boron/nitrogen co-doping was reported to produce high percentage of Semi-SWNTs or a specific chirality distribution SWNTs [10-13]. These pioneering studies indicate the possibility for selective synthesis of Semi-SWNTs by heterodoping method.

S contained compound has often been used as an additive in the synthesis of CNTs [14] for increasing the yield of SWNTs or DWNTs. Even, Denis et al [15] reported S doping could modify the electronic structure of the SWNTs by using first-principles calculations. Recently, we tested a technique for the synthesis of SWNTs by graphite arc discharge in hydrogen with S doping. The as-synthesized S-doped SWNTs showed purely semiconducting. Theory calculations elucidate that the metallic chirality SWNTs can be converted into semiconductors by proper S concentrations doping into the tube wall structure.

S-doped SWNTs were synthesized by arc discharge between two graphite electrodes in hydrogen atmosphere. The graphite electrodes were graphite rods of ~6 mm in diameter and made with high purity graphite, iron (5 at%) and S (0.1-2.0 at%). Briefly, the synthesis apparatus consists of graphite electrodes, a water-cooled trap, and a DC power supply which is capable of providing the voltage of 150 V and the current of 100 A. During DC arc discharge process, the distance between the graphite electrodes was maintained about 2 mm. The optimum
parameters of current and voltage for the DC arc discharge were 40 A and 55 V respectively. A magnetic field of ~160 mT was applied to confine the discharge plasma, and aligned SWNTs thin film can be obtained by adjusting the orientation of the magnetic field.

The as-synthesized SWNTs have been characterized by scanning electron microscopy (SEM, JSM-7401F), high-resolution transmission electron microscopy (HRTEM; JEM-2010), UV-vis-NIR absorption spectroscopy and Raman spectroscopy (by 514.5 and 632.8 nm excitation). X-ray photoelectron (XPS) was used to estimate the contents of sulfur and characterize their bonding environments. The electronic properties of the as-synthesized SWNTs have also been measured by fabricating CNT-FET devices. The electrical properties were studied by two field effect configuration. One is thin film SWNTs FETs. The other is FETs based on several SWNTs bridging the two electrodes. The electrical properties of CNT-FETs were measured by Agilent 4156C.

Figure 1a shows the typical SEM image of as-synthesized S-doped SWNTs sample. It can be seen that the SWNTs with clean and smooth surface are homogenously distributed and entangled. HRTEM (Fig. 1b) provides direct evidence that the nanotubes were single-walled with the average diameter of ~1.2 nm. Figure 1c shows the XPS of as-synthesized SWNTs. Inset shows the high resolution S 2p XPS spectra, which has been curve-fitted by Voigt lines to detect bonding structure. In order to find whether S incorporated into the nanotubes, the surface layer of sample was etched away by Ar+ sputtering for 3 min. The broad band can be deconvoluted into two bands at 169.2 and 167.6 eV, which can be assigned to the C-O and C-S bonding structures, respectively. The S concentration in SWNTs powders estimated to be 1.4 at %. Figure 1d is the XRD patterns of the S-doped SWNTs and undoped SWNTs. The major peak at 2θ=25.952° is corresponding to (002) reflections of polyaromatic. It is worth while noting that the intensity and half width of the diffraction at 25.952° increase after S doping.

![FIG. 1. (a) A typical SEM image of as-synthesized S-doped SWNTs. (b) HRTEM image of as-synthesized S-doped SWNTs. (c) XPS spectrum of the as-synthesized S-doped SWNTs. (d) XRD patterns of S-doped and undoped SWNTs.](http://www.nmletters.org)

![FIG. 2. UV-vis-NIR absorption spectroscopy of the undoped and doped samples.](http://www.nmletters.org)
These indicate that S doping induces partial aberration of the geometry structure of SWNTs while the crystal structure of SWNTs is unchanged after S doping.

Figure 2 and Fig. 3 show the typical optical spectra of an undoped SWNTs sample. The UV-vis-NIR absorption spectroscopy in Fig. 2 shows that several peaks in the semiconducting band arise from the electronic transitions between the first pair of van Hove singularities (vHs) in semiconducting SWNTs (S_{11} band) and the second pair (S_{22} band). The intensities of the S_{11} band transition peaks of the as-synthesized S-doped SWNTs sample are greatly dominant relative to the undoped SWNTs sample while the M_{11} band shows little change, which is indicative of a higher Semi-SWNTs content in the as-synthesized sample. Moreover, red shift of S_{11} band (main peak shift) indicates that the band gaps of the S-doped SWNTs changed probably. The radial breathing mode (RBM) region of SWNTs Raman spectra can be used to assign and quantitatively evaluate metallic and semiconducting nanotubes [16-18]. As-synthesized SWNTs samples were sonicated in ethanol for 10 min, and then the suspensions were dropped on glass slides and dried in air. Figure 3 shows the measured Raman spectra in RBM region. The intensities of semiconducting S33 (514 nm excitation) and S22 (633 nm excitation) from as-synthesized S-doped SWNTs increase, whereas the intensities of the peak attributed to metallic SWNTs were disappear.

For better understanding the S-doping effects into metallic SWNT structure, calculations are carried out with the density functional theory implemented provided by Dmol³ package [19]. Figure 4 shows the band structures by first-principles calculations for an S-doped (7, 7) metallic SWNT. The all-electron Kohn-Sham wave functions were expanded in the local atomic orbital (double numerical polarization, DNP) basis set and generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) for the exchange-correlation potential [20]. The Monkhorst-Pack scheme was used in the Brillouin zone with 1×1×10 for all the geometry optimization and total energies calculations [21]. Self-consistent field procedure was done with a convergence criterion of 10⁻⁵ a.u. on the energy and electronic properties. As shown in Fig. 4a, a typical metallic (7, 7) SWNT has no energy band at the Fermi level. The band structures of S-doped SWNTs in different concentrations show that the energy gaps of about 0.24 eV for 0.71% (Fig. 4b) and about 0.29 eV for 1.43% (Fig. 4c) open at Fermi level. It is suggested that metallic SWNTs can be converted into semiconductors by sulfur doping with proper S concentrations.

SWNTs field effect transistors (FET) were used to test the electronic properties of the S-doped SWNTs. SWNTs solutions
were spin coated on a Si/SiO$_2$ wafer to form a random SWNTs thin film. The SiO$_2$ surface layer of 80 nm thick acted as a back gate electrode. On top of the films, source (S) and drain (D) electrodes with a channel distance ~10 µm were made of 10 nm Ti, followed by 30 nm Au by electron beam lithography technique. The schematic of the SWNTs field effect transistors (FET) structure and their electronic properties curves are shown in Fig. 5. Figure 5a demonstrates the source-drain current increase with increasing negative gate voltage. Figure 5b is the transfer characteristic of as-synthesized S-doped SWNTs-FET which shows that the on/off ratio is more than $10^3$ by sweeping gate voltage at room temperature. In contrast, similar thin film field-effect configuration based on the undoped SWNTs sample shows the on/off ratio of less than 10, which means that the undoped sample may contain a lot of M-SWNTs.

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Bilirubin adsorption property of mesoporous silica and amine-grafted mesoporous silica

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Nephritic, hepatic and immune failures would lead to the overload of endogenous toxic molecules (e.g. bilirubin, cholic acid, uric acid, creatinine etc.) in human bodies. It is fatal in most cases and extracorporeal blood purification (ECBP) is powerful first-aid therapy. Adsorbents are key parts of ECBP apparatus. Mesoporous silicas should be promising candidates for these medical adsorbents, but there is no report about this. Herein, pure and amine-grafted mesoporous silicas have been applied to adsorb bilirubin, cholic acid, uric acid, creatinine and phenobarbital for the first time. These mesoporous materials show high adsorption capacities for bilirubin and uric acid in phosphate buffer solution (PBS). Effects of pore sizes, amine-modification, temperature and ionic strength on their bilirubin adsorption capacities have been studied in detail.

Keywords: Mesoporous silica; Bilirubin adsorption; Amine-grafted

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Generally, there are exogenous and endogenous poisons overloading in human body [1]. Acute medicament (e.g. soporific) toxicosis is the most common exogenous case. Nephritic, hepatic and immune failures lead to overload of endogenous toxic molecules (e.g. bilirubin, cholic acid, uric acid, creatinine etc.) and pull patients to death's door. Extracorporeal blood purification (ECBP), including hemodialysis, hemofiltration, hemoperfusion and plasma exchange, is powerful first-aid therapy to remove toxins from human hematic system [2]. Adsorbents are the most important parts of ECBP apparatus. Active carbon, chitosan and resins have been applied in ECBP [3-6]. However, development of medical adsorbents with high adsorption capacity and excellent blood compatibility is still a great challenge. Mesoporous silicas, which have high surface area, uniform pore size and abundant Si-OH groups, have been used as adsorbents for heavy metal ions [7-10] and organic pollutants [10] and toxic gas [10], etc. Recently, they have also been applied to medicine storage and targeting therapy [7, 11, 12]. Mesoporous silicas should also be promising candidates for medical adsorbents of ECBP to remove the above-mentioned toxins from human hematic system. However, there are few reports about this. Herein this article, pure and amine-grafted mesoporous silicas have been prepared and applied to adsorb bilirubin, cholic acid, uric acid, creatinine, etc. Effects of pore size, amine-grafting, temperature and ionic strength on the bilirubin adsorption capacities of these materials have been studied in detail.

EXPERIMENTAL

A. Materials. Bilirubin (~99%) was supplied from Alfa Aesar Chemical Company. The molecular structure of bilirubin has been shown in Fig. 1. Cholic acid (~99%) was obtained from Fluka Chemical Company. Uric acid (~99%), creatinine (~99%), tetraethyl orthosilicate (TEOS, >99%), were got from SCRC (Sinopharm Chemical Reagent Company, China). All reagents are used as received.

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B. Preparation and amine-modification of mesoporous silica SBA-15. Mesoporous silica SBA-15 was synthesized using a triblock copolymer surfactant in acid media according to a published procedure [13]. In a typical synthesis, 4 g of block copolymer surfactant EO20PO70EO20 (Pluronic P123, BASF) was dissolved in 30 g of distilled water and 120 ml of 2 M HCl with stirring, followed by addition of 8.5 g of TEOS at 35–40 °C. This gel was continuously stirred for 24 h and then crystallized in a glass bottle at 100 °C for 48 h. After crystallization, the solid product was filtered, washed with distilled water, and dried in air at 100 °C. The material was calcined in air at 530 °C for 6 h to remove the surfactant template and obtain a white parent powder (SBA-15). For preparation of larger pore SBA-15, 2 g of P123 was dissolved in 75 ml 1 M HCl with stirring, followed by addition of 1.38 ml 0.5 M NH₄F and 8.5 g of TEOS at 35–40 °C. This gel was continuously stirred for 24 h and then crystallized in a sealed glass bottle at 110 °C for 48 h. FSBA-15 was then obtained after filtration and calcination.

Multi-amine grafted SBA-15 and FSBA-15 was prepared according to published procedures [14, 15]. Functional groups (amine, diamine and triamine groups in this case) were introduced to the pore surfaces of mesoporous silica by refluxing the mixture of 1 g of the calcined SBA-15 or FSBA-15 and 5 ml of γ-aminopropyltriethoxysilane (APTS), N-[3-(trimethoxysilyl)-propylethylene] diamine (TPED), trimethoxysilyl propyl diethylenetriamine (TPDT) in 100 ml of dry toluene under nitrogen atmosphere for at least 12 h. The resulting hybrid materials (denoted as 1N-SBA-15, 2N-SBA-15, 3N-SBA-15, 2N-FSBA-15 and so on) were filtered out using toluene thoroughly and dried in vacuum at 70-80 °C.

C. Preparation of mesoporous silica KIT-6. The mesoporous silica with cubic Ia3d symmetry (designated as KIT-6) was prepared according to the published procedure using tri-block copolymer Pluronic P123 as template by adding of n-butanol in an acidic aqueous solution [16]. Typically, 6 g of surfactant P123 and 6 g of n-butanol were dissolved in the solution of 217 g of distilled water and 11.4 g of concentrated HCl (37 wt%). To this homogeneous solution, 12.9 g of TEOS was added under stirring at 37°C and continuously stirred for 24 h. After that, the mixture was transferred to Teflon-lined autoclaves and heated at 100°C for 24 h. The solid product was filtered, washed with distilled water and calcined at 550 °C for 5 h to get KIT-6.

D. Preparation of mesoporous silica MCM-41. Pure silica MCM-41 samples were prepared by the hydrolysis of cetyl-trimethylammonium bromide (CTAB) and TEOS in basic solution according to the published procedure. The final composition of the gel is 1.0 CTAB: 7.5 TEOS: 1.8 NaOH: 500 H₂O (molar ratio). The gel was hydrothermally treated at 110°C for 60 h and calcined at 550°C for 5 h to obtain MCM-41 [17,18].

E. Preparation of toxins solutions. Bilirubin stock solution was prepared by dissolving 250 mg of bilirubin in 10 ml 0.06 M NaOH solution and then diluting this solution to 250 ml by phosphate buffer solution (PBS, pH=7.4). Bilirubin solutions of lower concentrations were obtained by further dilution using PBS. All solutions were stored in refrigerator in dark.

Uric acid solution was prepared by dissolving 500 mg of uric acid in 250 ml of 0.02 M NaOH solution and then diluting this solution to 250 ml by phosphate buffer solution (PBS, pH=7.4). Bilirubin solutions of lower concentrations were obtained by further dilution using PBS. All solutions were stored in refrigerator in dark.

To prepare phenobarbital solution, five phenobarbital tablets (30mg per tablet, pet using only) were ground and

Table 1. Structure parameters of mesoporous silicas and their adsorption capacities for bilirubin.

| Samples   | BET surface area (m²/g) | BJH desorption pore diameter (nm) | BJH desorption pore volume (cm³/g) | Adsorption capacities for bilirubin (mg/g) |
|-----------|------------------------|----------------------------------|----------------------------------|------------------------------------------|
| MCM-41    | 708                    | 2.6                              | 0.60                             | 63                                       |
| KIT-6     | 684                    | 5.8                              | 0.79                             | 52                                       |
| SBA-15    | 775                    | 6.8                              | 1.20                             | 37                                       |
| FSBA-15   | 534                    | 8.8                              | 1.28                             | 37                                       |
| 1N-SBA-15 | 373                    | 6.0                              | 0.76                             | 51                                       |
| 2N-SBA-15 | 336                    | 6.1                              | 0.74                             | 47                                       |
| 3N-SBA-15 | 256                    | 6.1                              | 0.57                             | 42                                       |
| 2N-FSBA-15| 266                    | 7.9                              | 0.71                             | 51                                       |

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dissolved in 100 ml $H_2O$. Cholic acid was prepared by dissolving 50 mg of Cholic acid in 6 ml 0.05 M $NaOH$ solution and then diluting this solution to 100 ml using PBS.

**CHARACTERIZATION**

Concentrations of all toxins are characterized using UV-Vis absorbance, which was measured using Shimadzu UV-3101PC spectroscope. $N_2$ adsorption-desorption isotherms were carried out on Micromeritics Tristar 3000 analyzer at 77 K under a continuous adsorption condition. BET (Brunauer-Emmet-Teller) and BJH (Barrett-Joyner-Halenda) analyses were used to determine the surface area, pore size and volume.

A. **Effect of pore sizes of mesoporous silicas on bilirubin adsorption.** As shown in Tab.1, pure mesoporous silicas MCM-41, KIT-6, SBA-15 and FSBA-15 with pore diameters from 2.6 to 8.8 nm have adsorbed 63, 52, 37 and 37 mg/g bilirubin, respectively. Small pore diameters are favorable to get high adsorption capacity. The samples SBA-15 and FSBA-15 have the same adsorption capacities, which could be attributed to their microporous structure in pore wall frameworks. However, surface areas of these pure mesoporous silicas have little influence on their adsorption capacities for bilirubin.

B. **Effect of amine-modification of mesopore surface on bilirubin adsorption.** For comparison, amine-grafted mesoporous silicas SBA-15 have also been synthesized and applied to adsorb bilirubin. 1N-SBA-15, 2N-SBA-15 and 3N-SBA-15 have similar pore diameters (about 6 nm). Large pore volumes and high surface areas have lead to slightly increase of their adsorption capacities from 42 to 51 mg/g. More amine groups have not improved their bilirubin adsorption capacities. In order to study on the influence of pore diameter of amine-grafted mesoporous silicas on their bilirubin adsorption capacities, 2N-FSBA-15 has been also given as an example. 2N-FSBA-15 with pore diameter 7.9 nm has adsorbed 51 mg/g bilirubin. This adsorption capacity is higher than that of 2N-SBA-15 sample, although 2N-FSBA-15 has smaller surface area and pore volume than 2N-SBA-15. This indicates that large pore diameters rather than N numbers are beneficial to improve the adsorption capacities of amine-grafted samples. It can be attributed to the high flexibility of amine group chains in large pore channels.

For SBA-15 and FSBA-15, as shown in Table 1, the surface areas, pore diameters and volumes all decrease after the introduction of amine groups (2N-SBA-15 and 2N-FSBA-15). However, all amine-grafted mesoporous silicas show higher adsorption capacities than their pure parent mesoporous silicas. The same results can also be obtained from Fig. 2. Their bilirubin adsorption capacities of 2N-SBA-15 and 2N-FSBA-15 are higher than those of SBA-15 and FSBA-15, which is independent of the treatment time. As reported in literatures before [19], introductions of hydrophobic groups in adsorbents can effectively improve their adsorption capacities for bilirubin.

**FIG. 2.** Influence of the adsorption time on the adsorption capacities of the mesoporous silica adsorbents for bilirubin. Initial concentration of bilirubin: 300 mg/L, 10 ml; mesoporous adsorbent: 10 mg; temperature: 310K.

**FIG. 3.** Influence of initial concentrations of bilirubin on the adsorption capacities of mesoporous silica adsorbents for bilirubin. Adsorption time: 3 h; temperature: 310K; bilirubin solution: 10ml; mesoporous silica adsorbents: 10mg.

**FIG. 4.** Influence of temperature on the adsorption capacities of mesoporous silica adsorbents for bilirubin. Initial concentration of bilirubin: 500 mg/l, 10 ml; adsorption time: 3 h; mesoporous silica adsorbents: 10 mg.

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Table 2. Adsorption properties of mesoporous silicas for cholic acid, uric acid, creatinine and phenobarbital.

|                  | SBA-15 | MCM-41 | 1N-SBA-15 | 2N-SBA-15 | 3N-SBA-15 |
|------------------|--------|--------|-----------|-----------|-----------|
| Cholic acid      | 52     | 70     | 0         | 0         | 0         |
| Uric acid        | 118    | 108    | 74        | 104       | 122       |
| creatinine       | 0      | 0      | 0         | 0         | 0         |
| phenobarbital    | 0      | 0      | 0         | 0         | 0         |

Initial concentration of Cholic acid: 1500 mg/l, 10 ml; temperature: 293 K; mesoporous adsorbents: 10 mg; adsorption time: 6 h.

Initial concentration of Uric acid: 2000 mg/l, 10 ml; temperature: 293 K; mesoporous adsorbents: 10 mg; adsorption time: 6 h.

liposoluble bilirubin. Herein the grafting of amine-containing silane chains onto the pore surface makes these mesoporous adsorbents more hydrophobic and leads to increasing adsorption capacities.

C. Effect of initial concentrations of bilirubin. Figure 3 shows the influence of initial concentrations of bilirubin on the adsorption capacities of pure and amine-grafted mesoporous silicas. Their adsorption capacities all increase with the increase of initial concentrations of bilirubin. Amine-grafted mesoporous silicas show higher adsorption capacities than pure mesoporous silicas, which is unreliable to the initial concentrations of bilirubin. 1N-SBA-15 and 2N-FSBA-15 adsorbed similar amount of bilirubin because of the similar flexibility of amine group chains in their pore channels. 2N-SBA-15 show less bilirubin capacity than 1N-SBA-15 and 2N-FSBA-15, which can be ascribed to its small pore size and less flexibility of amine-containing organic chains.

D. Effect of temperature on bilirubin adsorption. Experiments on the bilirubin adsorption under different temperatures have been conducted and the results are shown in Fig. 4. The bilirubin adsorption capacities of SBA-15 increase while those of amine-grafted SBA-15 decrease when the experiment temperatures become higher. For pure mesoporous silicas, hydrogen bonds between Si-OH groups of mesoporous silicas and the -COOH, -NH- groups of bilirubin can be formed in PBS. With the increase of temperature, diffusion of bilirubin molecules into the pore channels of mesoporous adsorbents have greatly improved and accordingly the amount of hydrogen bonds also increased, thus their adsorption capacities increase. As for amine-grafted mesoporous silicas, adsorption mainly bases on the electrostatic interaction or the ionic bonds between -NH2/-NH-groups of mesoporous adsorbents and -COOH groups of bilirubin molecules. These charge effects have been greatly weakened under high temperature because the diffusion of bilirubin in the pore channels of adsorbents is accelerated.

E. Effect of ionic strength on bilirubin adsorption. Figure 5 shows the influence of ionic strength (NaCl concentrations) of the PBS solution on their adsorption capacities of pure and amine-grafted mesoporous silicas. With the increase of the concentration of NaCl, the ionic atmosphere around -COO¯ groups of bilirubin increases. On the one hand, the formation of the ionic atmosphere makes the bilirubin molecules get more hydrophilic. Therefore, bilirubin adsorption capacities for pure mesoporous silica SBA-15 increase when the ionic strength of the solutions increases. On the other hand, the ionic atmosphere around -COO¯ groups of bilirubin also leads to obvious steric hindrance. At the same time, the ionic atmosphere around amine groups on the pore surface of amine-grafted mesoporous silicas also causes obvious steric hindrance. These steric hindrance effects make adsorption capacities of amine-grafted mesoporous silicas decrease. Meanwhile, the improved hydrophilic bilirubin is favorable to get high adsorption capacity. The balance between these two facts makes the bilirubin adsorption capacities of 3N-SBA-15 keep between 40-50 mg/g when the ionic strength has been changed.

F. Adsorption for other toxins. Pure and amine-grafted mesoporous silicas have also been applied to adsorb other toxins, such as cholic acid, uric acid, creatinine. As shown in Table 2, pure mesoporous silicas also show high adsorption
capacity for cholic acid. However, amine-grafted mesoporous silicas do not adsorb cholic acid at all. Both pure mesoporous silicas and amine-grafted mesoporous silicas show high adsorption capacities for uric acid. Neither pure mesoporous silicas nor amine-grafted mesoporous silicas have adsorption capacities for creatinine and phenobarbital. Further studies on the adsorption of these toxins on mesoporous adsorbents are still in progress.

CONCLUSION

Both pure and amine-grafted mesoporous silicas show high adsorption capacities for bilirubin and uric acid. Pure mesoporous silicas with smaller pore size show higher adsorption capacities for bilirubin. For amine-grafted samples, larger pore diameters, rather than N numbers, are beneficial for the enhancement of their adsorption capacities, which can be attributed to the high flexibility of amine-containing silane chains in large pore channels. Amine modification of mesoporous silicas can increase their adsorption capacities for bilirubin because the grafting of amine-containing silane chains onto the pore surface makes these mesoporous adsorbents more hydrophobic and then leads to increased adsorption capacities of hydrophobic bilirubin. Increase in temperature leads to the enhanced bilirubin adsorption capacities of pure mesoporous silica because diffusion of bilirubin molecules into the pore channels have greatly improved and the amount of hydrogen bonds between Si-OH and -COOH/-NH- also increases. However, the bilirubin adsorption capacities of amine-grafted samples decrease at increased temperature because of the faster bilirubin diffusion in the pore channels of adsorbents and the weaker ionic bonds between the -NH2/-NH- of mesoporous adsorbents and -COOH of bilirubin at higher temperature. With the increase of ionic strength, the bilirubin adsorption capacities of pure mesoporous silicas increase due to the formation of the ionic atmosphere which makes the bilirubin molecules more hydrophilic. The bilirubin adsorption capacities of amine-grafted mesoporous silicas change little resulted from the counteraction from the steric hindrance effect of the ionic atmosphere. Pure mesoporous silicas also have affinity to cholic acid. Neither pure mesoporous silicas nor amine-grafted mesoporous silicas can adsorb creatinine and phenobarbital.

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Graded doped structure fabricated by vacuum spray method to improve the luminance of polymer light-emitting diodes

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An increase in luminance of a polymer light-emitting diode (PLED) was obtained by fabricating a graded doping structure using a vacuum spray method. The small electron transport molecule, Tris(8-hydroxyquinolinato) aluminum(III)(Alq₃), was graded dispersed along the film in the direction of growth in the hole transport polymer poly(3-hexylthiophene-2,5-diyl) (P3HT, regiorandom) layer of the PLED, despite being dissolved in the same organic solvent as the polymer. The PLED reported here, which is composed of a graded structure, emitted brighter light than PLEDs composed of pure polymer or of a blend of active layers prepared by spin coating and/or vacuum spray methods.

Keywords: Polymer light-emitting diodes; Luminance; Graded doped; Vacuum spray

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Organic and polymer light-emitting diodes (OLEDs and PLEDs [1], respectively) have attracted a great deal of interest for application in emissive flat panel displays and as new light sources. One reason is that the OLEDs and PLEDs are composed by several layers on the substrate; thickness of these layers is less than 200 nm. Therefore, these devices are lightweight and thin, and can be fabricated on flexible substrate. Now many efforts have been made to improve their luminance and lifetime. It has been shown, for example, that the luminance of an OLED can be improved by producing a bilayer (or multilayer) structure by successive sublimation steps. However, for PLEDs, it is usually difficult to fabricate a bi- [2] or multilayer [3] structure with common processes due to the dissolution between polymer layers.

Good balance between electron and hole injection is very important for the functioning of both OLEDs and PLEDs. In PLEDs, the most common way to achieve this balance is by blending the electron and hole transporting materials. The electroluminescent (EL) efficiency is higher when the electron and hole transport materials are separated and attached to the cathode and anode layers, respectively. Another way to achieve this balance could be by producing a structure in which the two materials are graded along the film direction of growth. As there is no interface between the electron and hole transport materials in this structure, it is expected that there will be an increase in the lifetime of the devices. For small organic molecules, graded structures can be fabricated by codeposition processes [4-7] and annealing [8], but for polymers it is difficult to control the gradient profile in the active layer due to dissolution by the solvent. There have been attempts to achieve polymer graded structures, such as molecular-scale interface engineering [9], self-organization [10], and thermal transfer process [11]; however, the processes involved are not simple.

We have developed a vacuum spray (VS) method [12-16]

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that allows fabrication of polymer films with a controllable dye distribution along the film direction of growth, by which graded and/or bilayer structures can be prepared. This report describes the production of PLEDs based on films with homogenious and graded structures prepared using this VS method. For reference studies, devices based on spin-coated films were also investigated.

Figure 1 shows a schematic illustration of the preparation of a graded structured polymer film by the VS method. The polymer and small molecules are diluted separately in the same solvent. These two solutions are then mixed by an apparatus that is part of a gradient high-performance liquid chromatography (HPLC) pump, which includes a program that calculates and controls the precise output ratio of these solutions. This mixed solution is sprayed into a vacuum chamber through a pinhole nozzle, generating a solution mist that is then deposited on a rotating substrate. In the film preparation by VS method in this work, the vacuum chamber was evacuated below $5 \times 10^{-6}$ Pa by a turbo molecular pump, during the spray process, the chamber was maintained below $1 \times 10^{-1}$ Pa. The spray flow rate was set at 1.7 ml/min by HPLC pump, the high spray pressure (from 35 to 40 MPa) was achieved. In addition, the substrate is heated with halogen lamps and the temperature ($T_s$) can be precisely controlled. In this work, $T_s$ was controlled at 353 K. Substrate heating combined with the low pressure in the chamber leads to rapid and complete evaporation of the solution when the mist reaches the substrate. As polymer and small molecules hardly migrate without solvent on the substrate, the concentration distribution of small molecules in the polymer matrix, in the film direction of growth, is determined by their arrival ratio. Films with homogeneous structures were prepared by spraying a homogenously blended solution into the chamber. To prepare a graded polymer film containing increasing concentrations of small molecules along the film direction of growth, the concentration of small molecules was increased linearly relative to the polymer concentration during the deposition process. The thickness of the film is controlled by the solution concentration, flow rate, and spraying time.

PLEDs were produced by spin-coating a hole-injecting material, i.e., poly (3,4-ethylenedioxythiophene) poly (styrene-sulfonate) (PEDOT:PSS; Aldrich), on the indium-tin-oxide substrate. An active layer 110 nm thick was then produced by the VS method where the Tris(8-hydroxyquinolino)aluminum(III) (Alq$_3$; Aldrich) electron-transporting molecules were dispersed in the poly (3-hexylthiophene-2, 5-diyl) (P3HT) (regiorandom; Aldrich) hole-transporting polymer. Finally, a Mg:Ag (10:1) cathode 50 nm thick was deposited on top by thermal evaporation. Each PLED cell was 2 mm×2 mm in size.

Three types of active layer were prepared by the VS method with substrate temperature fixed at 353 K. Pure P3HT layers were prepared with P3HT/chloroform solution at concentration of 0.06 wt%; blend P3HT:Alq$_3$ (4:1) layers with P3HT:Alq$_3$(4:1)/chloroform solution, in which P3HT concentration was 0.048 wt% and Alq$_3$ concentration was 0.012 wt%; and graded layers of P3HT and Alq$_3$ with P3HT/ chloroform and Alq$_3$/chloroform solutions both at concentration of 0.06 wt%. During the production of the graded layers, the
Alq$_3$:P3HT ratio was increased linearly. For reference studies, P3HT and P3HT:Alq$_3$ blend films were prepared by spin coating. The P3HT spin coating film was prepared with P3HT/chloroform solution at the concentration of 1.0 wt%. The P3HT:Alq$_3$ blend spin coating film was prepared with blend solution in which the concentration of P3HT was 0.8 wt% and the concentration of Alq$_3$ was 0.2 wt%.

Figure 2 shows the electroluminescence properties of the PLEDs prepared by spin coating and VS methods. While the $I$-$V$ characteristics (Fig. 2a) did not differ with production method for PLEDs composed of a pure P3HT layer, the $L$-$V$ characteristics showed that PLEDs prepared by the VS method emitted brighter light. This may have been because there is less solvent residue in the polymer layer prepared by the VS method.

Adding an electron transport material to the hole transport material is one way to achieve better electron injection and to balance the carriers, and thus higher luminance can be expected. In this study, the electron transport material (Alq$_3$) was added into the hole transport (P3HT) material and the results are shown in Fig. 2. In the case of PLEDs with uniformly blended layers, both the current and the luminance of PLEDs prepared with the spray layer were higher than those of PLEDs prepared with the spin-coated layer. This may be because solvent residue is left in the spin-coated layer and/or that Alq$_3$ aggregates easily in layers prepared by the spin coating process due to the solvent residue. With the VS method, where almost no solvent residue is left in the layer, Alq$_3$ molecules did not migrate after reaching the substrate, which markedly impeded the aggregation.

As a general trend, PLEDs with a blend structure have higher working voltage [17], and in this study the turn-on voltage ($V_{on}$ at the minimum luminance of 0.1 cd/m$^2$) of the PLEDs with a spin coating layer (see Table 1) confirmed this trend. However, the $V_{on}$ of the PLEDs with a blend layer prepared by VS method was about the same as that of PLEDs composed of pure structures. This low $V_{on}$ is an advantage of the VS method for PLED applications. Unfortunately, the highest measured luminance ($L_{max}$) of the PLEDs with a blend layer was lower than the $L_{max}$ of PLEDs with pure structures. In the blend structure case, the efficiency was even lower than that of the PLEDs with a pure P3HT active layer.

To improve the luminance of PLEDs, the blended layer was exchanged for a graded doped layer where the structure consisted of a P3HT matrix in which the concentration of Alq$_3$ was increased linearly from 0 to 20%. Thus, while there is no Alq$_3$ in the polymer near the interface with the PEDOT:PSS layer, the concentration of Alq$_3$ increases linearly in the polymer until about 20% in the region near the interface with the cathode. We have reported the structure of these graded layers prepared by VS method analyzed by scanning transmission electron microscopy (STEM) [14,15]. Although in the present study the polymer film was thinner, the graded structure is expected to be similar to that reported previously.

The graded structure device has a turn-on voltage of 9 V, which is about the same as that of the pure and blend structure devices (Tab. 1), however, it emits much brighter light than the pure and graded structure devices (Fig. 2b). As the heterojunction interfaces are virtually eliminated in the graded structure, this increase in brightness was probably because there is a better balance of charge carrier in such a way that there is a higher recombination probability of holes and electrons [5], leading to a large increase in PLED performance. In the present study, the optimized highest ratio of Alq$_3$ to P3HT was about 1:4, but suitable ratios have still to be determined for other combinations of electron and hole transport materials.

All PLEDs showed very similar EL spectra to that of the graded structured PLED shown in the insert of Fig. 2b. In addition, all PLEDs emitted yellow-orange light and the preparation method and structure of active layers did not influence the color. Thus, only P3HT emit light, while Alq$_3$ acted only as an electron transport material without emitting light.

In summary, this report described the successful fabrication of a PLED in which the polymer active layer had graded doping with electron transport molecules by the VS method. The results showed that the graded structure improves the performance of PLEDs.

| Device Structure | Spin coating | VS method |
|------------------|--------------|-----------|
|                  | $V_{on}$ (V) | $L_{max}$ (cd/m$^2$) | $V_{on}$ (V) | $L_{max}$ (cd/m$^2$) |
| Pure P3HT        | 7            | 159.4     | 9            | 415.1         |
| P3HT:Alq$_3$ (4:1) blend | 23          | 94        | 9            | 218.8         |
| Graded           |              |           | 9            | 1028.0        |

Table 1. Turn-on Voltage ($V_{on}$ at the minimum luminance of 0.1 cd/m$^2$) and highest luminance ($L_{max}$) of PLEDs.
method. The graded doped PLED emitted much brighter light than those produced with a pure polymer layer and with a blend layer, regardless of whether the layers were prepared by the spin coating or spray method. Due to the excellent controllability of the doping process of the VS method, other structures such as bilayer, multilayer, or more complicated profiles can also be prepared. The conversion efficiency of not only PLEDs but also polymer solar cells can be improved by using a graded structure. Therefore, the VS method is very promising for the fabrication of polymer optoelectronic devices, not only PLEDs but also polymer solar cells.

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The electrical switching characteristics of single copper tetra-cyanoquinodimethane nanowire

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In this paper, method combined vapor transportation with in-situ chemical reaction is employed to synthesize Cu(TCNQ) nanowires. The typical diameter of nanowires is 50-500 nm with high uniformity. The electrical switching characteristics of single nanowire are observed. The ON-OFF resistance ratio for switching reaches $10^4$. The investigation reveals a linear relationship between the switching threshold and the spacing between the two electrodes. The temporal response of the switching process is 30 ns and the switch exhibits good reproducibility. The collapse of the nanowire under the condition of current surge is also discussed. It is believed that the Cu(TCNQ) nanowire could be promising for applications in nanoelectronics.

Keywords: Cu(TCNQ); Nanowire; Electrical switching; Charge transfer Complexes

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Metal-TCNQ (7,7,8,8-Tetracyanoquinodimethane) charge transfer complexes have long been considered as organic logical and memory materials due to their electrical switching phenomena induced by the structural phase transition in the mix-stack columns in the form of solitons [1]. The phenomenon and mechanism of the switching effect has been widely discussed in Metal-TCNQ formed with different metals, such as Ag(TCNQ), Cu(TCNQ), K(TCNQ), and Rb(TCNQ) over the past 40 years [2-6]. However, the difficulty in device integration and large switching delay time for traditional bulk and film materials has restricted their application in high-density electronic devices.

Since its recently discovered quasi-one-dimensional nanostructures, Cu(TCNQ) has attracted renewed attention because of its large surface to volume ratio and size effects which exhibit perfect crystal structure and opens up prospects for high-density nanoelectronics devices [7,8]. Recently, some researches on the switching properties and prototype device fabrication of the Cu(TCNQ) nanostructures have been reported. Liu [9] and Xiao [10] reported the directed integration of Cu(TCNQ) nanowires by a lateral bridging growth method and the observation of a bistable electrical switching; R. Muller [11] investigated the electrical properties of Cu(TCNQ) nanotubulars in Au/CuTCNQ/Au nanojunction formed by electroplating method and obtained nonvolatile electrical switching with an ON-OFF current ratio of $10^3$. Although such researches have significantly enhanced the understanding of the CuTCNQ nanostructure materials, the above-mentioned nanostructures are difficult to reveal the intrinsic switching characteristics of Cu(TCNQ) nanostructure and not well suited for reproducible device since all these nanostructures were formed by multiple nanounits (nanowire, nanotubular) which were disorderly arranged and loosely packed between the electrodes. In previous work, we introduced a method combined with physical vapor transportation and in-situ chemical reaction to synthesize single crystalline nanowires of Ag(TCNQ), Cu (TCNQ) and K(TCNQ) [12]. In this paper, single Cu(TCNQ) nanowire was assembled between the two Ni/Au electrodes via photolithography, and the electrical switching of the nanowire...
has been measured which exhibited a current ON-OFF ratio of $10^4$. Moreover, the temporal process, the reproducibility and the stability of the switching process were discussed. We believe that single Cu(TCNQ) nanowire could be employed as a switching unit with promising controllability and uniformity, which could avail the logical device application in the future.

a) Nanowires synthesis:

Cu(TCNQ) nanowires were synthesized by a method that combines physical and chemical vapor deposition techniques. A 10 nm Cu film was deposited first on a silicon (111) substrate in a thermal evaporator in vacuum. Then Cu thin film was placed together with TCNQ powder (98% Aldrich) in a glass tube. After the tube pumped down to $2 \times 10^{-3}$ Pa, it was sealed and put into a furnace, where the temperature was ramped to 100°C and the nanowires would form. The Cu film was under saturated vapor of TCNQ in this condition. The reaction was expressed as follows:

$$\text{Cu}^0 + \text{TCNQ}^0 \rightarrow \text{Cu(TCNQ)}$$

The phase structure and chemical state of as-obtained nanowires were identified by a Rigaku X-ray diffractometry with Cu Kα incident radiation and Raman spectrometer with an excitation wavelength of 632.8 nm. A Philips XL30FEG SEM was employed to observe the morphology of the Cu(TCNQ) nanowires.

b) Measurement on the electrical switching of the nanowire:

In order to measure the I-V properties of individual Cu(TCNQ) nanowire, as-obtained nanowires were separated from the substrate by ultrasonication in alcohol. The suspension was then deposited onto a silicon chip capped with a layer of 200-500 nm SiO$_2$. Photolithography was employed to form a square electrodes array which consisted of 10 nm of Ni and 100 nm of Au, as can be seen in Fig. 1A. Individual nanowire with good contacts on both ends were then located using SEM as shown in Fig. 1B. During the measurement the load resistor placed in series with the sample should be carefully picked in order to avoid the collapse of nanowire resulting from the heating effect of the current which will be discussed below.

SEM image (Fig. 2) shows vertically grown nanowires on the Si substrate with a typical diameter around 50-500 nm. The growth of Cu(TCNQ) nanowires conformed to a Vapor-Liquid-Solid mechanism [13]. TCNQ vapor diffused into liquefied droplets of Cu and reacted with it to form co-melting droplets of Cu and Cu(TCNQ) as illustrated in Scheme 1A. The excess Cu(TCNQ) with high surface activity precipitated gradually and formed nuclei as illustrated in Scheme 1B. Then the dissolved Cu(TCNQ) continued to precipitate and stacked in the existing interface on the droplets to grow in the preferential direction as illustrated in Scheme 1C.

Figure 3A showed Raman spectrum of the as-obtained nanowires and neutral TCNQ. The band at 2229 cm$^{-1}$, 1205 cm$^{-1}$ and 1607 cm$^{-1}$ was assigned to the C≡N stretching, C=CH bending mode and the C=C ring stretching mode of Cu(TCNQ) molecules, respectively. Compared with the Raman spectrum of neutral TCNQ, the C-CN stretching mode in the as-obtained nanowires shifted from 1455 to 1374 cm$^{-1}$, indicating a charge transfer between Cu and TCNQ [14,15]. Figure 3B showed XRD powder pattern of the nanowires. The intense features in the low-angle region identified that the as-prepared nanowires belonged to phase I [16].

To confirm the electrical switching of Cu(TCNQ)

![Scheme 1. Schematic illustration for the growth of aligned Cu(TCNQ) nanowires.](image_url)

![FIG. 3. (A) Raman, (B) XRD pattern of Cu(TCNQ) nanowires.](image_url)
nanowires, we fabricated prototype device to measure the current-voltage (I-V) characteristics of individual Cu(TCNQ) nanowire (as shown in Fig. 4A). The sample for measurement here was 400 nm in diameter and the spacing between the two electrodes was 2.1 µm (Fig. 1B). When the voltage applied to the device was increased to the threshold of 34 V, the current rapidly increased, indicating the sample transfer from a high-resistance to a low-resistance state. After the voltage was swept down to 0 V, the sample turned back to high-resistance. The nanowire resistance in the high-resistance state and low-resistance state was approximately 10 GΩ and 2.83 MΩ, respectively. The actual ON-OFF resistance ratio for switching reaches in 4 orders as can be seen in the logarithmic plot for I-V in Fig. 4A.

No previous researches on the single Cu(TCNQ) nanoribbon with 20 µm in length showed switching effect during the electrical measurement [9]. This can be explained by the the field driving solitons transportation model for traditional MTCNQ crystal [2] which also has been proved in our experiment for nanoscaled structures. After we carefully selected the spacing between the two electrodes during the I-V measurement, the proportional relationship between the threshold voltage of Cu(TCNQ) nanowire and the length of the nanowire between the electrodes has been revealed, indicating the local field dependence of the phase transition. Therefore, the free motion of the minority of charged defects solitons is hindered by the interstack repulsion at low fields. When the electric field is raised to a critical threshold, a positive feedback process occurred in which the field-induced motion of defects leads to an accelerated loosening of the interstack interaction and consequently ends in a sudden break of the long-range BOW state [2]. That is the switching effect would not happen until the nanowire reach its threshold of local electric field, which was 12.1 V/µm for Cu(TCNQ) nanowire as illustrated in Fig. 4B.

Figure 5A demonstrates the temporal response of the switching process after a positive pulse voltage V₀, with 75 V in amplitude and 150 ns in width was applied to the nanowire. The length of the nanowire between the two electrodes here was 2.4 µm. Once the voltage on the sample V₁ reached the switching threshold voltage of 26 V it transited from a high-resistance to a low-resistance state, and afterwards V₁ fell down rapidly. The fall time of approximately 30 ns was the temporal response of the switching process. Compared with traditional M-TCNQ bulk or thin film materials average charge transfer process in molecules, the temporal response of Cu(TCNQ) nanowires appeared to be faster. In particular, the previous temporal response measured on Ag(TCNQ) [17] and K(TCNQ) [6] thin film exhibits a slower delay time T_d in μs order when the voltage on sample rises from 0 V to its switching threshold as illustrated in Fig. 5B, whereas such effect could be neglected in Cu(TCNQ) nanowire. The reason for this was that the switching we observed resulted from the charge transfer in huge amount of molecules instead of one single molecule [2]. The nonlinear increasing of V₁ shown in Fig. 5B indicates an energy absorbing process occurs during the break of the long-range

FIG. 4. (A) I-V characteristics of individual Cu(TCNQ) nanowire, and the arrow demonstrated the sequence of applying the voltage. State I and II indicated the electrical ‘OFF’ and ‘ON’ states, respectively. (B) The spacing between the two electrodes versus the switching threshold.

FIG. 5. (A) The temporal measurement describing the break of the nanowire, (B) I-V characteristics of M(TCNQ) thin films and (C) The reproducible measurement of the nanowire.

FIG. 6. The temporal measurement describing the collapse of the nanowire.
BOW state. Owing to the size effect of every individual nanowire, the required energy for the macroscopically current switching is much lower and thus can be supplied within an ultrafast time.

The switching process also exhibited good reproducibility as shown in Fig. 5C. When the applied pulse voltage was substituted with a periodical triangle signal, a periodical change in current could be observed that almost no current flew through the device in high-resistance state (I) while a current in $\mu$A order could be measured in low-resistance state (II). The resistance change of the switching device in two states was also plotted in Fig. 5C.

It should also be mentioned that, in order to avoid the collapse of nanowire, a proper load resistor should be placed in series with the sample. Figure 6 illustrates the temporal measurement showing the collapse of the nanowire during the electrical measurement. The spacing between the two electrodes here was 3 µm. The load resistor used here was 10 KΩ, much lower than the resistor of 1 MΩ–10 MΩ employed in normal measurement. A triangle scanning voltage was applied to the sample. $V_0$ was the output voltage of the power source, and $V_1$ was the voltage on the sample. As shown in the inset, when the voltage applied to the sample was below 38 V, $V_1$ was almost equal to $V_0$ indicating the nanowire was in high-resistance state. The switching occurred at the threshold of 38 V with a sharp decline of $V_1$. Consequently, however, the surge of the current would rapidly heat the nanowire to collapse and $V_1$ suddenly increased at the voltage of 41 V.

The future application for the as-prepared structure is diversified in terms of these properties. For instance, due to the quick switching response, the device can serve as over-voltage protector when connected in parallel with other device. When a large voltage occurs, the switching device will swiftly transfer to low-resistance state and ‘short-circuit’ the system preventing other device from break.

Cu(TCNQ) nanowires were successfully synthesized by method combined vapor transportation with in-situ chemical reaction. The electrical switching effect with high ON-OFF ratio of approximately $10^4$ was observed in individual Cu(TCNQ) nanowire. The measurement demonstrated that the threshold voltage of the switching was proportional to the length of the nanowire between the electrodes. The electrical switching of the nanowire exhibited fast temporal response of 30 ns and fine reproducibility. These unique properties indicate their promising applications in nanoelectronics.

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A vacuum nano-casting route to magnetite cores/mesoporous silica shell composites

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Hollow mesoporous silica spheres with magnetite cores (HMSMC) have been fabricated by Vacuum Nano-casting Route. The amount of magnetite cores and saturation magnetization value can be easily adjusted by changing the concentration of iron nitrate solution used in the synthesis procedure. Furthermore, the as-prepared HMSMCs still maintain narrow mesopore distribution, high surface area and large pore volume after the hollow cores of hollow mesoporous silica spheres were filled with magnetite particles. Specially, when the saturation magnetization value of as-prepared HMSMCs reaches 22.0 emu/g, the surface area and pore volume of corresponding HMSMCs are 149 m$^2$/g and 0.19 cm$^3$/g, respectively, and the pore size is 2.30 nm. The corresponding samples are characterized by X-ray diffraction, N$_2$ sorption isotherms, transmission electron microscopy and vibrating-sample magnetometer.

Keywords: Hollow mesoporous silica spheres; Magnetite cores; Vacuum nano-casting

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A number of literatures have described the formation of hollow mesoporous spheres in the past few years [1-8], and it is generally accepted that hollow spheres with mesoporous shells will exhibit more advantages in mass diffusion and transportation compared with conventional hollow spheres of solid shells [4,8]. On the other hand, magnetic particles embedded in mesoporous materials have been intensively pursued for its emergent applications in biomedicine and efficient separable catalysis [9-14]. Due to their large pore size, high surface area, spherical morphology and magnetism, mesoporous spheres incorporated with magnetic particles have attracted great attention [15-19]. There have been some reports on the preparation of magnetic particles coated with mesoporous shells. Magnetic core/mesoporous silica shell structures were synthesized by sol-gel reaction on hematite particles followed by H$_2$ reduction [16,17]. The magnetic nanocrystals and GdSe/ZnS quantum dots were embedded in mesoporous silica spheres by sol-gel reaction [18]. In these reports, hematite particles and magnetic nanocrystals were firstly synthesized, and then were coated with mesoporous silica shell. It can be seen that these procedures required very strict control over the synthesis conditions and the yield is relatively low. Fuertes and co-workers [19] recently reported an incipient wetness impregnation technique to synthesize carbon capsules with a variety of inorganic materials. This method is attractive. However the inorganic solution has to be added dropwise until incipient wetness, and the procedure should be repeated many times for desired loading amount. Herein, we use a new route to fabricate hollow mesoporous silica with magnetite cores (HMSMC) and the amount of magnetite cores can be easily adjusted by changing the concentration of iron nitrate solution used in the synthesis procedure.

The strategy for the synthesis of the magnetic cores embedded in HMS is designed and presented in Fig. 1. First, the

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uniform hollow mesoporous spheres (HMS) were obtained via the way reported by Tan (TEM images of as-synthesized HMSs are shown in Electronic Supplementary Materials (ESM) Fig. 1). A certain amount of dewatered HMSs was vacuumized for a few minutes, and then the vacuum pump was turned off, and the ethanol iron nitrate solution (0.25, 0.5 or 1.0 M) and air was let to be filled into the system till normal air atmosphere. So the HMSs were immersed in solution. After a few minutes, the iron nitrate solution was removed and the precipitate was dried at 333 K. The resulting powder was washed twice by ethanol, and dried again. After that, the powder was calcined at 773 K for 2 h to yield the hollow mesoporous silica spheres with hematite cores (HMSHC). The reduction was carried out by the thermal treatment of the HMSHC particles in mixed H\textsubscript{2} (5% volume percentage) and Ar (95% volume percentage) gases at 683K for 5 h, and the final HMSMCs were obtained.

Powder XRD patterns were recorded on a Rigaku D/Max-2550V diffractometer using Cu K\alpha radiation (40 kV and 40 mA). The scanning rate was 6 °/min. Nitrogen sorption isotherms at 77 K were measured on a Micrometitics Tristar 3000 system. Before measurement, samples were pre-treated at 373 K for 12 h under nitrogen. The specific surface area and the pore size distribution were calculated from the BET and Barrett-Joyner-Halenda (BJH) data, respectively. TEM images were obtained on a JEM-2010 electron microscope operated at 200 kV. A vibrating-sample magnetometer (PPMS Model 6000 Quantum Design) was used to study the magnetic properties.

The TEM images of HMSHCs (Fig. 2a (0.25M-HMSHC), b (0.5M-HMSHC), c (1.0M-HMSHC), here 0.25, 0.5 and 1.0 M represent the concentrations of iron nitrate solution) show that the hematite are loaded into the hollow cores of HMSs, and the loading amount of hematite increases with the increase of the iron nitrate concentration used in the synthesis. HMSs were also immersed in 0.5 M iron nitrate solution under normal atmosphere for 24 h as a reference for comparison, which was named as C-HMS. The TEM image of C-HMS (ESM Fig. 2) shows the HMSs have no hematite cores. In the XRD pattern of HMSHCs (ESM Fig. 3), all the diffraction peaks match well with the standard PDF data (JCPDS Nos. 33-0664) of hematite, confirming the formation of α-Fe\textsubscript{2}O\textsubscript{3} and the peak intensity increases with the increase of the iron nitrate concentration used in the synthesis of HMSHCs, which also depicts that the loading amount of hematite cores can be adjusted by changing the concentration of iron nitrate solutions. Comparatively, the XRD pattern of C-HMS gives no apparent diffraction peaks, in accordance with the TEM results. The TEM images of the reduced HMSMCs (Fig. 2d (0.25M-HMSMC), e (0.5M-HMSMC) and f (1.0M-HMSMC)) show that the cores have shrunk and the amount of magnetic cores increases with the increase of hematite amount loaded. In the XRD pattern of Fig. 3, all diffraction peaks matching well with the standard PDF data (JCPDS No. 19-0629) confirm that the reduced cores are single-phase of magnetite Fe\textsubscript{3}O\textsubscript{4}. The reduction products can be controlled, according to the typical reduction process of hematite: α-Fe\textsubscript{2}O\textsubscript{3} → Fe\textsubscript{3}O\textsubscript{4} → FeO → Fe, by altering the reduction temperature or time [16,20]. The diffraction intensities of different samples increase in accordance with the increase of the loading amount of magnetic particles in the hollow cores. So we can easily control the loading amount of hematite and
magnetic cores by adjusting the iron nitrate concentration in the synthesis of HMSMCs.

The magnetization curves of the HMSMCs at room temperature (Fig. 4) shows magnetic hysteresis loops, which demonstrates the magnetic response to a varying magnetic field. The saturation magnetization values of HMSMCs are 2.2, 7.2 and 22.0 emu/g for 0.25M-, 0.5M- and 1.0M-HMSMC, respectively. The coercivity values are approximately 250 Oe for 0.25M-, 0.5M- and 1.0M-HMSMC, as estimated from the inset of Fig. 4.

The N$_2$ adsorption/desorption isotherms were recorded to investigate the pore properties of as-prepared HMS, 0.25M-, 0.5M- and 1.0M-HMSMC (ESM Fig. 4). All isotherms show the characteristic of mesoporous materials: type-IV isotherms with a marked leap in the adsorption branch at relative pressures P/P$_0$ between 0.2 and 0.4. This indicates that the mesostructure of HMSs has been kept after loading the magnetite cores. The structure parameters of all samples are summarized in Table 1. Here, similar pore size distributions for all samples, around 2.4 nm, can be found in Table 1. And the surface area is found to decrease gradually from HMSs, 0.25M-HMSMC, 0.5M- HMSMC to 1.0M-HMASMC, and the pore volume also decreases in the same order. The main reason for such decreases can be attributed to the presence of magnetite cores, which have higher density than silica.

In conclusion, we have successfully fabricated hollow mesoporous silica spheres with magnetite cores by a vacuum nano-casting route. The loading amount of the magnetite cores and saturation magnetization values of HMSMC can be adjusted by simply changing the concentration of iron nitrate solution used in the synthesis procedure. Relatively high surface area (149 m$^2$/g), large pore volume (0.19 cm$^3$/g), and mesoporous shell can be obtained for the HMSMC which has a saturation magnetization value of 22.0 emu/g.

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Schottky photodiode using submicron thick diamond epilayer for flame sensing

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The sensing of a flame can be performed by using wide-bandgap semiconductors, which offer a high signal-to-noise ratio since they only response the ultraviolet emission in the flame. Diamond is a robust semiconductor with a wide-bandgap of 5.5 eV, exhibiting an intrinsic solar-blindness for deep-ultraviolet (DUV) detection. In this work, by using a submicron thick boron-doped diamond epilayer grown on a type-Ib diamond substrate, a Schottky photodiode device structure-based flame sensor is demonstrated. The photodiode exhibits extremely low dark current in both forward and reverse modes due to the holes depletion in the epilayer. The photodiode has a photoconductivity gain larger than 100 and a threshold wavelength of 330 nm in the forward bias mode. CO and OH emission bands with wavelengths shorter than 330 nm in a flame light are detected at a forward voltage of -10 V. An alcohol lamp flame in the distance of 250 mm is directly detected without a focusing lens of flame light.

**Keywords:** Flame sensing; Boron-doped diamond; Schottky photodiode

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flame sensing. Semiconducting diamond with a bandgap of 5.5 eV is an attractive material due to its weak sensitivity in the visible wavelength range and high sensitivity in the DUV range (i.e., it has solar blindness).

Intrinsic diamond shows a cut-off wavelength of 225 nm beyond the flame UV emission. It is basically difficult to use only thick intrinsic diamond for flame sensing. However, the submicron thin film technology and impurity engineering provide the opportunity to apply diamond to flame sensing. By using submicron thick boron-doped homoepitaxial diamond layers on type-Ib diamond substrates and proper device structures, it is able to tune the overall properties of diamond photodetectors [3]. For example, the dark current can be extremely low due to the depletion of free holes in the submicron epilayer [4]. The threshold wavelength of the diamond detector can be tailored to be larger than 225 nm [4-7]. The photoconductivity gain can be as larger as 100 upon DUV light illumination. Thus, the diamond photosensor developed is able to detect the CO and OH emission bands in the hydrocarbon flame.

In this work, we demonstrate the solid-state flame sensor by using the high-sensitivity diamond DUV photosensor. In addition, we show the flame sensing performance of the diamond photosensor.

The p-diamond epilayers were homoepitaxially grown on Ib-type nitrogen-containing diamond (100) substrates with a dimension of 2.5×2.5×0.5 mm by a microwave plasma-enhanced chemical vapor deposition technique. The growth conditions were described in the previous paper [5,6]. The thickness of the epilayer was about 0.5 μm, and the [B] in the epilayer and the [N] in the substrate were measured by secondary-ion mass spectroscopy to be mid 10^{15} and mid 10^{19} cm^{-3}, respectively. Prior to fabricating the device, the surfaces of the epilayers were oxidized in a boiling acid solution of H_2SO_4 and HNO_3 to remove the surface conductive hydrogenated layers. Planar-type Schottky photodiodes (SPD) with semi-transparent WC Schottky and annealed Ti/WC Ohmic contacts were fabricated on the epilayer [5,6]. A WC Schottky contact with a nominal thickness of 3-5 nm was deposited in a defined circle pattern with a diameter of 0.98 mm. The interspacing between the Schottky and Ohmic contacts was 10 μm. Finally, the photodiode chip was packaged in a TO5-type can with a sapphire window.

The current-voltage characteristics were measured in a vacuum chamber at a pressure of 0.1 Pa by using a two-point probe method. The photoresponse properties were measured by illuminating monochromatic light with a wavelength between 210 and 630 nm using a 500-W xenon lamp. The incident light power was calibrated using a UV-enhanced Si photodiode. The time response of the SPD photodiode was measured by a digital oscilloscope. The flame sensing properties were measured using an alcohol lamp. Photoluminescence of the alcohol lamp flame was measured using the spectrometer system.

Figure 1 shows luminescence spectra of alcohol lamp flame and solar radiation through a room window glass. The major peaks of the flame are OH- and H-related emissions at 310 and 590 nm, and a shoulder band from 240 to 300 nm is observed in the DUV wavelength region [8]. In order to detect the flame optically under the existence of solar radiation, we have to develop the DUV photosensor with a large responsivity for...
wavelengths lower than 300 nm and a large discrimination ratio between the DUV and visible light.

Figure 2(a) illustrates the Schottky photodiode by using submicron boron-doped p-type diamond grown on a HPHT type-Ib diamond substrate. Figure 2(b) depicts the responsivities of the diamond photosensor for 220 and 280 nm-lights illumination as a function of applied bias voltage, where forward and reverse biases correspond to negative and positive voltages, respectively. The dark current of the photosensor was lower than 0.1 pA in the forward and reverse bias modes. Since the nitrogen in the diamond was known to behave as a donor with thermal activation energy of 1.7 eV [9], the high density of nitrogen in the Ib-type substrate is believed to deplete the hole in the thin epilayer, which results in the extremely low current even in the forward bias mode. Note that this leads to enhancement of the detectivity by using the Ib-type substrate. The voltage dependence of responsivity shows the clear rectifying properties, which indicates that the current transport is controlled by photo-generated holes. This is the characteristic feature of the diamond SPD as reported previously [5]. The responsivities as large as 136 A/W for 220 nm light and 38 A/W for 280 nm light is obtained in a forward bias voltage of -10 V. The corresponding quantum efficiency values are $7.7 \times 10^4$ % for 220 nm light and $1.7 \times 10^4$ % for 280 nm light, which indicates the photoconductivity gain property as reported previously [4,5]. The gain mechanism is explained by existence of electron trap with high capture rate and low emission rate, which provides the significant increment of the hole lifetime and the hole concentration [3,6]. This model is supported by the predominant current transport due to hole. Since we also observed the gain property of the MSM photoconductor at an applied voltage lower than 1 V [7], the interaction between the epilayer and the Ib-substrate is believed to be responsible for the kinetic gain mechanism.

Figure 3 shows time dependences of (a) responsivity of 220 nm light at -10 V, where curve (b) shows the 220 nm light pulse for comparison. The transient behavior to the 220 nm light of the current circled SPD is similar to the interdigitated SPD operated at forward biases [4]. The response time is evaluated to be as small as 5 ms. The response time for 280 nm light pulse is absolutely the same as that for the 220 nm light. Note that the present SPD has the high DUV-sensitivity and the response speed enough to detect the flame.

The d.c. spectral response of the SPD at a forward bias of -10 V is shown in Fig. 4. Differed from the reported diamond photodetectors [5,7], the threshold wavelength shifts from 270 nm to around 330 nm. This value does not change as the Schottky contact diameter increases from the previous 400 µm to the current 980 µm [4]. However, the visible-blind ratio (210/400 nm) increases greatly as the Schottky diameter increases. This value reaches up to around eight orders of magnitude in the present SPD due to the increased UV sensitivity. The cut-off wavelength and the high visible-blind ratio offer the current diamond SPD a potential candidate for flame sensing.

Figure 5 is a photograph of sensing the alcohol lamp flame by the diamond SPD under bulb light illumination background, where an inside photograph shows the photosensors packaged in the TO5 can. The diamond photosensor is set on the left-hand side at 250 mm in length apart from the alcohol lamp flame. The photosensor is able to detect the flame in the distance of 250 mm at a forward voltage of -10 V, and the photocurrent level is around 100 pA. Note that the flame can be detected without using a focusing lens. Since the threshold wavelength
of the present SPD was around 330 nm, the CO and OH emission bands with wavelength shorter than 330 nm is believed to be predominantly detected. This is the distinct demonstration which is really capable of sensing the hydrocarbon flame using the diamond DUV photosensor.

In summary, by using a submicron thick boron-doped diamond epilayer on a type-Ib diamond substrate, the cut-off wavelength of the diamond SPD was extended to be around 330 nm at forward biases. By virtue of this property, we developed the flame sensor by using the diamond SPD packaged in the TO5 can with the sapphire window and demonstrated sensing the alcohol lamp flame. Although we did not use the focusing lens of DUV light, the photosensor was able to detect the flame reproducibly in the distance of 250 mm. The development of the flame sensor opened a new application avenue for diamond photosensors.

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Ballistic current induced effective force on magnetic domain wall

C. Wang and K. Xia*

The collective dynamics of magnetic domain wall under electric current is studied in the form of spin transfer torque (STT). The out-of-plane STT induced effective force is obtained based on the Landau-Lifshitz-Gilbert (LLG) equation including microscopic STT terms. The relation between microscopic calculations and collective description of the domain wall motion is established. With our numerical calculations based on tight binding free electron model, we find that the non adiabatic out-of-plane torque components have considerable non-local properties. It turns out that the calculated effective forces decay significantly with increasing domain wall widths.

Keywords: Magnetic domain; Spin Transfer torque; Spintronics; First principle study

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The application of spintronics [1] requires effective ways of spin manipulations in nanoscale devices. Recently, growing interest has been focused on the current induced magnetic dynamics. Electric currents can be spin-polarized by passing through magnetic domains, and the polarized spins of the conducting electrons can exert spin transfer torque (STT) to the localized magnetizations when going through a magnetic domain wall. On the other hand, the spins of electrons will be altered by the localized magnetizations in return [2,3]. Beautiful experiments have been conducted using STT effect in devices [4-7]. However, the dynamics of magnetic domain walls (DWs) in the presence of electric current are still not well understood, especially for the components of spin transfer torques perpendicular to the plane where the local magnetization’s directions change. Shibata et al [8,9], studied the DW motion based on the s-d electron model and collective coordinates of the DW. They found that the DW motion will be dominated by the effective force on the DW, which is rooted from the reflection of the electrons incident on the DW. On the other hand, S. Zhang and Z. Li [10,11] pointed out that the out-of-plane STT was crucial for the stead current induced DW motion and proposed a non-adiabatic STT due to spin-relaxation mechanism. Another non-adiabatic STT was proposed by J. Xiao [12], which is due to the misalignment of non-equilibrium spin density and local effective field. The out-plane spin transfer torques can stem from either spin relaxation or non-local non-adiabatic effects [9]. However, the link between the microscopic STT and the effective force on the DW is missing.

In this paper, we start from the Landau-Lifshitz-Gilbert (LLG) equation, including the microscopic STT Terms from our numerical calculation, theoretically analyze the motion of the DW. The relation between the effective forces on DW and STT are established. The connections between the different components of STT and the effective forces and STTs on domain wall are established. Then we discuss the relationships between our results and other models in the end of Section II. In Section III the STT in DW is studied numerically for free electron model. Our calculations of out-plane torques show that the parameter $c_j$ describing the non-adiabatic torque in LLG equation is not constant but position dependent, implying its non-local characters. The DW width dependence of the...
Effective force is obtained.

**EFFECTIVE FORCE AND OUT-OF-PLANE STT**

The current-driven domain wall dynamics is studied based on the Landau-Lifshitz-Gilbert equation, the connection between effective force and out-of-plane STT on each site is obtained. The LLG equation reads,

\[
\frac{d\mathbf{M}}{dt} = -\gamma \mathbf{M} \times \mathbf{H}_{ef} + \frac{\alpha}{M_s} \mathbf{M} \times \frac{d\mathbf{M}}{dt} + \mathbf{T}_i + \mathbf{T}_z
\]

where the magnetization \(\mathbf{M}\) can be written as the function of polar angles as indicated in Fig. 1:

\[
\mathbf{M}(\theta, \phi) = M_s (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)
\]

We assume that the magnitude of the magnetization will not change when the DW moves. We can rewrite the on sites LLG equations Eq. (1) with sphere polar angle coordinates \((\theta_i, \phi_i)\) and then apply the Walker ansatz so that Euler angles are treated as functions of position and time.

The DW is parallel to the \(z\) direction, \(\theta\) and \(\phi\) are the function of position and time. \(\theta = \theta(z - X(t)), \phi = \phi(z, t)\), \(X\) is defined as the wall center’s position within the “rigid wall” approximation, and \(\phi(z, t)\) is simply reduced to \(\phi(t)\) in the model used in following derivation. The variable \(X\) and \(\phi\) can serve as collective coordinates to describe the wall motion. Namely, we can get the dynamic information of the domain wall if we know the time evolution of \((X(t), \phi(t))\). In the simplest model \((\phi = 0)\), the plane reduces to \(x-z\) plane.

\[
\mathbf{H}_{ef} = \mathbf{H}_{ex,i} + \mathbf{H}_{K,i} + \mathbf{H}_{demagi} + \mathbf{H}_{ext}
\]

\[
= H_{ex} 4\pi M_s (m_{i,x} + m_{i,x}) + H_{ex} m_{i,y} e_y' - 4\pi M_s m_{i,z} e_z' + \mathbf{H}_{ext}
\]

contains respective contributions from exchange interaction, anisotropy, demagnetization field, and external field where subscript \(i\) denotes different sites in the wall. The nearest neighboring approximation and assumption of constant magnitude of \(M\) were applied. The unit vectors in Cartesian coordination can be transformed into polar coordination.

And spin transfer torques can be explicitly expressed as,

\[
\mathbf{T}_i = -\frac{1}{M_z} \mathbf{M} \times (\mathbf{M} \times \frac{\partial \mathbf{M}}{\partial z}), \mathbf{T}_z = -c_1 \frac{1}{M_z} \mathbf{M} \times \frac{\partial \mathbf{M}}{\partial z}
\]

Putting all the above terms into the Eq. (1), we eventually obtain the LLG equation written in polar coordination with variable \((\theta, \phi)\) as,

\[
\begin{align*}
ev^\theta \phi : \theta &= \gamma 2M_s \sin \theta \sin 2\phi - \alpha \sin \theta \\
&+ T_{i,x} / M_s \cos \theta - T_{i,z} \sin \theta / M_s
\end{align*}
\]

\[
\begin{align*}
ev^\phi \phi : \phi \sin \theta &= \gamma (H_{ex} M_s 2\pi \frac{1}{2} + H_K / 2 + 2\pi M_s \cos^2 \phi) \\
&\cdot 2 \sin \phi \cos \theta + \alpha \theta + T_{i,z} \sin \phi / M_s
\end{align*}
\]

The above two sets of equations can be solved numerically for arbitrary STT form and effective field. However, when current and applied magnetic fields are not very large, rigid wall is a good approximation to study the DW motion. Applying Walker’s ansatz [16], the localized spins in Neel domain wall structure (Shown in Fig. 2) expressed in spin polar coordination satisfies

\[
\cos \theta (z,t) = \frac{\tanh \left( \frac{z - X(t)}{\lambda} \right)}{\lambda}
\]

Considering the magnetization \(\mathbf{M}\) of the domain wall and...
the localized macroscopic spin $\vec{S}$ satisfy the relationship:
\[ \dot{M} = -J\vec{S} / a^3, \]
we can express this relationship by pole angles:
\[ \cos(\pi - \theta_j(z,t)) = \text{tanh}(\frac{z - X(t)}{\lambda}), \phi_{0j}(z,t) = \phi_{0j}(t). \]
And we can see the time dependent behavior of $\theta$ is completely determined by the wall(center) position’s dynamics property:
\[ \dot{\theta}_m = -\frac{1}{\lambda} \sin \theta \cdot \dot{X}. \]

For the convenience in connecting to our first principles calculation, we use the $\vec{S}$ in the following of the paper. Using the relationship of magnetic moment and spin angular momentum $M_S = \gamma_0 \frac{1}{a} S$, the Eq. (5) (6) could be expressed by localized macroscopic spins. Summing all the equations on each site together, we obtained the corresponding equations for the collective coordinates. Replacing the summation by integration for the simplicity, the region of integration is set as where $L = Nd$ is the wall length, $d$ is the distance between neighboring sites, and $N$ is the total number of sites in a domain wall which can be extended to $\infty$. Since $\cos \theta$ varies from -1 to 1 in a symmetric way, the sum over position is $\int \cos \theta (z, \tau) dz = 0$. Considering the two collective coordinations $(X, \phi)$ are independent on position, the sum of equations on all the sites along the wall results in
\[ \begin{align*}
\bar{e}_\theta : \dot{X} - \alpha \dot{\phi} &= 2\pi \frac{\gamma_0}{\alpha} S \lambda \sin 2\phi \\
&+ \frac{\lambda}{S L} \int_{-L/2}^{L/2} d\tau \frac{1}{\sin \theta} \left( T_{||x} - T_{||z} \right) \tag{8}
\end{align*} \]
\[ \begin{align*}
\bar{e}_\phi : \phi + \alpha \dot{X} &= \int_{-L/2}^{L/2} d\tau \frac{1}{\sin \theta} T_{||z} \tag{9}
\end{align*} \]

So the equations portraying the dynamic behavior of the rigid wall are obtained. Recalling the expressions of spin torque in LLG Eq. (4), the spin torque exerted on localized spins in the right side of equations above can be simplified by
\[ (T_{||x} \frac{\cos \theta}{\sin \theta} - T_{||z}) / S = \frac{1}{\lambda} \bar{b}_j, T_{||z} \frac{1}{S \sin \theta} = \frac{1}{\lambda} \bar{c}_j \tag{10} \]

With the obtained results, we can immediately obtain the velocity, effective force and torques exerted on the domain wall in the following. If we regard $b_j$ and $c_j$ are independent on position (we will discuss the validity of this simplification with our calculations section III), the current-driven domain wall motion velocity, as the time derivative of wall position $X$, can be expressed by $b_j$ and $c_j$ using Eq. (8) (9) (10):
\[ \dot{X} = -\frac{1}{\alpha^2 + 1} (b_j + \alpha c_j) \tag{11} \]

Our results Eq. (9) and (10) also imply that for $t \rightarrow \infty$ in which $\phi = 0$, the magnitude of the domain wall ultimate velocity is determined by $c_j$ while the initial speed is mainly determined by $b_j$. The expression of velocities agrees well with other groups’ previous outcome [10]. In order to further clarify the roles of different components of STT, we combine our results with what obtained from s-d model Hamiltonian $H_{sd} = -J_{sd} \int d^3 x \cdot S \cdot \vec{S}$. We can immediately come to some interesting results after comparing Eq. (8) (9) with effective forces and effective torques [9]. It turns out that the out-plane spin torque $T_{||z}$, which appears in Eq. (9) corresponds to the force on domain wall, while the in-plane spin torque $T_{||x}$ contributes to the $z$ component of torque on the wall as a whole:
\[ \frac{\lambda}{N_s S} T_{||z} = \frac{\lambda}{S NL} \int_{-L/2}^{L/2} dx \frac{1}{\sin \theta} T_{||z} \tag{12} \]
\[ \frac{\lambda}{N_s S} F = \frac{d}{S NL} \int_{-L/2}^{L/2} dx \frac{1}{\sin \theta} T_{||z} \tag{13} \]

Eq. (12) tells that force exerted on the rigid domain wall is also originated from the STT(but only the perpendicular element $T_{||z}$), while Eq. (13) shows that the summed effective spin transfer torque along $z$ is determined by integration involving different positions’ $T_{||x}$ and $T_{||z}$. After we apply Eq. (10) and define $\bar{b}_j$ and $\bar{c}_j$ as the average values of the two parameters, the two integrations in Eq. (12) and Eq. (13) become
\[ \frac{\lambda}{N_s S} T_{||z} = \frac{\lambda}{\alpha} b_j \tag{14} \]
\[ \frac{\lambda}{N_s S} F = \frac{1}{\alpha} c_j \tag{15} \]

Although it is widely accepted that different components of STTs can be written in the form of Eq. (4), the origin of out-of-plane STT could be stem from different physics. In our calculation, we focused on the nonadiabatic term pointed out by J. Xiao and M. Stiles [12].

**NUMERICAL CALCULATION AND DISCUSSION**

In the following, numerical calculation is used to
investigate the torque as the function of domain wall width $\lambda$.
After introducing the calculation methods we used, we subsequently investigate the in-plane and out-plane STTs. The obtained calculations are in accordance with our model and can be helpful to the discussion about effective force.

A. Calculation of STT in Domain Wall

The structure used in the calculation is current in plane (CIP) domain walls in ferromagnetic materials. We apply free electron model in our calculations where the current is along (110) direction in fcc structure using the lattice constant of Cobalt $a = 3.549 \, \text{Å}$. And we set the energy split between majority and minority spins in free electron energy band as 1.69eV, which equals the value of exchange energy split of bulk Cobalt. Our numerical approach is based on the Tight-binding linear muffin-tin orbital formulism [13,14]. Scattering wave function is obtained by the wave function matching method [15]. The rigid potential approximation is employed to simulate the DW. Here STTs in our study can be defined as the difference between the incoming and outgoing spin current at R site.

$$\mathbf{\vec{T}} = \frac{\hbar}{2} \sum_{s, s'} \mathbf{\tilde{\gamma}}_{s, s'}(k_i) V_{s, s'}$$

Here summation over the 2D Brillouin zone is performed. Combining with the expression of current passing through R-site, the STT per unit current is obtained:

$$\mathbf{\vec{T}} = \frac{\mathbf{\vec{F}}}{G \cdot V_{s, s'}}$$

Given a specific current density ($\sim 10^{10} \, \text{A/m}^2$), we can calculate corresponding torque. The calculated spin transfer torques along the DW is presented in different components in Fig. 3. From the Eq. (12) and Eq. (13) the force and $z$-component's effective torque can be calculated.

![Fig. 3. Position dependence of different components of spin transfer torque in the domain wall structure.](http://www.nmletters.org)

![Fig. 4. Distribution of out-plane STT components in DW with $\lambda=6\text{ML}$. The inset shows the decaying oscillations of $T_{y}$ at sites away from DW centers.](http://www.nmletters.org)

![Fig. 5. The values of $c_j$ near the wall center. We make a cutoff and only consider the contribution of sites not far from the wall center.](http://www.nmletters.org)

B. Out-plane STT and Effective Force

Let us focus on the out-plane component of STTs. From our numerical calculations, we find a decaying oscillation for out-of-plane STT $T_{z, y}$ as shown in Fig. 4. From the inset in Fig. 4 we can see the decaying oscillation of $T_{z, y}$ at the sites away from DW centers. We can see that $T_{z, y}$ deviate significantly from zero only within a certain distance from wall center. We can fit these STTs with Eq. (10) to obtain the on site parameter $c_j = \lambda T_{z, y}/(S \sin \theta)$. Numerical difficulty comes from the position far away from the DW center, where $\sin \theta$ is very small and out-of-plane STTs oscillate as the function of position. Considering that the STT mainly dominated by the DW near the center where the angle of local magnetization changes significantly, a cut off is applied so that our focus is...
concentrated to regions near the wall centers. The calculated \(c_j\) as a function of position is presented in Fig. 5. From Fig. 5 we can see that \(c_j\) obtained from our model are position dependent rather than constant. This is reasonable because the non-adiabatic torques is nonlocal and has vibrating behaviors. Combining the calculated results, we will discuss the DW velocities expressed in Eq. (11). When the rigid wall still holds, it is suitable to express the terminal velocities \(v(t \to \infty) = -c_j/\alpha\).

Considering \(c_j\) is not constant but oscillating, we may use the average \(c_j\) to express the terminal velocity. When the wall is thicker, the increase of inertia or wall mass makes it harder to move, thus the velocities get smaller and consequently larger driving currents are required. In our model, the velocities will indeed drop significantly when the out plane torques \((c_j)\) terms vanish in thicker walls, as depicted in Fig. 6. However, we need to keep in mind that the Walker’s model we use to describe rigid walls will break down under high external field [16,17] or high current density [9]. In that case, the domain wall would be oscillating so the definition of DW velocities is no longer available.

The forces at different wall structures are calculated from integration within the narrowed region of \(c_j(z)\) using 
\[
F = \langle \bar{S} \hat{L}_z \rangle \sum c_j(z) \overline{c_j(z)}
\]
and presented in Fig. 6. We can see from the result that the forces exerted on the walls decrease significantly as the walls get thicker, implying that the non-adiabatic effect is obvious in thin domain walls. And the forces or the integrated non-adiabatic torques decay approximately parabolic exponentially with the increase of DW width.

FIG. 6. The force is calculated in wall structures with different widths. Our average \(c_j\) only take account of the contributions from sites near the wall center where the value of \(\sin\theta(z, t)\) is nonzero. The red line is a parabolic exponential curve.

CONCLUSION

In sum, domain wall motion under electrical current is studied focusing on spin transfer torque effect. Under the approximation of rigid wall the relationships between the force, velocity and different components of STT are clarified. And the results of our calculation successfully testify the validity of adiabatic limit. For out-plane component, the calculated torques show oscillating and decaying behaviors. The calculated non-adiabatic torque dependence on wall width is in good accordance with the physical illustration that an extremely thick wall would become completely adiabatic and thus the forces and terminal velocities originated from non-adiabatic terms vanish.

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Colloidal silicon nanocrystallites for low-cost solar cell development

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In this letter a formation of solution based of bulk-heterojunction based on freestanding silicon nanocrystals (Si-ncs) and conjugated ((poly(3-hexylthiophene) (P3HT) polymer is demonstrated. Surfactant free Si-ncs prepared by low-cost electrochemical etching are applied for fabrication of bulk-heterojunction and photo-conductive blends. We show that the optimum blend performance is at 40 wt% nanocrystallites concentration within the P3HT polymer matrix. Furthermore, we illustrate that solar cell transport properties can be improved by nanosecond laser fragmentation of the nanocrystallites micrograins in ethanol. It argues that the Si-ncs/polymer blend with refine nanocrystalline structure may impact the development of low-cost solar cells by environmental-friendly mean.

Keywords: Silicon; Nanocrystals; Electrochemical etching; Solar cell

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Solar cells have become nowadays ever more attractive as an alternative source of green energy [1-3]. A conjugated polymer based solar cells particularly present one perspective choice for the development of solar cells industry on large areas and at low cost [3-5]. Most of the polymer solar cells today rely on the formation of bulk-heterojunction i.e. a interpenetrating network of donor and acceptor material [4-6]. In last decade the fast photo-induced charge transfer from a conjugated polymer to fullerene showed to be very efficient and this system considerably speed up polymer based solar cell development [7,8]. Nowadays polymer based solar cells having a electrical conversion efficiency in the range of 3-8% [9-12]. However, still vigorous period of research is needed to refine the structure processing and to develop the solar cell fabrication techniques.

One-way to improve the efficiency is blending of polymer with a second inorganic nano-composite. On the other hand, it is accepted in photovoltaic community that to achieve a considerable improvement in solar cell efficiency a new physics as quantum-confined structures have to be applied [13-15]. One of such approach involves so called “hybrid” photovoltaic structures, consisting of blending of organic polymers with inorganic semiconductor nanocrystals (quantum dots), possessing of quantum confinement size effect (e.g. CdS, CdSe, and CdTe) [16]. Better yet, similar to fullerene, the nanocrystal can also serves as an acceptor for electrons [17] or potentially as a donor when it is doped.

Silicon nanocrystals (Si-ncs) are one potential low dimensional nanocomposite that fulfills all criteria for the next generation of solar cell development [13]. It has been demonstrated that it can be also efficiently used for bulk-heterojunction formation when blended with conjugated polymers [17,18]. Natural micro/nano phase-separation between the polymer and the solid state Si-nc get the morphology/structure to obtain photogenerated carrier separation [17,18]. In addition, it is expected that Si-ncs with quantum confinement size effect may provide a significant boost in carrier generation efficiency from a phenomenon so called carrier multiplication [19-22]. The principle of the phenomenon is sketched in Fig. 1. Illuminated nanocrystal
responds to an absorbed photon by producing multiple electron-hole pairs. So far in many types of nanocrystals the phenomenon has been widely reported [20-22]. It has to be stressed higher multiplication rates were reported for low band gap nanocrystals (e.g. CdSe). However, since the Si-ncs possess non-toxicity for the environment, abundance and established silicon based photovoltaic technologies Si-ncs even lower carrier multiplication rate could be more favorable material for solar cell production process at lower cost.

Processing of freestanding Si-ncs allows homogenous dispersion in almost any liquid, polymers included. It enables tuning of nanocrystals concentration in the host matrix very simply and high concentration assuring percolation trajectories for Si-ncs can be simply achieved [17]. Those might directly impact the blend performance. Even more, the interface between the organic and soluble nanocrystal can be controlled by using chemical or physical methods. Such flexibility considerably improves the opto-electronic interaction with host polymer matrix and allows better energy transfer within the system (nanocrystal/polymer). Recently introduced laser fragmentation of silicon micrograins can tune efficiently the surface chemistry and allows closed pack integration of Si-ncs within self-organized structures without using any surfactant [23]. It is believed that a nanosecond laser processing of the Si-ncs in liquid and blending with suitable conjugated polymer may considerably impact solar cell performance.

Here we demonstrate a fabrication of bulk heterojunction based on blending of freestanding Si-ncs with ((poly(3-hexylthiophene) (P3HT) polymer. Cheap electrochemical etching is applied for preparation of free standing and surfactant free Si-ncs with bright-red photoluminescence (PL) at room temperature. Si-ncs blended with polymer show an improvement in photoconductivity response and the optimum performance is observed at ~ 40 wt% concentration. Further, we show that an improvement of the nanocrystals surface passivation and morphology by nanosecond laser fragmentation processing in liquid media enhances the transport properties of the solar cell device.

In this work the freestanding doped Si-ncs are prepared by electrochemical etching of a silicon wafers. Boron doped wafer with a resistivity of 0.5-0.75 $\Omega \cdot$cm (p-type, <100>) was used. The wafers were electrochemically etched in a mixture of hydrofluoric acid with pure ethanol (HF:C$_2$H$_5$OH = 1:4, current density 3.2 mA/cm$^2$ and etching time 60 min). After etching the Si-ncs were collected by mechanical scratching and sedimentation [24].

For blend formation a commercially available (ALDRICH) polymer (poly(3-hexylthiophene) (P3HT) was used. Blends were prepared by dissolving 10 mg of polymer in 10 g of chlorobenzene. Then freestanding Si-ncs were introduced at different concentrations. In order to study photoconductivity measurement 300 nm thin films were spun cast on a glass covered by interdigitated platinum contacts. The interdigitated contacts consisted of 20 fingers, with a length of 6 mm and a width of 200 $\mu$m, separated by 200 $\mu$m. At the same conditions another set of samples just with pure polymers (P3HT) were fabricated for comparison. After processing all samples were dried at 140°C for 30 min in vacuum.

At the 40 wt% concentration of Si-ncs the solar cell device has been made by following way. Glass substrates with an indium tin oxide electrode were used for solar cells fabrications. In order to smooth the ITO surface the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid (PEDOT: PSS) was deposited by spin coating (3000 rpm, dried at 135°C). Subsequently, the Si-ncs/P3HT solution was spin-coated on the PEDOT:PSS/ITO substrate. Then, an alumina top electrode of 100 nm was deposited on top of the active layer by vacuum
evaporation. The active area of the cell was 4 mm$^2$.

It has to be noted that the PL, conductivity and the photoconductivity measurements were conducted in air atmosphere and ambient conditions. To measure PL the samples, an HeCd laser with a wavelength of 325 nm (3.82 eV) was used. In order to measure I-V characteristics a voltage from a regulated DC power supply was applied and the resulting current was measured with a KEITHLEY 6430. For photoconductivity measurement a white light of 1.5 AM was used. Spectrally resolved photocurrent of the solar cell was measured under illumination with monochromatic light from a Xe lamp. In all cases the irradiation intensities were calibrated by a standard a-Si solar cell.

Figure 2(a) shows a schematic sketch for a collection of fine silicon crystallites dispersed in ethanol. After a scratching procedure [19] and dispersion of powder in ethanol the largest micrograins get sediment on the bottom of the glassware. The finest used for further blend fabrication are harvested from the upper liquid after evaporation of ethanol. Figure 2(b) shows a typical photo of the upper solution after sedimentation for 4 hours. When the largest agglomerates sediment the upper solution becomes transparent that suggests that only the smallest nanocrystals remained. In order to test the presence of Si-ncs bright room temperature PL feature is used to witness them. When the laser beam is shined through the solution red PL is observed (Fig. 2(b)). This proofs that we deal with the Si-ncs with quite good quality. Low concentration defects (surface or bulk) do not hinder emission significantly. Further structural analysis [25] witnessed the presence Si-ncs with diamond-like structure with average size about 3 nm. Corresponding PL spectra is shown in inset of the Fig. 2(b). The PL spectrum is rather broad with maximum centered at 2 eV. As reported elsewhere the PL in Si-ncs with grain size of less than 5 nm originate mostly from quantum confinement effects [25-27]. Similar arguments could be used to describe luminescence properties of our sample. Therefore one can expected that a significant spectrum broadening could be ascribed to large nanocrystal size distribution.

Recently it has been demonstrated that such a way prepared Si-ncs blended with conjugated polymer form a bulk-heterojunction [17,28]. As the freestanding Si-ncs concentration within the polymer can be easily tuned, the photoconductivity response of the blend at different nanocrystallites concentration has been optimized. It has been observed that the photo- and dark-conductivity ratio varied as a function of Si-ncs concentration (Fig. 3). As the Si-ncs concentration is increased also the ratio between photo and dark increases and reaching maximum at around 40 wt.%. After reaching the peak the ratio again decreased. It has to be noted that the photoexcitation in silicon nanocrystals is fundamentally different from those in polymers or organics nanoparticles. Particular, whereas light absorption in Si-ncs (quantum dot) results to the direct generation of mobile charged carriers, however, the higher (more than 10 times) light absorption in polymer leads to the generation of excitons [17]. The exciton in polymer is associated with binding energy in excess of 0.2 eV. Therefore the exciton and the charged carrier transport in higher absorbing polymer [28] is the heart of the photocarrier generation of the blend. As a result an excitionic energy transfer might be an efficient mechanism to pump Si-ncs through the excitation of conjugated polymers [17]. We stress that the exciton is charge-neutral and is transported due to the diffusion process only. Contrary to that a charged carrier is transported by both diffusion and/or drift in the built-in electric fields. In our case field results from difference in work function of P3HT polymer and ionization potential of the nanocrystal that

![FIG. 3. Photo-/dark-conductivity ratio as a function of Si-ncs concentration in P3HT polymer matrix.](http://www.nmletters.org)
dissociates photogenerated excitons [17]. When the concentration is further augmented, most likely the P3HT lamella-like structure become more perturbed, which results in a hole mobility decrease [29]. Those perturbations then limit carrier transport and photoconductivity response of the blend at higher Si-ncs concentrations as 40 wt%.

Furthermore, we have fabricated solar cell based on the blend with silicon nanocrystallites concentration around 40 wt%. This allowed us to test the blend properties in sandwiched device-like configuration Fig. 4(a) shows energy level diagram of Si-ncs conjugated polymer based hybrid solar cell (ITO/PEDOT:PSS/(Si-ncs/P3HT)/Al). The PEDOT:PSS is used as the hole collector in this structure and alumina as the electron. While the polymer band structure is well known (having the highest at (~ 5 eV) and lowest unoccupied molecular orbital (LUMO) level at ~ 2.9 eV) the ionization potential of the Si-ncs is not well determined yet. Meanwhile it is assumed that it does not differ significantly to bulk silicon and adjust to band gap of the Si-ncs [17]. It is considered that band offset decreases due to quantum confinement and wide band gap of Si-ncs. Red photoluminescent Si-ncs having optical band gap around ~2 eV and work function being around ~ 4.1 eV that can be favorably aligned with P3HT polymer. Then, different electron affinity and ionization potential between the nanocrystal and polymer provides a driving force for dissociating the excitons. It has to be noted that similar to parallel configuration as the concentration of Si-ncs is increased also the generation of the photocurrent in solar cell is enhanced by reaching maximum around ~ 40 wt%.

Figure 4(b) represents photocurrent generation as a function of wavelength for the blends with around 38 wt%.

Figure 5(a) represents corresponding I-V characteristics of Si-ncs (38 wt. %) embedded in P3HT polymer. (b) I-V characteristic of the device made from Si-ncs micrograins fragmented in ethanol and blended with P3HT at ~38. wt.% concentration. Red lines are recorded under AM1.5 illumination and the black curves in dark. preparing Si-ncs in less oxidizing liquids by newly developed techniques (i.e. laser processing). In order to show the potential of laser processing we elaborated Si-ncs micrograins in ethanol by nanosecond laser fragmentation. Figure 5(b) presents I-V characteristics of the device made from such defragmented Si-ncs micrograins and blended with P3HT (at same weight concentration (~ 38%)). Red lines are recorded under AM1.5 illumination and the black ones in dark. We could clearly observe that defragmentation increased the generation of the photocurrent in the solar cell and an improvement in fill factor has been recorded as well. This is mostly due to the formation of thinner oxide shell around nanocrystals during the fragmentation process in ethanol as compared to exposure to the air. However, due to the fabrication of larger sized nanocrystalites a decrease in energy band gap occurred. This could be beneficial factor for better matching with solar spectra, however balance between the fragmentation conditions and Si-ncs size has to be find. Otherwise decrease in band gap reduces the open circuit voltage (VOC). Unfortunately, since in this work we focused primarily to show the principles, the structure morphology was not optimized yet. Therefore, further structural changes can occur when the fragmentation is performed in less oxidizing liquids at optimal fragmentation conditions. It has to be noticed that the fragmentation in liquid at the same time allows tuning of nanocrystallites surface properties without any

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additional surfactant [22], which might considerably improve the solar cell properties.

In conclusion, we fabricated by electrochemical etching top-down approach freestanding and surfactant-free photoluminescent silicon nanocrystals (Si-ncs). We showed that the blending with poly(3-hexylthiophene (P3HT) conjugated polymer allowed formation of solution based bulk-heterojunction. The different electron affinity and ionization potential between the Si-nc and P3HT dissociates excitons and allowed photocurrent generation. We demonstrated that the largest rate between photo- and dark-conductivity has been achieved at Si-ncs concentration around ~40 wt%. Furthermore, we showed a strategy for an improvement of photocurrent generation in solar cells by applying of Si-ncs prepared by nanosecond laser fragmentation in ethanol.

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Optical properties of ZnO and Mn-doped ZnO nanocrystals by vapor phase transport processes

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In this paper we investigated the optical properties of ZnO and Mn doped ZnO nanocrystals that were fabricated by a vapor phase transport growth process, using zinc acetate dihydrate with or without Mn in a constant O₂/Ar mixture gas flowing through the furnace at 400~600 °C, respectively. The as grown ZnO nanocrystals are homogeneous with a mean size of 19 nm observed by scanning electron microscope (SEM). The optical characteristics were analyzed by absorption spectra and photoluminescence (PL) spectra at room-temperature. For ZnO nanocrystals, a strong and predominant UV emission peaked at 377 nm was found in the PL spectra. For Mn doped ZnO nanocrystals, in addition to the strong UV emission, a strong blue emission peaked at 435 nm was observed as well. By doping Mn ions, the major UV emission shifts from 377 nm to 408 nm, showing that Mn ions were not only incorporated into ZnO Ncs, but also introduced an impurity level in the bandgap. Moreover, with the concentration of Mn increasing, the relative intensities of the two emissions change largely, and the photoluminescence mechanism of them is discussed.

Keywords: ZnO and Mn-doped ZnO nanocrystals; Optical properties; Vapor phase transport growth

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Zinc oxide (ZnO), a promising II-IV group semiconductor material with hexagonal wurzite structure, has been widely applied in various fields [1] such as transducers, transparent conduction electrode, solar cells, and wide ultraviolet (UV) optoelectronic devices [2], due to its direct band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV. To realize the light-emitting devices, an important issue is the fabrication of p-type conduction ZnO with a high concentration of hole and a low resistance. However, it is difficult to achieve low resistivity p-type ZnO film because of problems such as self-compensation, deep acceptor level, and low solubility of the acceptor dopants [3].

Recently, studies present that the doping of transition metal element Mn into ZnO offers a feasible mean of realizing p-type ZnO offers a feasible mean of realizing p-type ZnO film because of problems such as self-compensation, deep acceptor level, and low solubility of the acceptor dopants [3].

Mn impurity can be incorporated into ZnO during its growth by many approaches, including pulsed laser deposition [7], hydrothermal method [8], electron spin resonance [9], which are complicate technologies. In other researches, ZnO Ncs are grown using wet chemical methods [10, 11], but the wet modality limits the device applications. In our experiment, we try to synthesize and dope ZnO nanocrystals on Si and quartz substrates by a simple vapor phase transport (VPT) process [12]. The surface morphology of the products was investigated by

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scanning electron microscope, and the optical characteristics were analyzed by photoluminescence spectra at room temperature. The photoluminescence mechanism for both pure ZnO nanocrystals and Mn doped ZnO are discussed as well.

ZnO nanocrystals were fabricated by a simple vapor phase transport (VPT) process, as shown in Fig. 1, where the system consisted of a large horizontal quartz tube furnace, a vacuum system, a gas meter, and a temperature controller. Pure zinc acetate dihydrate as the source material was placed at the bottom of a one-end sealed slender quartz tube that was positioned at the center position of the furnace. For uniform growth, cleaned Si (111) and quartz wafers as the substrates were placed at the end of the large tube, in front of the slender tube but far away from it. Prior to the fabrication, the furnace was pumped at vacuum and heated to 100 °C and kept for 2 hours to remove the water moisture in the zinc acetate dehydrate. Then the furnace was heated to the growing temperature of 500 °C. At the same time, a mixture gas of O₂/Ar was loaded through the furnace and kept a constant flowing during the growing process. The growing process was carried out for 30 min, and the samples were taken out when the system cooled down to room temperature.

For Mn doped ZnO Ncs, the synthesis process is identical with above except that the source material is the mixture of zinc acetate dihydrate and manganese acetate tetrahydrate with different ratios. After the mixture decomposing at a high temperature of 500 °C, the mixed vapor of Zn/Mn was drawn out of the small tube by the flowing gas and condensed on the substrate as well. When the mixed Zn/Mn liquid droplets deposited and crystallized, ZnO Ncs were uniformly doped with Mn.

The morphology of the products was investigated by a Shimadzu SS-550 super scanning electron microscope (SEM). And the composition was analyzed by X-ray diffraction (XRD) on a RINT2000 vertical goniometer with Cu Ka radiation (λ=0.1541 nm). The photoluminescence (PL) measurements were performed by using a tunable excitation source at room temperature.

Figure 2(a) illustrates the surface morphology of ZnO Ncs on Si substrate investigated by SEM. Clearly, ZnO nanoparticles with an average size of 18 nm are uniformly dispersed on Si substrate, and a few of them aggregate together, which because new small ZnO nanoparticles were nucleated continually in the growth process. At the same time, small ZnO Ncs has large surface effect than that of the bulk material, leading to the nanocrystals readily get together. Figure 2(b) is a SEM picture taken from the quartz sample, where the morphology of ZnO Ncs is similar to that of Fig. 2(a) except that the density of ZnO Ncs is lower, indicating that ZnO Ncs prefer nucleate on Si substrate to quartz. The X-ray diffraction pattern of the ZnO Ncs on Si is shown in the upper panel in Fig. 3, while the standard diffraction spectrum of the bulk wurtzite ZnO is in the down panel. We can see that the diffraction peaks and the interplane spacing are well matched to the standard diffraction pattern of wurtzite ZnO, demonstrating that our products have a distinct formation of wurtzite ZnO nanocrystals. The average diameter of ZnO DQs is 19 nm estimated from Scherrer’s equation. These results indicate that the ZnO Ncs obtained in our experiment are of high quality with standard crystal shape and acceptable size.
Figure 4(a) shows an absorption spectrum of the pure ZnO Ncs on Si substrate at room temperature. It can be seen that the absorption intensity decreases sharply as the wavelength is over 355 nm, which can be defined as the absorption edge, corresponding the absorption of the intrinsic bandgap of ZnO. From the value of the absorption edge, we can estimate the bandgap of energy of ZnO Ncs to be about 3.54 eV. Figure 4(b) shows the photoluminescence (PL) spectrum of ZnO Ncs measured at room temperature. In the PL spectrum, ZnO Ncs exhibit a strong and predominant UV emission peaked at 377 nm, originating from the band to band emission of ZnO Ncs. And a much lower blue-green peak is positioned at 435 nm that is attributed to the surface defect from oxygen vacancies or zinc interstitials. For comparison, the PL spectrum of bulk ZnO is also given in a red line, where the date is magnified of 100 times. The UV and the blue emissions is absent in the bulk ZnO at room temperature, while a weak large band peaked at 500 nm (Kelly color) is appeared, attributing to the emission from the surface energy levels. Therefore, the predominant strong UV emission in ZnO Ncs results from the quantum-confined band-edge emission and the quantum size effects. Additionally, in the conventional growth methods, in order to obtain a prominent UV emission, the as grown ZnO Ncs usually require some accessional treatments, such as surface modification and annealing. In our experiment, ZnO Ncs sample achieves a very strong UV emission through a simple VPT process without any additional treatment in the experiment, showing that the as grown ZnO Ncs are of high quality.

Figure 5 shows the absorption spectrum of the Mn doped ZnO Ncs sample measured at room temperature. There are two absorption bands, one is located at 208 nm, and the other is a large band with a sharp absorption edge at 357 nm. The former corresponds to the absorption of MnO that has a larger band gap (4.2 eV), which makes the first absorption edge taking a blue shift. The latter is a combined absorption of ZnO:Mn Ncs, pure ZnO Ncs, and the surface defect states. Figure 6 shows the photoluminescence spectra of ZnO:Mn Ncs sample. For comparison, the PL spectrum of the pure ZnO Ncs is shown in panel (a). Figure 6(b) shows the PL spectrum of ZnO: Mn Ncs when the material ratio of Zn/Mn at 95:5. We can see that the PL property has taken a significant change by doping Mn impurity. The UV emission from the band edge of ZnO is almost quenching, replaced by two emissions with almost identical intensity in the spectrum, one is located at 409 nm, and the other is placed at 435 nm. The former can be considered as the UV emission shifting to longer wavelength of 408 nm because of Mn ions introducing an impurity in the energy band.
bandgap of ZnO. The latter originates from Mn relevant compounds, such as Mn$_2$O$_3$ etc. With the ratio of Zn/Mn increase to 95:10, the blue emission of 435 nm becomes stronger, while the UV emission decreases much a lot along with shifting from 408 to 390 nm, that is, the major UV emission shifts to short wavelength again.

From the PL spectra, we know that Mn impurity is triumphantly doped into ZnO Ncs. The doping way of Mn impurity in ZnO Ncs either is an interstitial doping or a substitutional doping. If the substitutional doping occurs, Mn ion will substitute Zn ion of ZnO to form MnO. MnO has a larger band gap (4.2 eV) that may lead to the UV emission taking a blue shift in the PL spectra. However, in our experiment the UV emission shifts to longer wavelength after doping Mn, hence we deduce that the doping is more an interstitial doping than a substitutional doping. In addition, the UV emission shifts to longer wavelength initially, then back to short wavelength again. The similar phenomena also happened in other’s researches on Mn doped ZnO [13,14], CdS and ZnSe. According to Bylsma’s [15] second-order perturbation theory on the similar phenomena in Mn doped ZnSe bulk materials, we can give a explanation. If the doping concentration of Mn is low enough (<2%), the d orbit of Mn has strong exchange interactions with the s and p orbits of ZnO, which can be considered as a short range disorder spin system. The first interaction decreases the energy of conduction band bottom, and the second one increases the energy of valence band top, so that the band gap of the product become narrower than before, resulting in the red-shift of UV emission. With the concentration of Mn increasing (>2%), the band gap is broadening, and the emission moves back to the UV field again.

Moreover, the relative intensity ratio of the UV and the blue (435 nm) emissions changes with the ratio of Zn/Mn in the source material. With the concentration of Mn increasing, the intensity of the blue emission increased much a lot, which comes from surface defect levels associated with oxygen vacancies, Mn$_3$O$_4$ etc. The enhanced blue emission is mainly attributed to the increasing of Mn impurities on the surface of ZnO Ncs. Because the decomposing temperature of Mn acetate is higher than that of Zn acetate, it decomposes later than Zn acetate in the growth process. Therefore, more Mn impurities are covered on ZnO Ncs than inter-doped them, on which Mn further combines with oxygen to form Mn$_3$O$_4$, a more stable structure, resulting in more oxygen vacancies and enhancing the green emission.

ZnO Ncs have been grown and doped with Mn by a simple technology of a vapor phase transport (VPT) process. The as grown ZnO Ncs in size of 19 nm have a distinct of wurtzite structure. Without any additional treatment, ZnO Ncs sample exhibit a strong and predominant UV emission in the PL spectra at room temperature. For Mn doped ZnO Ncs, a UV emission and a blue emission are observed, and the position of the UV emission shifts to longer wavelength direction because of Mn introduced an impurity level in the bandgap. With the concentration of Mn increasing, the blue emission enhanced much a lot due to the strong exchange interaction in the short range spin system and the excess Mn$_2$O$_3$ on the surface, respectively.

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Synthesis of Ni nanowires via a hydrazine reduction route in aqueous ethanol solutions assisted by external magnetic fields

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One-dimensional Ni nanostructures were synthesized via a hydrazine reduction route under external magnetic fields. The mixture of de-ionized water and ethanol was used as the reaction solvent and hydrazine hydrate as reducing agents. The morphology and properties of Ni nanostructures were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), and vibrating sample magnetometer (VSM). It was found that the magnetic field strength, concentration of Ni ions, reaction time and temperature as well as pH values played key roles on formation, microstructures and magnetic properties of Ni nanowires. The optimal wires have diameter of ~200 nm and length up to ~200 μm. And their coercivity is ~260 Oe, which is much larger than the commercial Ni powders of 31 Oe. This work presents a simple, low-cost, environment-friendly and large-scale production approach to fabricate one-dimensional magnetic materials. The resulting materials may have potential applications in conductive filters, magnetic sensors and catalytic agents.

Keywords: Ni fiber; Hydrazine reduction; Magnetic field; Magnetic properties

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One-dimensional (1D) magnetic materials such as Fe, Co and Ni have attracted much attention due to their unique magnetic, catalytic, and optical properties with promising applications in catalysts, magnetic sensors, high-density magnetic records, spintronics, magnetic memory bits or microwave circuits, etc [1-6]. Since most physical and chemical properties of these materials depend on their size and shape, it therefore becomes a new and interesting research field to precisely control the size and shape of these materials [7]. Accordingly, 1D nickel nanostructures including nanotubes, nanowires, nanorods, nanochains and nanorays, as a type of important magnetic materials, have been synthesized [8-12]. The common methods for preparation of magnetic nanowires are based on porous anodic aluminum oxide (AAO) templates [13]. AAO templates have been proved to be a simple and efficient method in controlling crystal growth and size of the products. Other templates such as polyaniline or polycarbonate membranes, diblock copolymer and mesoporous silica have also been used to fabricate nanowires with excellent quality [14-17]. In view of the complexity of multi-step preparation of the templates and the residue separation after production, template- or surfactant-free methods for the nanowire preparation are desirable. The use of magnetic field assistant in assembling nanoparticles to form 1D magnetic nanostructures have been proposed, which has been applied for preparation of Co or Fe nanowires. More recently, this method has been used to synthesize Ni nanowires [18]. Unfortunately, previous researches are mainly focused on the fabrication in organic solvents by hydrothermal or solvothermal methods which has drawbacks in purification or environment-friendly point of view.
Therefore, it is imperative to develop simple and template-free methods for fabrication 1D magnetic materials with expected advantages such as low cost, friendly environment, high purity and large-scale production prospection.

Preparation of nanostructures in the aqueous phase may be a preferred approach due to its significant advantages: nonflammable and nontoxic, environment friendly, safety and feasible for a large scale production. However, some limitation of the aqueous approach also should be considered. For example, the as-synthesized products obtained at relatively low temperature are often amorphous, and additional treatment protocols are required to achieve good crystalline of the resulting materials. Additionally, the as-synthesized nanometer-sized Ni particles tend to be oxidized in aqueous solutions.

In this study, we present an approach for fabrication Ni nanowires with good crystalline in an aqueous phase solution under normal pressure in absence of any inorganic or organic templates. The influences of magnetic field strength, concentration of Ni ions and pH values on the formation and morphology of Ni nanowires were investigated. The magnetic properties of Ni nanostructures with different morphology were also evaluated.

All chemicals were of analytical reagent grade and used without any further purification. In a typical process, nickel chloride (NiCl₂·6H₂O) was dissolved into the 100 mL mixture of deionized water and ethanol with a volume ratio of 5:4 to form a transparent absinthe-green solution. An appropriate amount of hydrazine hydrate (N₂H₄·H₂O, 85 wt%) solution as a reducing agent was added until the absinthe-green sedimentation turned to light blueviolet colour. NaOH solution (5 mol/L) was used to adjust the pH value of the mixture. The solution was then placed in a 60°C water bath and the bath was fixed in a magnetic field. The static magnetic field with interval of 30 cm and magnetic pole area of 1200 cm² was generated by direct current flow, and the strength can be controlled from 0.005 T to 0.5 T by adjusting the current intensity. After about 30 minutes, loose black floccules was formed and floated on the solution surface. The products were filtered and washed repeatedly with distilled water and ethanol by using magnetic field, and then dried at 60°C for 12 hours.

The size and morphology analyses were performed using field emission scanning electron microscope (SEM, Ultrazeiss, Zeiss). The phase structure was characterized by X-ray polycrystalline diffractometer (XRD, D8 Advance, Bruker) using Cu Ka radiation with graphite monochromator. The hysteresis properties were measured on a vibration sample magnetometer (VSM, Lake Shore 7400).

Figure 1 shows the SEM images of resulting products with Ni⁺ concentration of 0.01 M under different applied magnetic fields. It can be seen that the magnetic field has strong influences on the morphology of products. In the absence of the magnetic field, only some bulky particles were formed and no 1D material was observed (see Fig. 1a), whereas, under a low magnetic field of 0.05 T, some short, thick and flexural wires were observed (see Fig. 1b). When the strength of the magnetic field was increased to 0.2 T, the longer and thinner nanowires can be formed and no separated particles were observed. The wires have aspect ratio of about 1000 with average diameter of 200 nm and length of 200 μm (see Fig. 1c). There is little change observed on morphology of nanowires when magnetic fields increased from 0.2 T to 0.5 T.
The influence of concentration of Ni ions on morphology of Ni nanowires has also been observed. Figure 2 shows the SEM images of products with different Ni ion concentration under the same magnetic field of 0.2 T. It can be seen that the diameter of the nanowires increased with increasing Ni\(^{2+}\) concentration. It is about 200 nm for concentration of 0.01 M, and about 600 nm for 0.05 M. When the concentration increased to 0.1 M, there is no wires observed, whereas, the clusters with diameter from 200 to 600 nm were produced.

The reaction time has strong influence on the morphology of the products. There are no products observed less than 10 min. Some loose black floccules were formed and floated on the solution surface after 10 min later and for about 30 min the solution became transparent, clarifying and colorless. All the products were floated on the solution surface. However, as the reaction time elongated to 2 h, the nanowires will join together to form silvery-white flakes. For about 3 h later, the grey-colored nanowires disappeared gradually, and bright silvery-white films were formed on the beaker wall. The products dependence of reaction time was displayed in Fig. 3.

The XRD pattern of the Ni nanowires prepared at 0.01 M concentration under 0.2 T magnetic field is shown Fig. 4. Three diffraction peaks corresponding to different crystallization directions of [111], [200] and [220], respectively, indicate the nanowire has a cubic crystal structure which is in agreement well with the Nickel standard card (no. 65-0380). There is no other impurity observed, suggesting the prepared Ni nanowires have high purity.

Figure 5 shows the hysteresis loops of the Ni nanowires which prepared at magnetic field of 0.2 T. The magnetic property of commercial Ni powder which has particle size of about 1 um was also investigated. The nanowires have coercivity of 260 Oe which is much larger than 31 Oe of the powder. However, the saturation magnetization of the Ni nanowires is 41 emu/g, which is much less than the 55.5 emu/g of the powder sample. The large coercivity of Ni nanowire attributes to the shape anisotropy due to its large aspect ratio. This phenomenon has been observed on other Ni nanowires which prepared by templated-assisted methods. The reduced magnetization of Ni nanowires may result from the surface effect of Ni nanowire structures, in which lots of Ni atoms at the surface are not aligned along its magnetic anisotropy direction in order to reduce the the surface energy. Therefore, the magnetic moments of these Ni atoms cannot be aligned along the magnetic field due to the strong exchange interaction.

The possible mechanism for the formation of Ni nanowires in alkali solution under magnetic assistant may be understood as following: nickel ions were firstly reducted by strong reduction agent of hydrazine hydrate and turned to tiny spherical particles. Then the magnetic Ni particles aligned along the magnetic field direction under the magnetic driving force. The nickel nanowires retained their linear structure after kept in ultrasonic bath for 10 minutes, which proved that the nanowires...
showed a good mechanical strength.

It was found that the pH value of the reaction solution is sensitive to the reduction process of nickel ion by hydrazine hydrate. When the pH value was higher than 13.70, the nickel ion can be completely reduced within 30 min, whereas, when the pH value was adjusted to 13.00, it will need 2 hours to finish the reaction. If the pH value was lower than 13.00, the reaction would not take place and there was no any Ni nanowires or particles produced. This is attributed to the different oxidation reduction potentials \( \phi_0 \) of the reaction for different pH values. For a low pH condition, the reaction takes place as follows and the reduction potential can be calculated:

\[
\begin{align*}
N_2H_4^- - 4e^- & = 5H^+ + N_2, & \phi_0 &= -0.23 \text{ V} \\
Ni^{2+} + 2e^- & = Ni, & \phi_0 &= -0.25 \text{ V}
\end{align*}
\]

whereas, for a high pH condition, they will be:

\[
\begin{align*}
\text{Ni(OH)}_2 + 2e^- & = Ni, & \phi_0 &= -0.72 \text{ V} \\
N_2H_4 + 4OH^- - 4e^- & = N_2 + 4H_2O, & \phi_0 &= -1.15 \text{ V}
\end{align*}
\]

The oxidation reduction potentials at low pH condition are higher than those for higher pH values. This will lead to the reaction much easier for higher pH conditions.

In this method all the reaction agents are common and low-cost. The reaction process is simple and fast. It provides a new strategy to prepare other magnetic nanowires. In addition, the amount of products can be up to 100 g/day in our laboratory. It was found that the pH value of the reaction solution is up to 13 at 60°C. This will lead to the formation and morphology of nanowires. The pH value and the concentration of nickel ion has also strong influences on formation and morphology of nanowires. The wires increases with increasing strength of magnetic field, and there is no wires formed in absence of magnetic field. The pH value should be up to 13 at 60°C. This method provides a new approach to fabricate magnetic nanowires in an ambient condition and may be the most promising candidate to produce large-scale magnetic nanowires.

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