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Synthesis and Characterization of Rare Earth Ion Doped Nano ZnO

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Abstract: Zinc oxide (ZnO) doped with erbium at different concentrations was synthesized by solid-state reaction method and characterized by X-ray diffraction (XRD), scanning electron microscopic (SEM), UV-absorption spectroscopy, photoluminescence (PL) study and vibrating sample magnetometer. The XRD studies exhibit the presence of wurtzite crystal structure similar to the parent compound ZnO in 1% Er3+ doped ZnO, suggesting that doped Er3+ ions sit at the regular Zn2+ sites. However, same studies spread over the samples with Er3+ content >1% reveals the occurrence of secondary phase. SEM images of 1% Er3+ doped ZnO show the polycrystalline nature of the synthesized sample. UV-visible absorption spectrum of Er3+ doped ZnO nanocrystals shows a strong absorption peak at 388 nm due to ZnO band to band transition. The PL study exhibits emission in the visible region, due to excitonic as well as defect related transitions. The magnetization-field curve of Er3+ doped ZnO nanocrystals showed ferromagnetic property at room-temperature.

Keywords: Erbium doped zinc oxide; Solid state reaction; X-ray diffraction; Photoluminescence; VSM; Room-temperature ferromagnetism

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Introduction

The promise of nanocrystals as a technological material for applications including wavelength tunable lasers [1], bioimaging [2], and solar cells [3] may ultimately depend on tailoring their behavior by adding impurities through doping. Impurities are reported to modify electronic, optical, and magnetic properties of bulk semiconductors. Dopants can strongly influence optical behavior. Although undoped nanocrystals are highly fluorescent with a color that depends on size, lasers based on this emission are intrinsically inefficient. Several approaches can improve this situation [1], and one possibility is to incorporate dopants that provide carriers. Dopants in nanocrystals lead to phenomena not found in the bulk because their electronic states are confined to a small volume. For example, n- or p-type dopants can auto-ionize without thermal activation. This occurs because a carrier inside the crystalline occupy one of the confined electronic states, which increase in energy with decreasing nanocrystal size [4]. Below a critical radius, the confinement energy exceeds the Coulomb interaction between the ionized impurity and the carrier [5], which then automatically occupies a nanocrystal state.

The critical role that dopants play in semiconductor devices has stimulated research on the properties and the potential applications of semiconductor nanocrystals [4]. Semiconductors doped with rare earth ions are excellent phosphors of high efficiency and low degradation in addition to their unique physical and chemical properties [6]. II-VI compound semiconductors have been found to be unique host materials for doping of optically active impurities which exhibit luminescence at room temperature [7]. ZnO, an II-VI compound semiconductor with a wide band gap of about 3.4 eV, is an attractive material for applications in optical devices such as blue-, violet-, and UV-light emitting diodes (LEDs) and laser diodes (LDs). We have reported

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quantum confinement, influence of surfactant and temperature on the morphology of nano ZnO [8]. In the present paper, we report the influence of rare earth element erbium as dopant in ZnO.

The rare earth ion doped ZnO has the potential to be a highly multifunctional material with coexisting semiconducting, electromechanical and optical properties. The rare earth ions are better luminescent materials because of the sharp and intense emission due to their 4f intra shell transitions. Elements of the lanthanide series are characterized by a partially filled 4f energy levels, which are relatively host independent [9]. Among the lanthanides, erbium has attracted significant attention due to its enormous potential in various applications. The telecommunications industry has taken advantage of the PL characteristics of Er3+ ions to show emission frequencies, which are relatively host independent [9]. Among the lanthanides, erbium has attracted significant attention due to its enormous potential in various applications. The telecommunications industry has taken advantage of the PL characteristics of Er3+ doped optical amplifiers for application in high bandwidth data transmission lines [10, 11]. Although there are a few reports in literature on rare earth doped compounds, as bulk and nanostructures [12-16], their structural and luminescence properties are not very clear due to the difficulties in doping procedures. Further optimization of the procedures is needed for the development of complete understanding of doping processes. Present work is one such attempt in this direction. In this work, we are successful in doping erbium in ZnO, which showed improved luminescence characteristics. Compared to the conventional methods, the solid-state reaction has advantage of its low cost, high yield, and ability to achieve high purity in making oxide nano powders [17].

Experimental

ZnO nanopowder doped with erbium was prepared by solid-state reaction method to study their structural and optical properties. The chemicals used in the experiment are ZnO (99.9% pure), Er2O3 (99.9% pure) and LiOH.H2O (99.9% pure) brought from Merck company. The samples were prepared by thoroughly mixing Er2O3 and ZnO powders. Slurry was made with Lithium hydroxide (LiOH) solution and ethanol in a beaker and dried in an oven. LiOH is an inorganic and water soluble compound. In the present study, LiOH was used as a heat transfer medium, when ZnO doped with erbium. After drying, the mixture was ground for 45 min and sintered in air at 900°C. Samples were made in batches of approximately 5 g for different concentrations of erbium (1%, 2%, 4%, 6%, 8%, and 10%) (Table 1).

Measurements for all the samples were carried out at the same time and in the same setting of the instrument. The crystal structure of the synthesized sample was studied by using X-ray diffractometer (XRD) employing Cu-Kα radiation. The surface morphology and the grain size were estimated by employing a scanning electron microscope (SEM). PL excitation spectroscopy was done using Perkin Elmer spectrometer to study the available energy states and allowed transition between states. The magnetic hysteresis (M-H) loop was measured by using vibrating sample magnetometer (VSM).

Results and Discussion

Determination of lattice parameters from XRD

The XRD pattern of undoped and 1% erbium doped ZnO is shown in Fig. 1. The analysis of the diffraction peaks of both undoped and 1% erbium doped ZnO, revealed the presence of hexagonal wurtzite structure of bulk ZnO with lattice constants \( a = b = 2.8348 \) Å, \( c = 5.2478 \) Å and \( a = b = 2.8366 \) Å, \( c = 5.2492 \) Å, respectively. Diffraction peaks corresponding to reflections peaks of (100), (002), (101), (102), (110), (103), (200) crystal planes, which are consistent with standard JCPDS data of ZnO (Card No. 89-1397). It is suggested

![Fig. 1 XRD patterns recorded from undoped and 1% Er3+ doped ZnO.](image-url)
that the wurtzite structure is unchanged when the concentration of erbium in ZnO is minimum.

The XRD peaks of the increasing concentration (4%, 6%, 8%, and 10%) of erbium in ZnO showed the presence of extra phase related to Er2O3 in addition to the wurtzite phase of ZnO (Fig. 2). The peaks in the diffraction pattern of doped samples are slightly shifted as compared to undoped ZnO. This shows that small variation in the lattice parameters occurs as the Er3+ concentration increases. The nanocrystals exhibited changes in relative intensities and crystallite size with changes in the doping concentration of erbium. The nanocrystals, calculated using the formula ∆Eg = E_g^n - E_g^b = h^2/8a^2(1/m_e + 1/m_h), was found to increase slightly from 5.71 × 10⁻⁴ eV to 6.93 × 10⁻⁴ eV as the concentration of erbium in ZnO was increased (Table 2). The c/a ratio of Er3+ doped ZnO increased from 1.60 to 1.62 and the cell volume was found to increase from 23.749 Å³ to 24.706 Å³ (Table 2) as the concentration of erbium increased. The anion-cation bond length or the nearest neighbor distance was calculated to be 0.376 for all the concentrations of erbium in ZnO (Table 2). The iconicity of oxygen has played a major role in bonding, where the depleted d electrons of Zn would have formed a charge cloud around oxygen in bond formation. Hence, Er3+ doping has not influenced the nature of bonding, which is predominantly ionic in nature.

**Determination of dislocation density from XRD**

In materials science, dislocation is a crystallographic defect or irregularity within a crystal structure. The presence of dislocations strongly influences many of the properties of materials. Crystalline solids exhibit a periodic crystal structure. The positions of atoms or molecules occur on repeating fixed distances, determined by the unit cell parameters. However, the arrangement of atom or molecules in most crystalline materials is not perfect. The regular patterns are interrupted by crystallographic defects. The movement of dislocation is impeded by other dislocations present in the sample. Thus, a larger dislocation density implies a higher hardness. It is also known that above a certain grain size limit (~20 nm) the strength of materials increases with decreasing grain size.

The dislocation density (δ) in the sample was determined using expression,

\[
δ = 15β \cos θ / 4aD
\]

where δ is dislocation density, β is broadening of diffraction line measured at half of its maximum intensity (in radian), θ is Bragg’s diffraction angle (in degree), a is lattice constant (in nm) and D is particle size (in nm). The dislocation density (δ) was found to increase from 0.33 × 10¹⁵ m⁻² to 0.36 × 10¹⁵ m⁻² for 4% to 8% erbium doped ZnO in the (100), (002) and (101) orientations. This value increases to 0.5 × 10¹⁵ m⁻² to 0.6 × 10¹⁵ m⁻² when the concentration is increased to 10% (Table 3).

![Fig. 2 XRD pattern of undoped and Er3+ doped ZnO at different concentrations. Peaks corresponding to secondary phase appearing in the samples with Er3+ content >1% has been marked by “*”.](image)

| Concentration of erbium (%) | Average crystalline size (nm) | Difference in band gap (δE_g, eV) | Lattice constants | Cell volume (Å³) | Anion-cation bond length (μ) |
|----------------------------|------------------------------|----------------------------------|------------------|----------------|--------------------------|
|                            |                              |                                  | a (Å)            | c/a            |                          |
| 4                          | 65                           | 0.0005711                         | 3.2604           | 5.2232        | 1.602                    | 23.749                  | 0.37988                 |
| 6                          | 63                           | 0.0006076                         | 3.2660           | 5.232         | 1.602                    | 23.873                  | 0.37988                 |
| 8                          | 62                           | 0.0006274                         | 3.2655           | 5.232         | 1.605                    | 24.707                  | 0.40800                 |
| 10                         | 59                           | 0.0006928                         | 3.2600           | 5.296         | 1.625                    | 24.746                  | 0.37630                 |
Table 3 Dislocation density and specific surface area of Er doped ZnO

| Concentration of Erbium (%) | Dislocation Density ($\times 10^{15}$ m$^{-2}$) | Specific surface area (m$^2$/g) |
|-----------------------------|-----------------------------------------------|--------------------------------|
|                             | (100)                                       | (002)             | (101) |
| 4                           | 0.3359                                      | 0.3607            | 0.3717 | 16.465 |
| 6                           | 0.3353                                      | 0.3601            | 0.3710 | 16.988 |
| 8                           | 0.3358                                      | 0.3564            | 0.3614 | 17.262 |
| 10                          | 0.5943                                      | 0.3562            | 0.6670 | 18.140 |

Determination of specific surface area from XRD

Specific surface area is a material property of solids which measures the total surface area per unit of mass, solid or bulk volume, or cross-sectional area. It is a derived scientific value that can be used to determine the type and properties of a material. It has a particular importance for adsorption, heterogeneous catalysis, and reactions on surfaces. Specific surface area of the material can be determined using the expression,

$$S = 6 \times 10^3 / D_p \cdot \rho$$

where $S$ is the specific surface area, $D_p$ is the size of the particle and $\rho$ is the density of ZnO 5.606 g/cm$^3$. The specific surface area ($S$) of erbium doped ZnO nanocrystals was found to increase from 16.47 m$^2$·g$^{-1}$ to 18.10 m$^2$·g$^{-1}$ as the concentration of erbium in ZnO increased from 4% to 10% (Table 3).

X-ray line broadening—Williamson-Hall Technique

Williamson and Hall (W-H) plot is a classical method to obtain qualitative information of anisotropy in broadening peaks. Williamson and Hall [18] assumed that both size and strain broadened profiles are Lorentzian. Based on this assumption, a mathematical relation was established between the integral breadth ($\beta$), volume weighted average domain size ($D_v$) and the microstrain ($\varepsilon$) as follows:

$$\beta \cos \theta / \lambda = 1 / D_v + 2\varepsilon (2 \sin \theta / \lambda)$$

The plot of ($\beta \cos \theta / \lambda$) versus ($2 \sin \theta / \lambda$) gives the value of the microstrain from the slope and domain size from the ordinate intercept. If the points in the W-H plot are scattered, i.e., if ($\beta \cos \theta / \lambda$) is not a monotonous function of ($2 \sin \theta / \lambda$), the broadening is termed as anisotropic. The W-H plot of erbium doped ZnO is shown in Fig. 3. It is observed that the line broadening is not a monotonous function of the diffraction angle, indicating the anisotropic of the line profile. The strain value extracted from the W-H linear fit (Fig. 4) is 0.001 for all the samples.

Fig. 3 Williamson-Hall plot for 4%, 6%, 8%, and 10% Erbium doped ZnO at different deformations.
Morphological study

The SEM technique was employed to explore the size and distribution of particles in the materials. The images of 1% Er$^{3+}$ doped ZnO are shown in Fig. 5. It can be found that the sample synthesized through solid state reaction route crystallites are closely packed and have smaller sizes. The crystallites are nearly spherical shaped. The estimated particle size was 60 nm.

Optical studies

The interest in erbium doped ZnO stems from their possible use as fluorescence labels and as phosphor materials. For this the light emission characteristics of the prepared sample was studied using photoluminescence excitation spectroscopy. The PL spectrum of 1% Er$^{3+}$ doped ZnO with $\lambda_{\text{exc}} = 528$ nm is shown in Fig. 6. The PL spectrum exhibits strong near-band-edge emission at 381-394 nm with a full width at half maximum about 11 nm. The PL peaks from 381 to 394 nm derive from the quantum size effect. Broad emission peak at 478 nm can be ascribed to the mediated defect levels in the band gap such as oxygen vacancies which is a native defect of ZnO [19]. Oxygen vacancy acts as radiative center in luminescence process.

UV/Visible spectrum of 2% Er$^{3+}$ doped ZnO is shown in Fig. 7. The absorption spectrum of Er$^{3+}$ doped ZnO shows pronounced shoulder at 388 nm, corresponding to the energy band gap of 3.2 eV. A strong UV absorption band at 388 nm is assigned to the ZnO band-to-band transition. The decrease in band gap from 3.37 eV (bulk ZnO) to 3.2 eV is due to the effect
of the dopant, behaved as a substitutional impurity located in the lattice position of ZnO.

**Electrical studies**

The variation of resistivity with temperature for undoped ZnO and 1\% Er\(^{3+}\) doped ZnO is shown in Fig. 8. The resistivity measurements were taken from room temperature (303 K) to 463 K. It is observed that for undoped and 1\% Er\(^{3+}\) doped ZnO, the resistivity decreases as the temperature increases. The variation of resistance with temperature is marked in three regions in the resistivity-temperature plot. Initially the resistivity decreases very sharply from 303-320 K, it is lower in the shallow region from 320-340 K, and steady decrease beyond 345 K for undoped ZnO. For 1\% Er\(^{3+}\) doped ZnO, the resistivity decreases rapidly from 300-322 K, and it almost reaches a steady state in the range 322-362 K, and a rapid decrease from 362-382 K and a gradual decrease beyond 382 K is observed. This analysis indicates the increase in conductivity of both undoped and 1\% Er\(^{3+}\) doped ZnO. This is due to the negative temperature coefficient of resistance of Er\(^{3+}\) doped ZnO semiconductor, in which the occupancy of the conduction band goes up due to increase in temperature. Thus, 1\% Er\(^{3+}\) doped ZnO can be used in the temperature range 362-382 K for rapid current conducting device fabrication.

The Arrhenius plots that display the logarithm of kinetic constant (lnK) against inverse temperature of undoped and 1\% Er\(^{3+}\) doped ZnO is shown in Fig. 9. Arrhenius plots are used to analyze the effect of temperature on the rates of chemical reactions. For a singly-rate limited thermally activated process, an Arrhenius plot gives a straight line, from which the activation energy can be determined. Activation energy can be considered as the height of the potential barrier or energy barrier separating two minima of potential energy of the reactants and products of a reaction. For a chemical reaction to proceed at a reasonable rate there should exit an appreciable number of molecules with energy equal to or greater than the activation energy. The activation energy calculated from Arrhenius plots of undoped ZnO and 1\% Er\(^{3+}\) doped ZnO, increased from 0.77 eV to 1.16 eV. The increase in activation energy in 1\% Er\(^{3+}\) doped ZnO is due to the increased reaction rate and the effective collision per unit volume between the ZnO and erbium molecules.

**Magnetic study**

The significance of magnetism in non-magnetic materials has been focused extensively [20]. Multiple nanostructures of either organic or inorganic systems have
system can be characterized by delocalized band electrons, which can be described by extended states. The magnetic ion, on the other hand, is characterized by localized 3d or 4f shells. The localized magnetic moments associated with the magnetic ions and their interaction with the host semiconductor determines the magnetic properties. The interaction responsible for the desired magnetic behavior is s, p-f in the case of rare earth magnetic ions. Thus, erbium doped ZnO is observed to show dilute magnetic semiconducting behavior.

Fig. 9 Arrhenius plot of undoped ZnO and 1%Er$^{3+}$ doped ZnO.

been reported to show magnetic properties in the absence of magnetic elements [21-25], and even the suggestion of magnetism as a universal feature at the nanoscale has been proposed [26]. Sundaresan et al. [27] have shown that nanoparticles of metal oxides of non-magnetic materials, such as CeO$_2$, Al$_2$O$_3$, ZnO, In$_2$O$_3$ and SnO$_2$, exhibit room-temperature ferromagnetism. The present study focuses on the effect of rare earth ion Er$^{3+}$ on the magnetic behaviour of ZnO at room temperature. Erbium is one of the rare earth ions, which has more than a half-filled 4f electron shells. Magnetization of 6% erbium doped ZnO, as a function of magnetic field, measured at room-temperature, using VSM is shown in Fig. 10. The magnetization curve shows hysteresis, indicating a ferromagnetic ordering at room temperature. The coercivity measured from the plot is 386.55 G (0.038655 T) and the retentivity is $5.2524 \times 10^{-3}$ emu/g (5.2524 A/m) and the susceptibility calculated from the plot is 0.01237. The origin of ferromagnetism may be due to the exchange interactions between unpaired electron spins arising from oxygen vacancies at the surface of the nanoparticles. Sundaresan et al. [27] suggested that all metal oxides in nanoparticulate form exhibit room-temperature ferromagnetism. In general, the magnetic semiconducting behavior of ZnO can be characterized by a dilute magnetic semiconducting model.

Conclusion

In the present investigation, synthesis of Er$^{3+}$ doped ZnO by solid state reaction method seems to be an efficient, inexpensive and easy method. The structural characterization of the sample explored by XRD, shows polycrystalline structure with average crystalline size of 63 nm and ZnO has become zinc erbium oxide as the concentration of erbium in ZnO was increased. W-H plot generated for all the concentrations of erbium in ZnO showed that the broadening is highly anisotropic. Anisotropic line broadening of erbium doped ZnO was explained in terms of dislocation induced strain broadening and the dislocation density was found to be of the order of $10^{15}$ m$^{-2}$. UV/Visible absorption analysis of Er$^{3+}$ doped ZnO reveals the decrease in energy band gap of doped ZnO nanocrystals and created more defective sites on the ZnO surface. The increased surface defects are capable of absorbing more visible light. The emission peak at 387 nm observed from the photoluminescence study shows the improved luminescence characteristics of the Er$^{3+}$ doped ZnO. Electrical investigation showed an increase in conductivity of undoped and 1% Er$^{3+}$ doped ZnO. Activation energy calculated from Arrhenius plot increased for 1% Er$^{3+}$ doped ZnO in comparison with undoped ZnO. The observed hysteresis in the M-H behavior showed the presence of room temperature ferromagnetism (RTFM) in the rare earth ion doped ZnO nanocrystals.
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Solid-State Synthesis and Effect of Temperature on Optical Properties of CuO Nanoparticles

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Abstract: Modulation of band energies through size control offers new ways to control photoresponse and photoconversion efficiency of the solar cell. The $P$-type semiconductor of copper oxide is an important functional material used for photovoltaic cells. CuO is attractive as a selective solar absorber since it has high solar absorbance and a low thermal emittance. The present work describes the synthesis and characterization of semiconducting CuO nanoparticles via one-step, solid-state reaction in the presence of Polyethylene glycol 400 as size controlling agent for the preparation of CuO nanoparticles at different temperatures. Solid-state mechanochemical processing, which is not only a physical size reduction process in conventional milling but also a chemical reaction, is mechanically activated at the nanoscale during grinding. The present method is a simple and efficient method of preparing nanoparticles with high yield at low cost. The structural and chemical composition of the nanoparticles were analyzed by X-ray diffraction, field emission scanning electron microscopy and energy-dispersive spectrometer, respectively. Optical properties and band gap of CuO nanoparticles were studied by UV-Vis spectroscopy. These results showed that the band gap energy decreased with increase of annealing temperature, which can be attributed to the improvement in grain size of the samples.

Keywords: Band gap; CuO; Polyethylene glycol 400; Semiconductors; Solid-state reaction

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Introduction

Work demand for energy is expected high and finding sufficient route to produce clean energy is an ever more pressing problem. Science had identified the key research challenges if solar energy is to provide a significant fraction of our energy needs. The huge gap between our present use of solar energy and its enormous undeveloped potential defines a grand challenge in energy research. One of the most attractive methods currently being developed is “dye sensitization” in solar cells in order to increase the efficiency of conversion of solar radiation into electrical energy. Further, the most serious problem of fossil fuel as the energy source is the harmful effect produced on the environment due to the release of hazardous gases into the atmosphere. To avoid both environmental pollution and the future energy crisis, much attention has been devoted to the development of photovoltaic solar cells. The development of photovoltaic solar cells was initiated first by the French Scientist Edmund Bequerel [1]. During the last two decades, a substantial body of research has been directed toward the synthesis of metal nanoparticles in efforts to explore their special properties and potential applications. Nanocrystalline semiconductor particles have drawn considerable interest in recent years because of their special properties such as a large surface-to-volume ratio, increased activity, special electronic properties and unique optical properties as compared to those of the bulk materials [2-4]. The large
surface area to volume ratio can contribute to some of the unique properties of nanoparticles. The oxides of transition metals are an important class of semiconductors. Among various semiconductors, Cu and their oxides have attracted great deal of attention in both fundamental research and technical application because of their catalytic, optical, and electrical conducting properties [5,6]. Copper is an important material because of its high electrical and thermal conductivities. CuO is known as p-type semiconductor exhibiting narrow band gaps ($E_g = 1.2$ eV) and which makes it a promising material for gas sensors, magnetic storage media, solar energy transformation, electronics, semiconductors, varistors, and catalysis [7]. It has therefore been studied together with other copper oxides, especially with respect to its applications as a photothermally active and photoconductive compound [8]. Thus, great efforts have been made to study the preparation of nanosized CuO in the past two decades. Conventional methods for the preparation of CuO powders include one step solid-state reaction at room temperature, thermal decomposition of copper salts and mechanical milling of commercial powders [9-11]. Solid-state mechanochemical processing is an effective, useful and simple processing technique widely applied to the synthesis of quasicrystalline, nanocrystalline and crystalline materials, which is not only a physical size reduction process in conventional milling but also a chemical reaction that is mechanically activated at the nanoscale during grinding. The present method is a simple and efficient method of preparing nanoparticles with high yield at low cost. Thus, there is a renewed interest in understanding the fundamental physical properties of CuO, as well as for upgrading its performance in applications. PEGs are prepared by polymerization of ethylene oxide and are commercially available over a wide range of molecular weights from 300 g/mol to 10,000,000 g/mol. While PEG with different molecular weights find use in different applications and have different physical properties (e.g., viscosity). They are used in industry as surfactants, including food, cosmetics, toothpastes and pharmaceutics; in biomedicine, as dispersing agents. PEG 400 is less toxic and soluble in water, acetone, alcohols and benzene [12,13]. In this work, to prepare low-cost advanced materials for photovoltaic energy production, we report a simple one-step, solid-state reaction in presence of PEG 400 [H-(O-CH$_2$-CH$_2$)$_n$-OH] as size controlling agent for the preparation of CuO nanoparticles at different temperature. The process is carried out at room temperature. Band gap energy of all the synthesized nanoparticles was calculated using UV-vis spectroscopic data and synthesized the materials as in our previous paper (C. C. Vidyasagar, et al. Powder Tech. 2011).

Materials and methods

Materials

Copper dichloride and sodium hydroxide were procured from Merck (Mumbai, India). PEG 400 (Polyethylene glycol 400) was procured from s.d.finchem Ltd. (Mumbai, India). All the chemicals were of analytical grade and used as received for the experiments. Double distilled water was used for the preparation of the solutions.

Characterization of nanoparticles

X-ray powder diffraction (XRD) patterns were recorded on a Philips X’Pert X-ray diffractometer using Cu-Kα radiation. The size distribution and morphology of the samples were analyzed by Field emission scanning electron microscope (FESEM) fitted with an Energy-dispersive X-ray spectroscopy (EDAX) [Model: Nova Nano SEM600-FEI]. The absorbance of nanopowder samples were measured on a UV-Vis spectrophotometer [Model: USB 4000, Ocean Optics, USA].

Synthesis of CuO nanoparticles

In a typical synthesis, 5 g of CuCl$_2$ and 3 g of NaOH were ground separately for 5 min in an agate mortar. Thus obtained fine powder of CuCl$_2$ and NaOH were mixed with 6 ml of PEG 400 and subjected to further grinding for 30 min. The resultant paste was thoroughly washed with double distilled water and ethyl alcohol to remove the PEG 400. Finally, the product was dried at 70°C in an oven and the resultant solid was subsequently annealed at 400°C, 600°C and 800°C for 2 h.

Results and discussions

X-ray diffraction measurements were carried out to study the crystal structure and crystalline quality. Figure 1 represents the XRD pattern of synthesized CuO nanoparticles calcined at 400°C, 600°C and 800°C, respectively. All the diffraction peaks could be indexed to crystalline monoclinic structure. The major peaks located at 2θ values correspond to the characteristic diffraction of monoclinic phase of CuO (JCPDS NO-80-1268). No other peaks were observed belonging to any impurity such as Cu(OH)$_2$ and Cu$_2$O, indicating high purity of CuO nanoparticles. CuO particles annealed at higher temperature shows shift in (110), (002) and (200) planes compared to lower annealed temperatures. As the annealing temperature increases, the peak intensity of CuO nanoparticles increases with a decrease in the full width at half maximum (FWHM), which indicates a possible change in the grain size of CuO [12,14]. The diffraction peak (110) was narrower
than (002) peak, and in turn (002) peak was narrower than (200) peak. This clearly indicates the presence of asymmetry in the crystallite shape. The height of c-axis of the crystal is bigger than the basal diameter (crystal axis, \(a_1, a_2\)) [15]. The intensity of (110), (002) and (200) peaks gradually increases with increase in annealing temperature. However, the peak intensity of the annealed samples at 800°C was found to be increased. The lattice parameters for CuO nanoparticles were calculated from the XRD data. The lattice constants \(a, b, c\) for CuO annealed at 400°C were found to be 0.47153 nm, 0.33774 nm and 0.51247 nm, respectively. As for CuO annealed at 600°C, the lattice constant \(a\) decreases to 0.47141 nm, \(b\) increases to 0.34206 nm and \(c\) increases to 0.51264 nm. For CuO annealed at 800°C, \(a\) decreases to 0.46392 nm, \(b\) decreases to 0.33934 nm and \(c\) decrease to 0.50409 nm. Figure 1 illustrates the changes in (002) and (200) peaks position of the nano powders. As shown in Fig. 1, when the calcinations temperature changes from 400°C to 600°C, the peaks slightly shift towards lower angles. On the other hand the strongest shift towards higher angles has been observed in the sample annealed at 800°C. This can be seen from the enlarged view of the inset in Fig. 1. These shifts depend directly on the changes of the lattice constants [22]. It can be seen that the shifts of the peaks were detected as the lattice constants changed, which results in the changes of lattice constants along \(a, b\) and \(c\)-axis. As the peaks shift towards lower angle, the lattice constants increase and as it shifts towards higher angle, the lattice constants decrease [20]. The increases in peak intensity at higher annealing temperatures are attributed to the increase in crystallinity.

As the annealing temperature increases from 400°C to 800°C, the crystal size of CuO was also found to be increased from 65 nm to 454 nm) (Fig. 2(b) and 2(c)). With increasing in the annealing temperatures, the nucleation rate of the particles increases more rapidly. This is due to the increase in supersaturation of the reaction products, which accelerates the crystal core forming reaction within a short time. Under these conditions the controlling step of the reaction is transferred from grain growth to crystal nucleus formation. With the temperature continuing to rise, the phenomenon of “nuclear-aggregation” caused by the rapid formation of crystal nucleus is obvious, which results in aggregation among the crystal nucleus [12,16,17]. The rate of particle aggregation is a major factor that controls the morphology and structure (crystalline) of the final product [18]. With increasing the calcination temperature particle agglomeration was observed in FESEM images. Literature also indicates that with increase in calcination temperature the crystallinity of the particle increases as well as the surface area decreases. Variation in calcination temperature brought about changes in the crystallinity [21]. The micrographs clearly indicated that the crystallinity has increased with an increase in annealing temperature, which is in agreement with XRD results. EDAX spectra of CuO particles at different temperatures are shown in Figs. 2(d), 2(e) and 2(f), which indicates the high purity of synthesized materials where only Cu and O are present. Carbon signal are due to the Gold coating and carbon film supporting the specimen in FESEM observation [12]. Surfactants (PEG 400) would change nanoparticle’s shape, size and surface properties to different extent depending upon their molecular structure, for example, nature of head group, length of hydrophobic tail and type of counter ions. The termination of the nanoparticle growth and size is controlled by the diffusion and the attachment rates of surfactants (PEG 400) on the nanoparticle surface [23, 24].

Figure 3 shows the UV-Vis absorption spectra of the samples annealed at different temperatures. The exciton absorption is at about 650-900 nm. The CuO particles obtained from the higher annealing temperatures exhibits the relatively lower absorption in the visible range. As shown in Fig. 3, the increasing annealing temperature of CuO particles is considered to be the main factor for the intense decrease in absorption [19]. The crystallinity of the particles in our experiment was improved when the substrate temperatures increased from 400°C to 800°C (Fig. 2(a), b and c). With increase in the annealing temperature from 400°C to 800°C, the optical absorption edge slightly shifted towards longer wavelength, which may be attributed to the increase in grain size at higher annealing temperatures. The optical band gap \(E_g\) of the CuO was determined by using the formula, \(E_g = h c / \lambda\), where \(h\) is plank’s constant, \(c\)
is velocity of light and \( \lambda \) is wavelength [12]. The crystallinity of the CuO improved when the temperature increased from 400°C to 800°C. It is obvious that the conduction type of CuO is dependent on temperature. From UV-Vis results, the shift in the band gap may be attributed to the effect of temperature on the crystallinity of CuO samples. On the other hand, the crystallinity become better when \( E_g \) value red shifted from 1.72 to 1.58 eV. The changes in the optical band gap of CuO samples with increase in temperature are due to the change of crystallinity at higher temperature. The observed results show that the annealing temperature is very important in the band gap assignment.

### Conclusion

In summary, nanocrystalline CuO particles with a monoclinic structure have been synthesized through a simple, rapid, low-cost and one-step solid state reaction method using PEG 400 as a surfactant. The improved crystallinity was observed when annealed at higher temperatures. The grain size can between 21-450 nm. The intensity of peaks has been increased with increase in annealing temperature, as well as the optical band gap edge shifts towards longer wavelength region which may be attributed to the decreasing band gap of the CuO nanoparticles at higher temperatures.

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Effect of Synthesis Method on Photoluminescence Properties of Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ Nanophosphor

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Abstract: We have synthesized a series of single-composition emission Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ phosphor by traditional solid state reactions and novel combustion method. Formation of compound was confirmed by X-ray diffraction analysis. The photoluminescence (PL) emission spectra were observed at 376 nm when excited around 322 nm for the various concentrations in both cases. The PL emission spectra of phosphors showed strong Ce$^{3+}$ emission due to the 5d $\rightarrow$ 4f transition of Ce$^{3+}$ ions. The Ce$^{3+}$ emission intensity in Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ prepared by combustion was higher than that of solid state reactions.

Keywords: Nanophosphor; Luminescence; Halophosphate

Introduction

The applications of phosphor materials in different fields have resulted in its great growth. Halobased phosphors, such as halophosphate phosphors have attracted tremendous attention due to their intense luminescence intensities, high emission efficiencies, simple preparation techniques and wide application fields in illumination and display [1-5]. The present Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ phosphor is not studied yet for its optical properties and application in scintillation. Ce$^{3+}$ doping in phosphates results in emission spectra near ultraviolet (UV) region [6]. Recently, trivalent lanthanide dopants have received greater attention for fast and bright scintillators. In particular, Ce$^{3+}$ is a favored dopant in many scintillators due to its allowed optical 5d $\rightarrow$ 4f transition, which is relatively fast. Today, low temperature methods such as hydrothermal microwave [7], co-precipitation [8,9], sol-gel [10,11] and combustion [12] are used to prepare these phosphors. However, we synthesized Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ phosphor by both traditional solid state reactions and novel combustion method. Moreover, we investigate comparatively impact of synthesis method on the photoluminescence properties of same system. Orthophosphates have been extensively investigated, due to their structural diversity. This makes them suitable as hosts to accommodate active rare earth ions. The phosphate family symbolizes possibly one of the most attractive kinds of novel inorganic material, largely owing to the ability of the tetrahedral PO$_4^{3-}$ group to bond with other structural units. Recently, Dhoble and coworker reported some phosphate phosphors prepared by both solid state method and combustion method Ca$_3$(PO$_4$)$_2$ [13], Mn$_5$(PO$_4$)$_2$F (M=Ba, Sr, Ca) [14], Na$_3$Al$_2$(PO$_4$)$_3$:RE (RE=Ce$^{3+}$, Eu$^{3+}$ and Mn$^{2+}$) [15], Dy$^{3+}$, Mn$^{2+}$ or Gd$^{3+}$ activated NaCaPO$_4$ [16], trivalent dysprosium activated X$_6$AlP$_5$O$_{20}$ (where X=Sr, Mg, Ca) [17].
Ba, Ca and Mg) [17].

The effect of rare earth ion (i.e., Ce^{3+}) in the above system and its effect on the luminescence behavior of the materials were not focused by the researchers before and hence material is considered as the main attempt in the present investigation.

Experimental

Ce activated Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$halophosphate phosphor was prepared via combustion method and solid state method as well.

For Combustion Method: All starting AR grade materials (99.99% purity) taken were in nitrates form and urea was used as fuel for combustion. Materials were prepared according to the chemical formula Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$_{2}$. The mixture of reagents was mixed together to obtain a homogeneous solution. Ce ion was introduced in the form of (NH$_4$)$_2$Ce(NO$_3$)$_6$. The compositions of the metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valencies of the components, which served as the numerical coefficients so that the equivalent ratio is unity and the maximum heat liberated during combustion. After stirring for about 15 min, precursor solution was transferred to a furnace preheated to 500°C and the porous products were obtained.

For Solid State Method: All starting AR grade materials (99.99% purity) taken were in carbonate/oxide form. The raw materials with stoichiometrical ratio were weighed and mixed in mortar sufficiently. In order to obtain the target compound with pure phase, the mixture was heated at 900°C for 8 h in a covered alumina crucible then cooled down to the room temperature.

The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-Kα radiation) at a scanning step of 0.01°, continue time 20 s, in the 2θ range from 10° to 120°, the average crystallite size was calculated from the broadening of the X-ray line (311) using Scherrer’s equation. The morphology of the samples were investigated on scanning electron microscopy (SEM). The photoluminescence (PL) measurement of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample 2 g was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. All the measurements were conducted at room temperature.

Results and discussion

XRD and morphology of Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$

Figure 1 shows the XRD pattern of Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$ materials prepared by both solid state and combustion methods. The XRD patterns did not indicate presence of the starting constituents and other likely phases which are an indirect evidence for the formation of the desired compound. This result indicates that the final product was formed in crystalline and homogeneous form. The XRD spectra of prepared compounds cannot match the existing standards JCPDS file. However, some new diffraction peaks also emerge, which are characteristic diffraction peaks for the prepared samples, but cannot be attributed to any known compounds. These results imply that the prepared samples are not the simple physical mixtures of starting materials, but a new single-host Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$ compound. Only intensities varies in both the cases otherwise peak position and phases are quite resemblance to each other.

It is clearly seen that the grains prepared by combustion method are irregular in shape of particles with a size of about 0.5-1 μm. This shows that the combustion reactions of the mixtures took place well. The typical morphological images are presented in Fig. 2(b). The particles possess foamy like morphology formed from highly agglomerated crystallites, whereas, in Fig. 2(a) an average crystallite size is in sub-micrometer range and the particles of Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$ with agglomeration prepared by solid state method were uniform in grain size of about 2-5 μm seen in SEM image.
Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ prepared by Solid state method

As all the results were related to PL of Ce$^{3+}$, general features of the emission are mentioned first. The 5d-level spectroscopy of Ce$^{3+}$ is very simple. In the excited state, the 4f shell is empty and there is only one single 5d electron interacting with the crystalline environment. In the ground state, Ce$^{3+}$ ion has the (Xe) 4$^f^1$ configuration, which results in only two 4$^f^1$ energy levels, $^2F_{5/2}$ and $^2F_{7/2}$. The spatially diffuse 5d electron orbital extends outward from the ion to overlap the neighbouring ligand ions, and is more strongly influenced by their motion. In consequence, the optical properties depend strongly on the structure of the host crystals. Both absorption and emission have a usually broadband character, showing splitting characteristic of 2$F_j$ states. As the position of the 5d band itself depends on the host, not only the Stoke’s shift but also the spectral positions of both the excitation and emission bands are host-dependent. In phosphate, the emission is expected to be in the UV region. Figures 3 and 4 show the PL excitation and emission spectra of Ce$^{3+}$ ions in Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$ phosphor prepared by solid state method of different concentrations under light excitation at a wavelength of 320 nm. The splitting peaks are observed at 355 nm and 376 nm, which are assigned to the 5d-4f transition of Ce$^{3+}$ ions. With increasing concentration of Ce$^{3+}$ ions, the peak intensity of both peaks increases and maximum intensity is observed at 1 mol% of Ce$^{3+}$ ions (Fig. 4). This indicates that the Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$ lattices are more suitable for higher concentrations of Ce$^{3+}$ ions. Energy transfer between pairs of rare earth ions at dilution levels below the self-quenching limits is known to take place generally through multipolar interactions, such as dipole-dipole or dipole-quadrupole interactions [18-20]. The Ce$^{3+}$ ion can be used as a sensitizer as well as an activator, depending on the splitting of 5d excited levels by the crystal field symmetry.

![SEM images of Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$ prepared by (a) solid state method and (b) combustion method.](image)

![PL excitation spectra of Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ monitored at 376 nm (prepared by Solid state Method).](image)

![PL emission spectra of Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ excited at 320 nm (prepared by Solid state Method).](image)
to as (Ce\(^{3+}\))\(^s\), to the Ce\(^{3+}\) ground state [Xe]4\(f^1\) 5\(d^0\) (see Fig. 5). Trapping mechanisms on the host, such as self-trapped excitons, hole traps, or electron traps, can quench or reduce the transfer of energy to the Ce site. A necessary condition for scintillation and luminescence is that the Ce 4\(f\) and 5\(d\) levels must be in the gap of the host material. If the Ce 4\(f\) level lies in the valence band of the host or the 5\(d\) level is in the conduction band, there will be no Ce-activated scintillation or luminescence. Our theoretical calculations for the prediction of candidate scintillator materials are based on studies of the Ce 4\(f\) and 5\(d\) levels relative to the valence-band maximum and conduction-band minimum of the host material, respectively [21].

![Fig. 5 Schematic diagram for a Ce-activated scintillator showing the positions of the Ce 5\(d\) and 4\(f\) levels relative to the conduction and valence band of the host material.](image)

**Na\(_2\)Sr\(_2\)Al\(_2\)PO\(_4\)Cl\(_9\):Ce\(^{3+}\)** prepared by combustion method

Ce\(^{3+}\) is a very good candidate as activator as well as sensitizer, for studying the behavior of 5\(d\) electrons. Ce\(^{3+}\) has only one outer electron and only two spin-orbital splitting 4\(f\) states (\(^2\)\(F_{5/2}\), \(^7\)2\(_2\)\(^z\)). Thus, its excited state energy structure is simpler than that of the other trivalent rare-earth ions. Photoluminescence excitation and emission spectrum of Na\(_2\)Sr\(_2\)Al\(_2\)PO\(_4\)Cl\(_9\):Ce\(^{3+}\) phosphor shown in Figs. 6 and 7 respectively. Figure 6 shows the PL emission spectra of Na\(_2\)Sr\(_2\)Al\(_2\)PO\(_4\)Cl\(_9\):Ce\(^{3+}\) phosphor with different concentrations under the same excitation (i.e., 322 nm) wavelengths of light. Two emission peaks are observed from 350 to 376 nm, which are assigned to the 5\(d\)-4\(f\) transition of Ce\(^{3+}\) ions. The highest intensity observed at 376 nm due to \(^2\)\(D(5d) \rightarrow ^2\)\(F_{7/2}(4f)\) transition between two peaks. The concentration of Ce\(^{3+}\) ion increases the corresponding intensity of all peaks and at higher concentration (1 mol %) of Ce\(^{3+}\) ion. This indicates a change of the surrounding of the Ce\(^{3+}\) ions at higher concentration in the Na\(_2\)Sr\(_2\)Al\(_2\)PO\(_4\)Cl\(_9\):Ce\(^{3+}\) lattice. The emission intensity is related to the concentration of the Ce\(^{3+}\) activator ions. With the increase of the concentration of the activator ion, the luminescent centre increases and the emission intensity is enhanced. The highest luminescent intensity was obtained at a cerium concentration of 1 mol%, and lower or higher cerium contents result in a substantial decrease in emission intensity. The luminescence spectra depict the concentration of the activated elements, which increases as a result of the concentration quenching effect. At high concentration the clustering of activator atoms may change a fraction of the activator into quenches, and may induce the quenching effect; this decreases the emission intensity. The quenching concentration is about 1 mol%. The oxygen vacancies might serve as a sensitizer for the energy transfer to the rare earth ion, due to the strong mixing of charge transfer states, resulting in highly enhanced luminescence [22]. However, excess oxygen vacancies in the host would inevitably destroy the crystallinity, leading to quenching of luminescence [22]. There is no PL observed in the host material. This signifies that the incorporation of Ce\(^{3+}\) ion into the Na\(_2\)Sr\(_2\)Al\(_2\)PO\(_4\)Cl\(_9\) lattice causes a significant change to the PL properties compared with the host matrix.

![Fig. 6 PL excitation spectra of Na\(_2\)Sr\(_2\)Al\(_2\)PO\(_4\)Cl\(_9\):Ce\(^{3+}\) monitored at 376 nm (prepared by combustion Method).](image)

![Fig. 7 PL emission spectra of Na\(_2\)Sr\(_2\)Al\(_2\)PO\(_4\)Cl\(_9\):Ce\(^{3+}\) excited at 322 nm (prepared by combustion Method).](image)
are very close. We have also observed excitation spectrum for Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ prepared by solid state method (Fig. 3) that is almost identical to that for Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ prepared by combustion method. The emission band for Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ prepared by solid state method (Fig. 3) is almost identical to that for Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ prepared by combustion method. The emission band for Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ (Fig. 6) is located at slightly longer wavelength of 322 nm. A shoulder around 290 nm is observable. The changes may be due to different synthesis method consequently local higher concentration or different local environment in the precipitated powders.

Conclusions

From the results presented here novel Na$_2$Sr$_2$Al$_2$PO$_4$Cl$_9$:Ce$^{3+}$ phosphor involving as many as three constituents can be prepared by both traditional solid state and novel combustion method described here and formation of compound is confirmed by XRD. Strong luminescence of Ce$^{3+}$ can be observed in the as prepared powders without any further heat treatment. Peak position (at 376 nm) is not influenced by different concentrations of Ce$^{3+}$ and only relative intensities vary when excited around 322 nm. Only intensity varies may be due to different synthesis method. Present phosphor shows the near UV emission for development of energy transfer based co-activated advanced phosphors for lamp industry and scintillation. Besides, full understanding of the nature of the competing processes and the dynamics of holes trapping by Ce$^{3+}$ is still one of the challenging subjects in scintillation mechanism research.

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Synthesis of Cobalt Chromite Nanoparticles by Thermolysis of Mixed \(\text{Cr}^{3+}\) and \(\text{Co}^{2+}\) Chelates of 2-Mercaptopyridin N-Oxide

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Abstract: Pure greenish-blue cobalt chromite (\(\text{CoCr}_2\text{O}_4\)) nanoparticles with narrow particle range of 4.1±1.9 nm and surface area of 78.2 m\(^2\)·g\(^{-1}\) were synthesized through mixed chelates thermolysis of corresponding metals using 2-Mercaptopyridine N-oxide sodium salt as chelating agent. During the thermolysis procedure, high amount of gases were emitted that led to the formation of nanoparticles with high surface area. The product was characterized by TGA, DTG, XRD, TEM, SEM, LLS, BET and chemical analysis. Design of experiments was performed to fulfill the two levels \(L_4\) Taguchi design. It was found that the temperature and time of thermolysis process have significant effect on the particle size reduction. The Oxidation of trichloroethylene was carried out over \(\text{CoCr}_2\text{O}_4\) nanocrystallite. Catalytic activity analysis revealed that the synthesis \(\text{CoCr}_2\text{O}_4\) possesses high catalytic activity for this process.

Keywords: \(\text{CoCr}_2\text{O}_4\); Nanoparticle; Chelates Thermolysis; Taguchi experimental design; Combustion of trichloroethylene

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Introduction

Cobalt chromite is a potential industrial material. It is an insulating and normal spinel compound [1-5] and has various catalytic activity such as water gas shift reaction, combustion of halogenated hydrocarbons, alkylation of phenol, dehydrogenation and hydrogenation [6-11]. It is also used as ceramic material, heat resistant pigment [12,13], substrate for epitaxial growths [14,15], high density magnetic memory media, etc [16-18]. Cobalt chromite have been synthesized by sonochemical route [19,20], coprecipitation technique and heating \(\text{Co}^{2+}\) and \(\text{Cr}^{3+}\) ions with styrene maleic acid copolymer in DMF medium [21].

In this article we report a new and convenient method for preparation of fine nanoparticles of \(\text{CoCr}_2\text{O}_4\) with high specific surface area using thermolysis of mixed complexes of \(\text{Co}^{2+}\) and \(\text{Cr}^{3+}\) chelates with 2-Mercaptopyridine N-oxide sodium salt (MPNO-Na). The mole ratio of Co/Cr in the mixed chelate was 1:2. In this method, several parameters such as thermolysis temperature, time of thermolysis and concentration of \(\text{Co}^{2+}\) and \(\text{Cr}^{3+}\) in the initial materials affect the surface area and particle size of the metal oxide. \(L_4\) Taguchi experimental design was used to optimize the preparation conditions for the synthesis of cobalt chromite with low particle size [22]. To the best of our knowledge, there is no report about this process in the open literature.

Experimental

Materials

All chemicals used were AR grade and obtained...
from Sigma-Aldrich and used with without further purification. The starting materials were CoCl₂·6H₂O and CrCl₃·6H₂O as cobalt and chromium precursor respectively. 2-Mercaptopyridine N-oxide sodium salt (MPNO-Na) was used as chelating agent. Ammonium hydroxide was used as precipitating agent. Distilled deionized water was used in all experiments.

**CoCr₂O₄ preparation**

**thermolysis method**

The following procedure is based on the L₄ Taguchi experimental design which is discussed later. Aqueous solutions of CoCl₂·6H₂O and CrCl₃·6H₂O were placed in 250 ml flask equipped with mechanical stirrer and thermometer. Then appropriate amount of MPNO-Na was added with stirring and the flask was heated up to 100°C with an IR heating lamp (the pH of solution 2-3.5). After 5 min digestion the precipitation was filtered, washed several times with distilled deionized water to remove the impurities and then calcined at different conditions. The product of thermal decomposition was the brilliant greenish-blue nano cobalt chromite. The experimental design was arranged for three factors: A (thermolysis temperature, °C), B (time of thermolysis, h) and C (coefficient of stoichiometric concentration of Co²⁺ and Cr³⁺ in the initial materials). Two levels assigned factor are shown in Table 1.

**Table 1 Factors and their experiment levels**

| Level 1 | Level 2 | Factors                           |
|---------|---------|-----------------------------------|
| 800     | 600     | A (thermolysis temperature, °C)   |
| 5       | 3       | B (time of thermolysis, h)        |
| 0.6     | 0.2     | C (coefficient of stoichiometric concentration of Co²⁺ and Cr³⁺ in the initial materials) |

**Precipitation method**

For comparison, a cobalt chromite sample was prepared with conventional co-precipitation method with following procedure: initially, aqueous solutions of CoCl₂·6H₂O and CrCl₃·6H₂O were placed in 250 ml flask equipped with mechanical stirrer and thermometer. Then precipitation was carried out by adding aqueous ammonia to the above stirred solution. The pH of solution was adjusted to about 8.9. After that, the precipitate was washed and filtered and dried at 100°C overnight. The final solid was then calcined in a flow of air from room temperature to 600°C with a heating rate of 2°C·min⁻¹, and kept at this temperature for 3 h. The obtained powder was named as sample 6.

**Characterization**

An automatic C H N analyzer (CHN- Micro, Karlkoft 267-48) was used to analyze the cobalt and chromium chelates. Thermogravimetric (TGA) and differential TG (DTG) analyses were carried out in a Netzsch STA 409 system in a static air atmosphere at a heating rate of 10°C per minute. The XRD patterns were recorded on an X-ray diffractometer (Shimadzu XD3A) using a Cu-Kα monochromatized radiation source and a Ni filter in the range 2θ= 10° to 80°. The surface areas (BET) were determined by nitrogen adsorption at −196°C using an automated gas adsorption analyzer (The Tristar 3000, Micromeritics). The diagram of particle size distribution of sample was obtained with laser light scattering (LLS) instrument, (SEMATech 230v, 50 Hz). Transmission electron microscopy (TEM, Ziss EM 900) and scanning electron microscopy (SEM, Philips XL30) were used to observe the size and morphology of CoCr₂O₄ nanoparticle. Atomic absorption spectrophotometry (Philip, U9100) was used to analyze CO²⁺ and Cr³⁺ ions in synthesized cobalt chromite. The catalytic reaction products were identified by a gas chromatograph coupled with mass spectrometry (GC-MS, TRACE GC Ultra, column THERMO TR-5MS 30 m-0.25 mm ID, quadrupole MS TRACE DSQ).

**Catalyst evaluation**

Removal of volatile trichloroethylene (TCE) pollutants has been known as challenging technology [23-27]. In this work combustion of TCE was carried over cobalt chromite nanoparticles. This compound is nonflammable and it is used in metal degreasing and drycleaning industries. TCE in the presence of catalyst is oxidized to CO₂ according to the following reaction,

\[
2\text{C}_2\text{H}_3\text{Cl}_3 + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{CO}_2 + 6\text{HCl}
\]

Oxidative decomposition process was conducted in a glass-tube fixed bed reactor (I.D.=0.8 cm and Length=40 cm) at 330°C under atmospheric pressure with weight hourly space velocities (WHSV) of 60 Lg⁻¹·h⁻¹. The reaction feed was a mixture of 1500 ppm of TCE and 15000 ppm of H₂O with balance air. The reaction products were analyzed by an on-line gas chromatograph (GC) equipped with TCD and FID.

**Results and discussion**

MPNO-Na reagent form insoluble stable five-membered ring chelates with Co²⁺ and Cr³⁺ ions according to following reactions:
To confirm the formation of chelates by reactions (2 and 3), an automatic CHN analyzer was used to characterize chelates. Results of elemental microanalysis of cobalt and chromium chelates are given in Table 2. The thermal decomposition of mixed complexes in the presence of air can be formulated as follows:

$$\text{Co(C}_5\text{H}_4\text{NOS)}_2 + 2\text{Cr(C}_5\text{H}_4\text{NOS)}_3 + 54\text{O}_2 \xrightarrow{600\degree C} \text{CoCr}_2\text{O}_4 + 8\text{SO}_2 + 4\text{N}_2 + 40\text{CO}_2 + 16\text{H}_2\text{O}$$

(4)

Table 2 Analysis of Co$^{2+}$ and Cr$^{3+}$ chelates

| Complex                  | Theoretical | Experimental |
|--------------------------|-------------|--------------|
| N H C                    | N H C       |              |
| 8.50 2.51 37.61          | 8.70 2.68 37.32 | Co(C$_5$H$_4$NOS)$_2$ |
| 9.23 2.73 41.70          | 9.73 2.80 42.05 | Cr(C$_5$H$_4$NOS)$_3$ |

The thermal behavior of dried mixed complexes precursor was studied by TGA and DTG. The experimental curves are shown in Fig. 1. As can be seen, Fig. 1(a) shows that roughly there is no loss of weight up to 90$\degree$C, the loss is about 5% at 250$\degree$C. This can be related to removal of small amount of physically adsorbed water.

However dramatic weight loss are observed at above 300$\degree$C and eventually the curve is leveled off around 10.6% of its initial weight at 600$\degree$C. This loss of weight is attributed to the thermal decomposition of mixed complexes. A total theoretical weight loss of 88.84% would have been expected due to decomposition reaction (4), however, the total weight loss of 89.40% is shown in the experimentally observed TGA curve. It is clear that experimental weight loss (89.4%) is in agreement with the theoretical value. The TGA curve of this sample is also shown in Fig. 1(b). The initial small peaks are due to loss of small amount of water. The major peak is due to the decomposition of mixed complexes which take place at 387$\degree$C.

The L$_4$ Taguchi orthogonal array was used to study the optimum conditions for the preparation of smallest average particle size product. The L$_4$ Taguchi array with levels assigned and responses are shown in Table 3. Figure 2 shows the XRD patterns of samples synthesized at different conditions indicated in Table 3. All samples are crystalline in nature and the peaks are well matched with diffraction patterns (JCPDS No: 780711). The average crystallite size was determined by the peak broadening method. The full width at half maximum (FWHM) for the highest peak was measured and the average crystallite size (D) was estimated using Scherrer’s formula,

$$D = \frac{0.9}{\cos \theta \times \sqrt{B^2 - b^2}}$$

(5)

Fig. 1 (a) Termogravimetric (TGA) and (b) differential TG (DTG) curves for dried mixed complexes precursor of CoCr$_2$O$_4$.

Fig. 2 X-ray diffraction patterns of CoCr$_2$O$_4$ samples synthesized at different conditions indicated in Table 3.
where λ is the wavelength of radiation, θ is the Bragge’s angle, B and b are the FWHM observed for the sample and standard, respectively. Results are presented in the response column of Table 3. The experiment was carried out by random order.

### Table 3 The L₃ Taguchi design for 3 main factors at 2 levels

| Average Crystallite Size (nm) | Factors levels | Experiment No. |
|------------------------------|----------------|----------------|
| Response                     | C    | B    | A    |               |
| 4.1 (Y₁)                    | 1    | 1    | 1    | 1              |
| 6.9 (Y₂)                    | 2    | 2    | 1    | 2              |
| 7.2 (Y₃)                    | 2    | 1    | 2    | 3              |
| 7.2 (Y₃)                    | 1    | 2    | 2    | 4              |

Calculation of the average effects of factors follows,

\[
\bar{A}_1 = \left( \frac{Y_1 + Y_2}{2} \right) = \left( \frac{4.1 + 6.9}{2} \right) = 5.50
\]

\[
\bar{A}_2 = \left( \frac{Y_3 + Y_4}{2} \right) = \left( \frac{7.2 + 9.2}{2} \right) = 8.20
\]

\[
\bar{B}_1 = \left( \frac{Y_1 + Y_3}{2} \right) = \left( \frac{4.1 + 7.2}{2} \right) = 5.65
\]

\[
\bar{B}_2 = \left( \frac{Y_2 + Y_4}{2} \right) = \left( \frac{6.9 + 9.2}{2} \right) = 8.05
\]

\[
\bar{C}_1 = \left( \frac{Y_1 + Y_4}{2} \right) = \left( \frac{4.1 + 9.2}{2} \right) = 6.65
\]

\[
\bar{C}_2 = \left( \frac{Y_2 + Y_3}{2} \right) = \left( \frac{6.9 + 7.2}{2} \right) = 7.05
\]

The optimum combination of factors A, B and C and the lowest magnitude of the performance was calculated from the following equation,

\[
Y_{opt} = \bar{Y} + (A_x - \bar{Y}) + (B_x - \bar{Y}) + (C_x - \bar{Y}) \quad (6)
\]

\[
\bar{Y} = \left( \frac{4.1 + 6.9 + 7.2 + 9.2}{4} \right) = 6.85
\]

\[
Y_{opt} = 6.85 + (5.5 - 6.85) + (5.65 - 6.85) + (6.65 - 6.83) = 4.1
\]

Therefore, the optimum combination levels of A, B, C factors and the lowest average particle size belongs to the conditions of row 1 of Table 3 (i.e the preparation is robust). When the thermolysis of mixed chelates was carried out at 540°C which is less than 600°C, some oxides impurity were detected in the XRD spectrum of product (No. 5 in Fig. 2). To check the optimum value obtained for the average particle size (Row 1 in Table 3) the appropriate amount of cobalt chromite (0.1 g) was dispersed in 100 ml distilled deionized water containing 0.5 g pentaerytritol as dispersing agent by vigorous stirring. As can be seen, Fig. 3 shows that the size range obtained with laser light scattering (LLS) for optimum conditions was 2.2-6.0 nm. The mean diameter of particles was obtained from size distribution curve using RTG correlator software to be 4.2 nm (the result obtained from XRD spectrum was 4.1 nm). The estimated factor effects on the response were calculated from Table 3 by using the following equation [28,29],

\[
\text{Effect estimate} = \left[ \frac{\left( \sum \text{level 2 results} \right)}{\left( \sum \text{level 1 results} \right)} \right] / \left( \frac{r}{2} \right) \quad (7)
\]

where $r$ is the number of experiments. Considering the absolute value of factor effects. The order of variable effectiveness is,

\[
A = 2.7 \quad \text{(temperature of thermolysis, °C)} > B = 2.45 \quad \text{(time of thermolysis, h)} > C = 0.4 \quad \text{(coefficient of stoichiometric concentration of Co²⁺ and Cr³⁺ in the initial materials)}.
\]

It is clear that the concentration of initial material have lowest effect on crystallite size of particles. This is maybe due to fast chemical reaction produces insoluble chelate. Furthermore the amount of thermolysed sample is low, therefore the temperature lag between inside and outside of sample for different sample size does not produce crucial effect on the particle size. The main effective factors on the particle size of product are temperature and time of thermolysis. Figure 4 shows changes in the crystallite size (responses) against the thermolysis temperature at two different thermolysis times. It is clear that, increasing the thermolysis temperature increases the crystallite size. The higher time of thermolysis (5 h) lead to bigger crystallite size. As the higher temperature causes sintering and aggregation of crystallite, therefore the crystallite size is increased significantly when the thermolysis temperature is increased from 600 to 800°C.
Figure 4  Response (Crystallite size: Y1, Y2, Y3, and Y4) obtained against the thermolysis temperature.

Figure 5 shows the TEM analysis of the CoCr$_2$O$_4$ nanoparticle obtained according to the recommended procedure (experiment 1 in Table 3). This image shows that the particles are roughly spherical having diameters in the range of 2.0-6.0 nm which agrees well with XRD and LLS results. Figure 6 shows the SEM analysis of the CoCr$_2$O$_4$ obtained with conventional coprecipitation method (sample 6). As can be seen, the particles diameters are in the range of 30-60 nm. It is clear that the coprecipitation method causes the agglomeration of particle during precipitation. While the thermolysis method lead to the particles in range of 2-6 nm.

The specific surface area (SSA) of sample1 (Table 3) was measured based on the principle of N$_2$ sorption. The SSA obtained was high (78.2 m$^2$·g$^{-1}$). This is because of the generation of high volume of gases during thermolysis process. The evolution of hot gases causes the loss of heat from the solid phase and favours formation of small particle with high porosity.

To confirm the purity of CoCr$_2$O$_4$, about 0.2 g of sample was fused with ten times its weight of Na$_2$O flux and the melt was dissolved in HNO$_3$ [30]. After proper dilution the percentages of Co$^{2+}$ and Cr$^{3+}$ ions in cobalt chromite were determined by atomic absorption spectrophotometry. The average of duplicate results for each case are given in Table 4.

Table 4  Analysis of cobalt and chromium in synthesized CoCr$_2$O$_4$

| % Cr  | % Co  |
|-------|-------|
| 54.91 | 25.50  |
| 54.83 | 25.79  |
| +0.08 | -0.29  |

Experimental
Theoretical
Difference

Figure 7 shows the catalytic performance for the decomposition of TCE over CoCr$_2$O$_4$ catalysts at 330°C and WHSV of 60 L·g$^{-1}$·h$^{-1}$ under steady-state conditions. As indicated in Fig. 7, CoCr$_2$O$_4$ nanoparticle obtained according to the recommended procedure (experiment 1 in Table 3, average particle size is 4.1 nm)

![Figure 7](image-url)  
Fig. 7  TCE conversion over CoCr$_2$O$_4$ samples prepared by optimized thermolysis procedure (experiment 1 in Table 3) and conventional coprecipitation method (sample 6) at WHSV:60 L·g$^{-1}$·h$^{-1}$.
showed higher conversion (97%) than sample 6 (particle size in the range of 30-60 nm) obtained with conventional co-precipitation method which gave 70% conversion. Comparison of catalytic activity and crystallite size of samples confirmed that the catalyst with smaller crystallite size gives more favorable active sites for the decomposition of TCE.

Conclusion

A novel approach using new precursors is reported for the synthesis of cobalt chromite based on the decomposition of mixed chelates of Co$^{2+}$ and Cr$^{3+}$ ions with stoichiometric ratio using 2-Mercaptopyridine-N-Oxide Sodium salt as chelating agent. The characterization and the conditions for the complete conversion of mixed chelates to CoCr$_2$O$_4$ nanoparticles were confirmed by TGA, DTG, XRD, TEM, LLS, BET, SSA and chemical analysis. The L$_4$ Taguchi design was implemented to optimize the experimental conditions for the preparation of CoCr$_2$O$_4$ nanoparticles. The main factors having significant effect on the particle size reduction were found to be time and temperature of thermolysis process. The SSA of CoCr$_2$O$_4$ synthesized by optimized method was effectively increased. This is because of generation and evolution of high amount of gases in the thermolysis process. The particle size of product was 4.1±1.9 nm. The lowest reported value is 10±2 nm [5]. The SSA of CoCr$_2$O$_4$ was found to be 78.2 m$^2$/g. Furthermore CoCr$_2$O$_4$ nanoparticle with smaller crystallite size presented a better catalytic performance for oxidation of trichloroethylene.

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Preparation and Characterization of Free-standing Hierarchical Porous TiO$_2$ Monolith Modified with Graphene Oxide

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Abstract: Catalyst recovery is one of the most important aspects that restrict the application of TiO$_2$ photocatalyst. In order to reduce restrictions and improve the photocatalytic efficiency, a hierarchical porous TiO$_2$ monolith (PTM) with well-defined macroporous and homogeneous mesoporous structure was prepared by using a sol-gel phase separation method. P123 was used as the mesoporous template and graphene oxide was applied to increase the activity and integrity of the monolithic TiO$_2$. According to scanning electron microscopy and the Barrett-Joyner-Halenda measurements, PTM is mainly composed of 10 nm anatase crystallines with 3.6 nm mesopores and 2-8 $\mu$m macropores. Further characterization suggests carbon and nitrogen have been maintained in the PTM during calcinations so as to induce the visible light activity. The PTM with 0.07 wt% graphene oxide dosage shows high efficiency for methyl orange (MO) decolorization under both full spectrum and visible light irradiation ($\lambda > 400$ nm). Besides, the monolith remains intact and has good photocatalytic stability after four cyclic experiments.

Keywords: Photocatalysis; Titanium dioxide; Porous monolith; Graphene oxide

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Introduction

Heterogeneous photocatalysis of TiO$_2$ nanocrystalline is a promising technology to remove recalcitrant toxic organic pollutants in wastewater [1-3]. However, in engineering applications for water purification, catalyst recovery is still a big challenge due to the costly and inefficient separation process for TiO$_2$ nanoparticles. Efforts have been directed toward immobilization of TiO$_2$ nanoparticles onto various materials, such as glass, fiber optic cable, plastic, etc [4-8]. However, immobilization will result in a dramatical reduction of surface area and inhibited mass transfer efficiency, therefore, the inherent decrease of catalytic activity blocks their further scalable application of TiO$_2$ photocatalysis. Freestanding porous TiO$_2$ with a large length scale could be a favorable alternative [9,10] because the monolithic structure can be easily separated from aqueous solution and the porous structural characteristic facilitates the mass transfer so as to maintain a feasible reaction rate.

Hierarchically ordered porous structures in natural materials have attracted considerable attention for both fundamental and practical reasons [11,12]. Natural leaves are optimized systems with elaborate hierarchical porous structures and functional components, which play an elaborate crucial role in photosynthesis, including light harvesting, photogenerated charge separation...
and catalytic active center for efficient solar energy conversion [13,14]. Inspired by natural materials, several kinds of hierarchical porous TiO$_2$ replicas have been developed via a two-step infiltration process with leaves [15], egg shells [16] or butterfly wings [17] as templates. However, their methods cannot obtain a large-sized free standing TiO$_2$ monolith. To the best of our knowledge, little work has been done on free standing hierarchical porous TiO$_2$ by sol-gel method, because capillary pressure generated during drying treatment makes the TiO$_2$ sol-gel hard to form intact monolith. Cao et al. obtained free standing and crack free TiO$_2$-SiO$_2$ aerogel by drying the precursor with ethanol and CO$_2$ supercritical method [10,17]. Konishi et al. obtained titania monoliths in a phase-separation method [18,19]. We have developed this method to obtain a monolithic TiO$_2$ by controlling the amount of water in the precursor, and the resulting catalyst showed efficient activity in water purification [9].

Inspired by the hierarchical porous structure of leaves in the nature, we develop a hierarchical porous TiO$_2$ monolith with well-defined macroporous and homogeneous mesoporous structure in a sol-gel phase separation method. Graphene is a recent discovery of new 2D nano carbon materials and its strength is the highest of all the materials known so far, so the relevant topics have attracted much attention recently. In our study, graphene oxide (GO) is added to the monolithic TiO$_2$ and P123 has been used to obtain an ordered porous structure. The dosage of GO is optimized and the photocatalytic performance of the monolithic TiO$_2$ is tested and characterized.

Experimental sections

Preparation of PTM$_x$

GO was synthesized from oxidation of graphite by the modified Hummers method [20,21]. In a typical experiment, 0.5 g graphite powder and 0.5 g NaNO$_3$ were introduced to 23 ml concentrated H$_2$SO$_4$ in an ice-bath. 3 g KMnO$_4$ was added gradually under vigorous stirring and the temperature of the mixture was maintained below 20°C. The mixture was stirred at 35°C for 4 h. Then, 46 ml de-ionized water was slowly added into the solution and the mixture was stirred at 98°C for 15 min. The reaction was terminated by adding 140 ml de-ionized water and 1 ml H$_2$O$_2$ (30 wt%). The resulting graphite oxide was washed with de-ionized water. GO was obtained from the graphite oxide solution by using a JY92-2D ultrasonic crasher (Ningbo Scientz Biotechnology Co., Ltd.) for 40 min. Unexfoliated graphite oxide in suspension after ultrasonication was removed by centrifugation at 3000 rpm for 5 min. The suspension with GO was centrifuged at 8000 rpm for 20 min. The product was dried at 70°C for 12 h under vacuum and then re-suspended in water. The obtained suspension with GO (1.3 g/l) was then used for the following synthesis of GO/TiO$_2$ composites.

 Porous TiO$_2$ monolith was synthesized using a sol-gel method accompanied by phase separation. In a typical procedure, 1.5 ml of acetylacetone was added into 5 ml of tetrabutyl titanate (Ti(OBu)$_4$) under modest stirring and the mixture was named solution A. Another solution composed of 3.2 ml deionized water with 0.2 g P123 and a certain amount of GO dissolved in it was named solution B. Both solution A and solution B were prepared in an ice-bath. Afterwards, 1.86 ml of concentrated HCl was slowly added into solution A, then solution B and 0.15 ml of formamide were successively added dropwise into solution A. The resulting solution was vigorously stirred for 30 min, and then poured into plastic centrifugal tubes, which served as the molds. The sample was aged for one day at 30°C, and finally was dried in an oven at 60°C for 7 days. The obtained monolithic TiO$_2$ was carefully taken out and calcined at 350°C in air, named as PTM$_x$, wherein $x$ is corresponding to different dosages of GO, that is, 0-3 represent that the GO dosages in the porous TiO$_2$ monolith are 0 wt%, 0.03 wt%, 0.05 wt% and 0.07 wt%, respectively.

Characterization

The morphology of TiO$_2$ monolith was observed by a FEI Quanta 250 (20 kV) field emission scanning electron microscope (FESEM). X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2200/PC X-ray diffractometer. The measurements were made on the powder specimens prepared by grinding monolithic TiO$_2$. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an AXIS Ultra DLD system produced by Kratos company and Shimadzu company with Al-K radiation (h=1486.6 eV). UV-vis diffuse reflectance spectra (DRS) were recorded on a Lambda 950 UV/vis spectrophotometer (PerkinElmer Instrument Co., Ltd.) and converted from reflection to absorption by the Kubelka-Munk method. The specific surface area and pore size distribution were measured using a Nova 100 (Quantachrome Instruments) with nitrogen as the adsorption gas, and obtained using the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method, respectively.

Photocatalytic activity

The optical system for photocatalytic activity measurement is composed of a 1000 W xenon lamp and a cutoff filter ($\lambda$ >400 nm). In a typical test, one or two pieces of intact monolithic TiO$_2$ were put onto a stainless steel mesh, and 20 mL of methyl orange (MO) solution (initial concentration 10 mg/L) was added into the beaker. The solution with catalyst was stirred in
dark for 30 minutes to reach an adsorption equilibrium. Subsequently the light was switched on, and the sample was taken and analyzed at regular time intervals. The absorbance of MO was monitored with UNICO UV-2101 spectrometer at 464 nm.

The photocatalytic efficiency of the monolithic TiO$_2$ can be compared by the MO specific removal efficiency (SRE), whose definition is as follows:

\[ a = \frac{(C_0 - C_t)}{C_0} \times t \times m \]  

(1)

Wherein, $C_0$ is the initial absorbance of MO, $C_t$ is the absorbance of MO at time $t$, $t$ is the time when the absorbance of MO decreases to below 15% of $C_0$, and $m$ is the mass of monolithic TiO$_2$. Moreover, $a_1$ corresponds to the SRE under full spectrum irradiation, and $a_2$ corresponds to the SRE under visible light irradiation ($\lambda > 400$ nm).

Results and discussion

Photocatalytic performances of PTM$_x$

The photocatalytic activities of PTM$_x$ have been studied using MO as the model pollutant. As shown in Fig. 1, the photocatalytic performance of PTM$_x$ under visible light irradiation decreases in the order of PTM$_3$ > PTM$_2$ > PTM$_1$ > PTM$_0$ (Fig. 1(a)). Without addition of GO, the PTM$_0$ also has obvious activity for MO decolorization under both visible light and full spectrum irradiation, however, the structure of the monolith has a slight disruption after reaction. Consequently, from the time dependent curves in Fig. 1, it can be concluded that the sample PTM$_3$ shows better activity for MO removal.

To make the comparison more reasonable, SRE was calculated to evaluate the activities of the PTM$_x$ samples. Figure 2 shows specific removal efficiency of MO over PTM$_x$ under the full spectrum ($a_1$) and visible light irradiation ($a_2$). It can be seen that under visible light irradiation, with addition of graphene oxide, photocatalytic activity was improved as the percentage of graphene oxide increased. As for the full spectrum irradiation, the sample PTM$_2$ shows the best SRE value, a little higher than PTM$_3$. However, the time dependent curves indicate that although the initial decrease of MO is very fast over PTM$_2$, the rate slows down soon, and the final MO removal efficiency is lower than PTM$_3$. Therefore, PTM$_3$ with GO dosage of 0.07 wt% has the highest efficiency for MO decolorization, whose SRE value increases to 4 and 2.2 times of that of PTM$_0$ in the conditions of visible light and full spectrum irradiation, respectively. As is known, the reduced GO is an efficient substrate for electron transfer. Hence, the enhanced photocatalytic activity of the PTM with addition of GO can be attributed to the thermal reduced graphene oxide, which is in favor of photogenerated electron transfer and charge separation [22]. Therefore, taking into account both the activity and structure before and after irradiation, PTM$_3$ has been chosen as the proper photocatalyst for further investigation.

Characterization of PTM$_3$

Figure 3 shows the XRD patterns of PTM$_3$ and PTM$_0$ samples. In the XRD pattern of PTM$_3$, an intense peak at $2\theta=25.28^\circ$ corresponding to the (101) plane diffraction of anatase TiO$_2$ is observed and a
smaller peak appears at $2\theta=48.0^\circ$ corresponding to the (200) plane diffraction of anatase TiO$_2$ [23]. It can be seen that PTM$_0$ has a similar XRD pattern, but the peak corresponding to the (101) plane diffraction of anatase TiO$_2$ appears at $2\theta=25.48^\circ$. All diffraction peaks are indexed to pure anatase TiO$_2$ (JPCDS Card: 84-1286). According to Scherrer’s equation, $L_c=K\lambda/(\beta\cos\theta)$ (where $\lambda$ is the X-ray wavelength, $\beta$ is the FWHM of the diffraction line, $\theta$ is the diffraction angle, and $K$ is a constant, which has been assumed to be 0.9) [24], and according to the full width at half maximum (FWHM) of the peaks at 25.28$^\circ$ and 25.48$^\circ$, PTM$_3$ and PTM$_0$ have an average particle diameter of about 7.2 nm and 7.5 nm, respectively. It reveals that the addition of GO does not affect the crystalline phase of PTM. The result of PTM$_3$ is strongly consistent with the observation from TEM (Fig. 4). The TEM image manifests that titania particles are almost uniform in a small size (about 8-10 nm). The small dispersed nanoparticles indicate that the TiO$_2$ monolith consists of small TiO$_2$ nanoparticles with a quite large specific surface area, which is very important for the photocatalytic performance of PTM$_3$ sample.

The morphology of PTM$_3$ can be observed by the SEM images, as shown in Fig. 6. It reveals that the walls of the porous TiO$_2$ consist of small interconnected TiO$_2$ nanoparticles with sizes under micrometer scale. Besides, the SEM image with higher magnification (Fig. 6(b)) clearly shows the existence of homogeneous macropores. The macropores are self-organized, originating from the phase separation process. Combining the above analyses of nitrogen adsorption–desorption and XRD, a conclusion can be drawn that PTM$_3$ is mainly composed of 10 nm anatase crystallines with 3.6 nm mesopores and 2-8 µm macropores. Macropores ensure the light penetration depth and thus improve the efficiency of the light utilization, meanwhile mesoporous and microporous structures guarantee the
large specific surface area and better adsorption ability. Hence, the hierarchical porous structure results in a large BET surface area and good photocatalytic performance [26].

![Typical SEM images of PTM calcined at 350°C with magnification of 1000× (a); with magnification of 5000× (b).](image)

UV-Vis diffuse reflectance spectrum of PTM powder is employed to evaluate the optical absorption properties. The measurement is recorded using BaSO₄ as a reference, and then the reflectance spectrum is converted into equivalent absorption spectrum by using Kubelka-Munk function (Fig. 7) [27]. It can be seen that PTM exhibits an extended optical absorption in both ultraviolet light region and visible light region. The indirect band-gap energy of PTM is estimated according to the intercept of the tangent in the plot of \((F(R_\infty)h\nu)^{1/2}\) versus photon energy \((h\nu)\). The band-gap energy decreases to 3.02 eV with a threshold wavelength of about 410 nm, which is narrower than that of anatase TiO₂ (about 3.2 eV) [28], as shown in Fig. 6. The extended visible light absorption can be supported by the highly efficient decolorization of MO solution under visible light irradiation, which is attributed to the incorporation of carbon and nitrogen species. Moreover, the long tail in the region till 800 nm is also observed, indicating the presence of surface modified species.

![UV-vis absorption spectra of PTM and commercial anatase TiO₂.](image)

To further investigate chemical states of the existence of carbon and nitrogen elements in the PTM, XPS has been measured, as shown in Fig. 8. The binding energies are all calibrated by using the contaminant carbon at binding energy of 284.8 eV. From the high resolution core-level spectra of titanium, two peaks at 464.6 eV and 463.8 eV (Fig. 8(a)) can be seen, which are ascribed to the Ti2p3/2 and Ti2p1/2 of TiO₂ [29]. However, there is also a small peak at 461.3 eV, and we tentatively ascribe this peak to the Ti³⁺, which might be related with oxygen vacancy, and contributes much to the visible light activity of TiO₂ [30]. The peaks at 529.9 eV and 532.1 eV in Fig. 8(b) are attributed to the bulk O from TiO₂ and –OH adsorbed on the surface of PTM, respectively [29]. The larger area at 532.1 eV indicates the abundance of surface states.

The high resolution Cls core-level XPS spectrum is shown in Fig. 8(c). The first peak at 284.8 eV arises from the adventitious carbon contamination and the other two peaks at 286.0 eV and 288.4 eV suggest the existence of C-O and C=O bonds, respectively, which indicates the formation of carbonated species [31]. Fig. 8(d) shows the high resolution N1s core-level XPS spectrum, which could be deconvoluted into two peaks (401.7 eV and 403.4 eV). The main peak at 401.7 eV corresponds to the N atoms that replace the O atoms inside of the TiO₂ [32]. Another peak at 403.4 eV can be attributed to the N-O bond over the surface of TiO₂ powder [33]. Considering that PTM presents only the anatase phase in the XRD spectra, it can be inferred that some compounds containing nitrogen or carbon form over the TiO₂ surface and consequently increase the absorption ability of TiO₂ monolith for visible light.
Photocatalytic stability and structural integrity

To evaluate the photocatalytic stability of the PTM₃ catalyst, cyclic experiments are conducted, as shown in Fig. 9. In each test, one small piece of PTM₃ was applied as the catalyst, and the MO solution with a same initial concentration is illuminated under visible light for 2 h. We can see that after the first two rounds of the experiments, the photocatalytic activity of PTM₃ shows a slight decline. It is probably because that during photocatalytic degradation, some of the intermediate products adsorbed inside the catalyst and reduced the photocatalytic activity. In the following continuous tests, PTM₃ shows a stable photocatalytic performance in the cyclic experiments. Moreover, the digital pictures of PTM₃ before and after the degradation (inset pictures of Fig. 9) show that the structure of the PTM₃ catalyst remains intact after the cyclic experiments. In another control test, the absorbance of methyl orange has almost no change after two-hour irradiation in the absence of catalysts.

Consequently, by selecting a proper template and optimizing the synthesis parameters, it is promising to prepare a 3D monolithic material with structure similar to leaves in the nature. This material has a good application prospect in water purification, because it can keep an intact structure under a flowing media, consequently avoiding the complex steps like recovery or immobilization of photocatalysts.

Conclusion

Hierarchical porous TiO₂ monoliths with high photocatalytic activity have been successfully synthesized in
a sol-gel method accompanied by phase separation. The TiO$_2$ monolith is mainly composed of 10 nm anatase crystallites, and has a hierarchical porous structure with 3.6 nm mesopores and 2-8 µm macropores. P123 and GO play an important role in structural integrity and stability of the monolith, and the pore size can be tailored by adjusting the starting compositions. Due to the macroporous and homogeneous mesoporous structure, the BET specific surface area can reach 163 m$^2$/g. The porous TiO$_2$ monolith remains intact after being applied for the discolorization of MO solution. Therefore, it has a promising prospect in applications of photocatalytic water purification, mesoporous membranes, etc.

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Controllable Hydrothermal Synthesis and Properties of ZnO Hierarchical Micro/Nanostructures

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Abstract: A simple hydrothermal route has been developed for the fabricating ZnO hierarchical micro/nanostructure with excellent reproducibility. SEM and TEM analysis show that the hierarchical rod is a single-crystal, suggesting that many single-crystal micro/nanorods are assembled into ZnO hierarchical micro/nanostructures. The morphologies of the hierarchical rods can be conveniently tailored by changing the reaction parameters. And we also found citric acid plays a crucial role in the formation process of ZnO micro/nanostructures. Room-temperature photoluminescence spectra reveals that the ZnO hierarchical micro/nanostructures have a strong emission peak at 440 nm and several weak emission peaks at 420, 471 and 541 nm, respectively.

Keywords: Hydrothermal route; Micro/nanorod; ZnO

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Introduction

Bottom-up processes which commonly used to manipulate the growth of multi-dimensional nanostructures are very important for understanding advance fundamental nanomaterials and engineering novel functional devices [1,2]. One-dimension (1D) nanostructures or their ordered arrays have attracted considerable interest in recent years because they are expected to improve the performance of various nano-devices [3-7]. Meanwhile, hierarchical or complex architecture built up with well-ordered nanostructures plays a key role in their chemical, optical and electrical properties for functional micro/nanosystems [8]. Different dimension hierarchical ordered nanostructures may induce some novel properties resulting from its unique multi-dimensional shape and a combination of both micrometer-scale and nanometer-scale building blocks [9], such as multi-reflection [10], higher specific surface and porosity [11,12].

A wide range of 1D ZnO nanostructures, including wires, rods, belts and tubes has been prepared [13]. So far, much attention has been paid to the realization of three-dimensional (3D) ZnO structures based on these 1D structures due to its unique properties for novel applications in advanced catalysts or gas sensors [14]. To date, several techniques have been used for the fabrication of 3D ZnO structures, including chemical vapor deposition (CVD) [15], thermal evaporation [16], sonochemical method [17], hydrothermal route [18] and pyrolysis technique [19]. For example, Umar et al [15] reported flower-shaped ZnO nanostructures obtained on silicon substrates with different orientations by using modified cyclic feeding chemical vapour deposition (CFCVD) technique in which diethyl zinc and high purity oxygen (99.999%) gas were used as raw materials. Zhang et al [18] synthesized prickly sphere-and flower-like ZnO by decomposing \( \text{Zn(OH)}_2^{2-} \) precursor in an aqueous solution or \( \text{Zn(NH}_3)_2^{2+} \) precursor in ethanol. Moreover, Choppati et al [19] obtained 3D ZnO structures with hexagonal flower-like morphologies by using a polymeric precursor solution-based pyroly-
sis technique. Template methods using pre-deposited buffer layers or different surfactants (additives) were also reported by other groups on synthesis of 3D ZnO nanostructures [20]. However, previous efforts usually involved complicated experimental procedures, equipments, expensive substrates or surfactants. Control-

cable synthesis of hierarchical or complex ZnO structure is still a challenge for researchers.

Herein, we present a one-step hydrothermal route to synthesize ZnO hierarchical micro/nanostructure. The morphology can be simply controlled by chang-

ing the reaction parameters. We also investigated the optical properties of flower-like ZnO hierarchical mi-

cro/nanostructures using UV-Vis and photolumines-

cence techniques.

Experimental

All reagents were analytically pure and used without further purification. The precursor solution was prepared by mixing 0.025 mol Zn \((\text{CH}_3\text{COO})_2\cdot2\text{H}_2\text{O}\), 0.05 mol NaOH and 50 ml \(\text{NH}_3\cdot\text{H}_2\text{O}\) (25-28%) into deionized water with continuous stirring. Firstly white floccules appeared and after a while it dissolved completely. The as-formed solution was transferred into a volumetric flask, diluted to 250 ml with deionized water, and then a precursor solution with 0.1 mol/l \(\text{Zn}^{2+}\) concentrations was obtained. In a typical procedure, an aqueous solution of precursor and deionized water were mixed in an equal volume. A 0.3 g citric acid was added into the above solution whilst stirring for \(\sim 10\) min. Then 32 ml of this mixture with \(\text{Zn}^{2+}\) concentration of 0.05 mol/l were transferred into a 50 ml Teflon-lined stainless steel autoclave. After hydrothermal treated at 180°C for 12 h, the autoclave was cooled down to room temperature naturally. The white precipitates were collected and washed with deionized water and ethanol several times to remove impurities. The precipitates were dried in air at 60°C for 5 h.

The products were characterized with X-ray diffractometer (XRD, Rigaku D/Max-2550 PC, Cu Kα ra-


diation), scanning electron microscope (SEM; JSM-5600LV), transmission electron microscope (TEM; JEOL JEM 200CX 3000F) equipped with an X-ray en-


ergy dispersive spectrometer (EDS). The photolumines-


cence (PL) measurements were performed on a Perkin-


Elmer luminescence spectrometer LS55 at room tem-


temperature using a Xe lamp with a wavelength of 380 nm as the light source.

Results and Discussion

All as-obtained powders show similar XRD patterns. A representative XRD pattern is shown in Fig. 1, in which products were prepared when the volume ratio of \(\text{Zn}(\text{NH}_3)_4^{2+}\) precursor solution and water is 1:1. It can be indexed to a hexagonal ZnO phase with lattice constants of \(a=0.325\) nm and \(c=0.521\) nm (JCPDS card; 36-1451). No precursor impurities peaks, such as \(\text{Zn (CH}_3\text{COO})_2\cdot2\text{H}_2\text{O}\) and NaOH were detected within experimental error. The sharp and narrow lines indicate that the products are well crystallized.

![Fig. 1 XRD pattern of the product prepared with the volume ratio of \(\text{Zn}(\text{NH}_3)_4^{2+}\) precursor solution and water of 1:1.](image-url)

A low-magnification SEM image (Fig. 2(a)) reveals that the flower-like products have the average mean diameter of \(\sim 20-40\) µm. These flower-like micro/nanostructures consist of hierarchical rod alignments; as further shown in the high magnification SEM image (Fig. 2(b) and 2(c)), the hierarchical rod within the micro/nanostructure is composed of microrods on its lower part and a taper on its upper part. The microrods are regular hexagonal prisms with diameters of \(\sim 300\) nm and lengths of several micrometers, and the taper is consisted of the cone with a width of \(\sim 300\) nm and a cone-like nanorod end with a diameter of \(\sim 30\) nm. The high-resolution TEM image is taken from an

![Fig. 2 (a-c) SEM and (d) HRTEM images of the ZnO hierarchical micro/nanostructures synthesized using the volume ratio of \(\text{Zn}(\text{NH}_3)_4^{2+}\) precursor solution to water of 1:1.](image-url)
edge of a composed ZnO micro/nanorod within flower-like microstructures (Fig. 2(d)). It reveals that the hierarchical rod is a single-crystal, suggesting that many single-crystal hierarchical rods are self-assembled into ZnO hierarchical micro/nanostructures. Detailed analysis of the lattice fringes give an interplanar spacing of 0.524, which match well the distance of the (001) planes of a ZnO crystal, which may result from lattice orientation perfections among the prismatic rod [21]. The rod axis direction was parallel to the (001) crystallographic orientation of a wurtzite ZnO crystal. This is a frequent growth orientation for the hexagonal close-packed materials, which has been observed in many ZnO nanorods [22].

The morphologies of these ZnO hierarchical micro/nanostructures vary with the volume ratio of Zn(NH$_3$)$_2^{2+}$ precursor solution to water, as shown in Fig. 3. When the volume ratio of Zn(NH$_3$)$_2^{2+}$ precursor solution to water is 32:0 with unchanged other parameters, the ZnO micro/nanostructures are consisted of the cone-like microrod assemblies and many submicrometer particles, and the cone-like microrod of the assemblies has a diameter of ~1 µm and a length of several micrometers, as shown in Fig. 3(a) and 3(b). When the volume ratio is decreased to 3:1, the ZnO microstructures consisting of several microcones and particles are prepared (Fig. 3(c) and 3(d)). The cone has a diameter of ~3 µm and a length of ~6 µm, and the particle has a diameter of ~1 µm. With further decreasing the quantity of Zn(NH$_3$)$_2^{2+}$ precursor solution (the volume ratio is 1:3), the flower-like ZnO structures are destroyed (Fig. 3(e) and 3(f)), and it can be seen that the products are consisted of many cone-like microrods or particles with ~3 µm in diameter and several micrometers in length, which possess the typical tapering feature with the tips. Therefore, ZnO crystals with a series of different morphologies were successfully fabricated only by changing the volume ratio of Zn(NH$_3$)$_2^{2+}$ precursor solution to water; each ZnO micro/nanostructures is composed of the ZnO cones and particles.

The effect of the surfactant quantity on the morphology of the ZnO hierarchical micro/nanostructures was also investigated. SEM images of the products prepared using the different amounts of citric acid are shown in Fig. 4. Without using citric acid as the surfactant, the flower-like ZnO hierarchical superstructures are composed of sub-micrometer rod, and individual rods gradually tapered and tipped in the form of cone with a diameter of about ~1 µm (Fig. 4(a)). When the amount of citric acid was increased to 0.025 g or 0.05 g, the formation of the flower-like ZnO hierarchical structures consisted mainly of these micro-sized prisms, Fig. 4(b) and 4(c). When the amount of citric acid was increased to 0.1 g, the ZnO hierarchical structures are composed of sub-micrometer hierarchical rod or single hierarchical rod, and individual rod is prism-like and gradually tipped in the form of several nanocones with a diameter of about ~100 nm (see Fig. 4(d)). Besides, when the amount of citric acid was increased to 0.3 g, the hierarchical microrod with a taper on its upper part began to aggregate into flower-like micro/nanostructures (see Fig. 2).

![Fig. 3](image-url)

**Fig. 3** SEM images of the ZnO micro/nanostructures prepared at different volume ratio of Zn(NH$_3$)$_2^{2+}$ precursor solution to water: (a,b) 32:0; (c,d) 3:1; (e,f) 1:3.

![Fig. 4](image-url)

**Fig. 4** SEM images of the ZnO micro/nanostructures prepared at different amounts of citric acid: (a) without citric acid; (b) 0.025 g; (c) 0.05 g; (d) 0.1 g.

ZnO particles by the direct decomposition of soluble Zn(NH$_3$)$_4^{2+}$ precursor under hydrothermal conditions were fabricated, which follows the growth habit of ZnO crystals [23]. The crystal growth process involves two stages of nucleation and crystal growth [24]. External conditions may stress tremendous effects on the morphology and size of a given crystal by participating...
in the nucleation and growth [25]. In the present case, with the amounts of surfactant increasing gradually, the surfactant affects the overall size and the morphology by participating in the nucleation and growth. So, the surfactant plays a crucial role on the formation process of the ZnO micro/nanostructures.

We investigate the optical properties of ZnO hierarchical micro/nanostructures using a combination of UV-Vis and PL technologies. Figure 5(a) shows the UV-Vis spectra of ZnO hierarchical micro/nanostructures. The band gap energies ($E_g$) calculated on the basis of the corresponding absorption edges are 3.27 eV, which are comparable to the values of bulk ZnO. The PL properties of the as-prepared hierarchical micro/nanostructures were measured using 380 nm as an excitation wavelength at room temperature (Fig. 5(b)). It is clear that the spectra consist of a strong emission peak located at 440 nm and several weak emission peaks at 420, 471 and 541 nm, respectively. The near-UV emission at 420 nm agrees with the band gap of bulk ZnO (Gaussian peaks from 365 to 420 nm) [26], which comes from the recombination of free excitons. One possible reason for the variations in the position of the band-edge emission in ZnO nanostructures with relatively large dimensions are different concentrations of native defects [27]. The weak broad peaks at 440 and 471 nm are attributed to the exciton transitions [28] and the present of various point defects, either extrinsic or intrinsic, respectively. The green emissions at 541 nm are related to the singly ionized oxygen vacancy [29], and these emissions result from the recombination of photogenerated hole with a singly ionized charge state of the specific defect.

Conclusion

ZnO hierarchical micro/nanostructures with the different morphology are fabricated by a simple hydrothermal method with excellent reproducibility. These morphologies can be conveniently tailored only by selecting the reactant concentration and the quantity of citric acid. SEM and TEM analysis reveal that the hierarchical rod is a single-crystal, suggesting that many single-crystal micro/nanorod are assembled into ZnO hierarchical micro/nanostructures. The surfactant plays a crucial role on the formation process of the ZnO micro/nanostructures. Room-temperature PL spectra reveal that the ZnO hierarchical micro/nanostructures have a strong emission peak at 440 nm and several weak emission peaks at 420, 471 and 541 nm, respectively.

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Using Inductance as a Tuning Parameter for RF Meta-atoms

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Abstract: The resonant frequency of metamaterials structured with split ring resonator (SRR) meta-atoms is determined primarily through the capacitance and inductance of the individual meta-atoms. Two designs that vary inductance incrementally were modeled, simulated, fabricated, and tested to investigate the role inductance plays in metamaterial designs. The designs consisted of strategically adding sections to the SRR to increase the inductance, but in a manner that minimized capacitance variations. Each design showed a shift in resonant frequency that was proportional to the length of the added section. As the length of each section was increased, the resonant frequency shifted from 2.78 GHz to 2.18 GHz.

Keywords: Inductance; Meta-atom; Metamaterial; Split Ring Resonator; Radio Frequency; Resonance

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Introduction

Metamaterials are engineered materials commonly fabricated from metal structures deposited on electrically isolated dielectric substrates. These materials, according to Pendry \cite{1}, can result in unique material properties that do not exist in nature such as negative permeability ($\mu$) or negative permittivity ($\varepsilon$), and therefore lead to negative index of refraction ($n$). Smith \textit{et al.} \cite{2} demonstrated the first such material based on Pendry’s initial work.

The split ring resonator (SRR) is commonly used as the meta-atom in the structured layer. The SRR is a commonly used component in metamaterial research ranging from radio frequency (RF) to terahertz (THz) \cite{3-5}. The metamaterial design arranges periodic rings as elements to create an electromagnetic response to an incident electromagnetic (EM) wave at a specific frequency, from which the effective $\mu$ and $\varepsilon$ parameters for the rings are generated \cite{2,6}. The dimensions of the SRR, typically 10\% of the incident wavelength, determine the specific resonance of the meta-atoms and the overall metamaterial. The resonant frequency ($\omega_{\text{res}}$) is determined from the capacitance ($C$) and inductance ($L$) of the meta-atom based on the SRR structural dimensions and metal structure. For comparison, capacitance depends on the overlap area and dielectric materials between metal surfaces. Inductance depends on the metal dimensions with length being the main parameter for split-ring resonators along with the material permeability. When using capacitance as a shifting parameter, an advantage is the constant surface area associated with the parallel plate capacitor. A disadvantage is the high voltage required to shift the capacitance with electrostatic actuation of MEMS varactors \cite{7}. When using inductance, an advantage we observe is the improved null depth at the resonant frequency. A disadvantage for using inductance to shift the resonant frequency is the amount of surface area that is required to vary the inductance. Varying the length of SRRs

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is a novel method to shift the resonant frequency and provides an advantage to make the resonant frequency shift based on inductance. Many research efforts focus on the SRR to create metamaterials for applications at RF. Marques et al. provides ideas on various metamaterial designs [8]. Gil et al. demonstrated metamaterial transmission lines using subwavelength resonators imbedded in metamaterial transmission lines described in [9].

The Baseline SRR design is static with a fixed resonant frequency; therefore tunable methods are required to broaden the functions of metamaterial. Most research has focused on the changing capacitance for tuning purposes [10]. Tunable designs have successfully shown that altering the capacitance with varactors [11,12] or adding additional splits in the resonator [13] can shift the resonance in a smooth fashion. Also, incorporating microelectromechanical systems (MEMS) cantilever arrays has been shown to create frequency tuning by varying SRR capacitance [10].

There are only a few reports on changing the inductance to shift SRR resonant frequency [14,15]. In these papers, the s-shaped designs are modified to change inductance for tunable metamaterials, dual-band switches and s-shaped antennas. In this research, three designs are modeled, simulated, fabricated, and tested to determine the effects of inductance on meta-atom designs. Our approach is to identify a design that changes inductance while minimizing capacitance changes. To accomplish this, the Baseline SRR design is modified with loops on the vertical sides. Once promising designs have been identified with this static approach, future work will explore means for adaptively modifying the structure.

Theory

The SRR consisting of symmetrical rings is the basis for our current loop design. It is a resonant $LC$ circuit that is shown to produce effective permeability and permittivity on propagating electromagnetic waves [8]. The design is based on circular double split ring resonators designed, modeled and fabricated by Marqués et al. However, our design and modeling deviates from Marqués et al. modeling based on two different characteristics [16]. First, our design is a rectangular double split ring resonator design, not a circular design. By using the rectangular design, we are able to divide the split ring resonators into sections and calculate capacitance for each section which differs from Marqués et al. modeling which uses the radius of the gap between the inner and outer split ring resonators. Also, the rectangular design provides the design freedom to change the design to increase the self-induction with small deviations to the total capacitance, a novel approach to shift the resonant frequency. And second, parallel traces are added to the sides of the double split ring resonators to create a low frequency plasma that effects the relative permittivity [17]. The combination of the rings and traces create a resonant frequency based on the component dimensions and metal structure.

In this work, three designs were investigated to determine the effect of increased inductance on the SRRs resonant frequency response. The relationship the inductance has on the resonance is approximated by

$$\omega_{res} \cong \frac{1}{\sqrt{LC}}$$  \hspace{1cm} (1)

where, $L$ and $C$ are the inductance and capacitance, respectively. From Equation (1), the resonant frequency shifts toward lower frequencies as the inductance increases.

For the Baseline design, the resonant frequency equation can be expressed, where the inductance is self inductance of the outer and inner split ring resonator ($L_{Outer}, L_{Inner}$). Capacitance is determined by the capacitance at the gaps in the split ring resonators ($C_{Section_B}, C_{Section_C}$) along with the horizontal sides of the adjacent split ring resonator which is based on the series combination of the structure. Additional capacitance is generated from the vertical sides of the split ring resonator ($C_{LeftSide}, C_{RightSide}$) and capacitance due to the traces ($C_{Traces}$). Figure 1 shows the baseline design divided into the four sections around the split ring resonators used to determine the capacitance. Figure 1 (b) shows the series resonant $LC$ band stop filter circuit model tailored to represent the response of the meta-atom. This model provides a response equivalent to the meta-atoms that are experimentally tested within our RF strip-line measurement setup. Furthermore, this circuit model relates the resonant frequency analytical model ($\omega_{res}$) which defines the resonant frequency location to our design.

$$\omega_{res} = \frac{1}{\sqrt{\frac{1}{L_{Outer}} + \frac{1}{L_{Inner}} \left( C_{Section_B} + C_{Section_C} + C_{LeftSide} + C_{RightSide} + C_{Traces} \right)}}$$  \hspace{1cm} (2)
To minimize the change in capacitance, the design must reduce the amount of capacitance shift while increasing the amount of inductance. The resonant equation is based on [8] and [17], but is modified based on parameter values obtained from analytical modeling and CoventorWare® Finite Element Method (FEM) simulations. The simulation computes capacitance values on each element based on the interaction with other elements. In [17] and [18], the analytic model uses capacitance of the split ring resonator gap and capacitance between the split ring resonators. Using our model, the rectangular split ring resonator is divided into sections to calculate the capacitance values.

\[ L = \frac{\psi_{ij}}{I_j} \quad \text{for} \quad I_k = 0 \quad \text{if} \quad k \neq j \]  

(3)

where \( \psi_{ij} \) represents the magnetic flux in the loop due to a current \( I_j \) in the loop \( j \) [19]. From this definition, the self-inductance of any wire, loop, or filament can be described using the dimensions of the structure and the induced current.

In [19], Ruehli provides a derivation of partial self-induction per length which leads to a simplified equation for infinitely thin conductors

\[ \frac{L_{m}}{l} = \frac{\mu}{6\pi} \left\{ 3 \ln \left[ u + \left( u^2 + 1 \right)^{1/2} \right] + u^2 + u^{-1} + 3u \ln \left[ \frac{1}{u} + \left( \frac{1}{u^2} + 1 \right)^{1/2} \right] - \left[ u^2 + \left( \frac{1}{u} \right)^2 \right]^{3/2} \right\} \]  

(4)

where \( \mu \) is the permeability and \( u \) is defined as the ratio of the \( l \) to the \( w \). For this simplified equation, the ratio of the thickness to the width of the conductor is considered less than 0.01. From this derivation, the calculation of the partial self-inductance for complex traces or circuits can be solved analytically using Equation (4). Based on this analytic equation, solvers have been developed to determine inductance of structures. CoventorWare® determines the inductance of the three designs using an integral equation approach combined with a multipole-accelerated solution algorithm [20]. Additionally, a FEM simulation is used to evaluate complex design layouts, prior to fabrication, by showing how SRR modifications affect the overall capacitance of the meta-atom structure.

**Design**

Figure 1 shows the Baseline design that consists of a meta-atom with inner and outer rings along with two parallel traces. The inner ring has a length of 6.0 mm for each side and a capacitive gap of 1.2 mm. The outer ring has a length of 9.6 mm for each vertical side. The outer ring’s horizontal sides are 8.8 mm with a capacitive gap of 1.2 mm. The width of the rings at the capacitive gap is 1.66 mm, while the other sides of the rings have a width of 0.8 mm. The gap between the inner and outer ring is 0.6 mm. The traces adjacent to the rings are 12 mm long and have a width of 0.20 mm. The traces are spaced 0.20 mm from the outer ring. From the baseline design, structural modifications are made to increase the amount of inductance with minimal changes in the structure’s capacitance.

To modify the design with minimum capacitance change, the capacitive area of each element must have minor changes. The separation gap between elements has to remain a fixed distance. To accomplish the modification, the outer ring is modified with a 0.15 mm gap in the middle of the vertical sides. Loops are added to the outer ring design which increased the overall length of the outer ring. The increased length produces a change in the inductance based on the increased path for current flow. From the baseline design, two modi-
Modifications are implemented with each design increasing the length of the loop which in turn increases inductance of the outer ring. Figure 2 shows the two designs used to demonstrate changes in resonant frequency as a function of the increasing length for the outer SRR.

![Fig. 2 Baseline, Loop A and Loop B Meta-atom designs, (a) prototypes on printed circuit board and (b) designs made by microelectronic fabrication techniques on quartz substrates.](image)

On all the designs, the separation between adjacent meta-atom is 2.4 mm. Within the RF strip-line, the meta-atom arrays are kept apart by a 10 mm distance to form a two dimensional array above and below the center conductor. The 0.15 mm gap in the vertical sides of the outer ring is maintained on all modifications to connect the loops of the various designs. After completing the three designs, a computer simulation of each design is accomplished using CoventorWare® to determine the self-inductance and capacitance of each ring and trace.

**Fabrication**

Two sets of the three designs were fabricated; one set was prototyped on FR4 printed circuit board (PCB) with single sided copper and the second set was fabricated using microelectronic techniques on a quartz substrate. Figure 3 shows how the Loop B design appears when inserted into the RF strip-line. As the wave propagates down the RF strip-line, the meta-atoms affect the applied electric field (E) and magnetic field (H) when placed above and below the center conductor. In this configuration, the applied fields emulate a plane wave illumination of a larger metamaterial array.

![Fig. 3 Meta-atoms inserted in the RF strip-line between the center and outer conductor. The signals propagating down the strip-line generate planar electric and magnetic wave from the center to the outer conductor.](image)

The prototype designs, on the FR4 PCB, were completed using a T-Tech Inc. Quick Circuit 5000 milling system. From the PCB prototype devices, the fabrication transitioned to microelectronic fabrication where the meta-atoms were fabricated on semiconductor substrates (76 mm quartz substrates). The reason for using microelectronic fabrication is to broaden the available fabrication options. Microelectronic fabrication allows several design of experiments based on various metals, dielectrics and substrates. The fabrication process used to create these structures consisted of evaporating titanium (Ti) adhesion layer and gold (Au) seed layer. A photolithography process was used to define the SRR and the traces. The SRRs and traces were electroplated with gold onto the seed layer to define the final structures. The extra titanium and gold evaporated layers were then removed leaving only the SRRs and traces on the quartz substrate. Figure 2 shows the completed samples made on the FR4 PCB and on the quartz substrates. The FR4 PCB samples have rough edges, resulting from the milling process; while the samples fabricated using the microelectronic techniques have much smaller minimum feature sizes and greater resolution. The rough edges and minimum feature sizes have the effect of reducing the magnitude of the resonant null and location of the resonant frequency.

**Simulations**

Simulations of the three designs are performed in CoventorWare®. This simulation package provides its own unique approach to solve for capacitance and inductance parameters. The CoventorWare® package was used to simulate the designs and determine the capacitance and induction of each design based on FEM and integral equation approach, respectively. The simulations are completed on a single meta-atom using periodic boundary conditions to obtain the design’s effective parameters.

The three designs are meshed to perform finite element modeling and boundary element modeling on the 3D designs to obtain the capacitance values. The static designs are simulated in frequency range from 1 MHz to 10 GHz to determine the capacitance and inductance of the design across a broad spectrum. To obtain inductance values, the simulated designs are biased with one volt across the gaps of the inner and outer rings. The one volt bias stimulates a current flow through the rings similar to an induced current on the rings at the SRR capacitive gaps. Figure 4 shows the imaginary current...
density of each design simulated with CoventorWare® used to solve for capacitance and inductance. As shown in the Fig. 4, the magnitude of the imaginary current density increases relative to the increase in inductance.

The metal SRR structures are constructed with copper (FR4 PCB prototypes) or gold (microelectronic fabrication) to eliminate any unwanted inductance shifts as a function of the metal or frequency. The range of operation is well below the plasma frequency of copper or gold where metals lose their complex refractive index form and become transparent.

![Image](image.png)

Fig. 4 CoventorWare® plots showing magnitude of imaginary current density incident on the (a) Baseline, (b) Loop A and (c) Loop B versions of the meta-atom designs.

The CoventorWare® simulations show a large inductance change can be achieved with minimal capacitance change. Table 1 lists the inductance and capacitance values obtained from the modeling and simulations. All designs show a shift in the resonance towards a lower frequency.

| Table 1 | Inductance and capacitance values obtained during modeling and simulations |
|---------|---------------------------------|
| Design  | Baseline | Loop A | Loop B |
| Outer Ring Inductance (nH) | 26.19 | 31.73 | 46.94 |
| Inner Ring Inductance (nH) | 13.87 | 13.87 | 13.87 |
| C_{Section B} (pF) | 0.04 | 0.04 | 0.04 |
| C_{Section C} (pF) | 0.037 | 0.037 | 0.037 |
| C_{Left Side} (pF) | 0.128 | 0.15 | 0.153 |
| C_{Right Side} (pF) | 0.128 | 0.15 | 0.153 |
| C_{Traces} (pF) | 0.053 | 0.106 | 0.106 |
| Resonant Frequency (GHz) | 2.70 | 2.33 | 2.20 |

Test Results

Two samples of the 1 x 4 array of each SRR meta-atom design (Baseline, Loop A, Loop B) were tested between the inner and outer conductor using an RF strip-line test fixture. The meta-atom arrays are inserted into a 4 GHz strip-line oriented normal to the transverse electromagnetic mode for RF testing (i.e., parallel to the propagation vector). An Agilent Technologies E8362B programmable network analyzer was then used to measure S-parameters within the 1.5-3.5 GHz spectrum incident on the meta-atom arrays.

![Image](image.png)

Fig. 5 (a) Data collected on meta-atoms fabricated on FR4 printed circuit board. (b) Data collected on meta-atoms fabricated on quartz substrates. The samples are measured in a 4 GHz strip-line to obtain the small signal S-parameters.

The resonance frequency shifted based on the different designs as expected, matching the simulation results for the Baseline, Loop A, and Loop B designs. The resonant frequency for the Baseline, Loop A and Loop B designs fabricated on printed circuit board (FR4 PCB) are 2.68, 2.37 and 2.18 GHz, respectively. The designs fabricated on quartz wafers showed resonant responses at 2.78, 2.45, and 2.24 GHz, respectively. The difference is attributed to the dielectric constants of the two substrates and the level of resolution for the two fabrication methods. The resonant frequency of each fabrication process design is shown in Fig. 5. The experimental data collection is close to the simulation results shown in Table 1. Figure 5 (a) shows the data collected from two arrays of FR4 PCB meta-atoms spaced...
10 mm apart which form a 2D structure. Figure 5 (b) shows the data collected from two arrays of quartz substrate meta-atoms spaced 10 mm apart also forming a 2D structure. Increasing the loop size causes the resonance to shift to a lower frequency with the greatest shift occurring on the Loop B design which the loop equals the vertical side of the outer SRR ring as shown in Fig. 2. Adding more meta-atom arrays and increasing the size of the 2D structure in the RF stripline increases the magnitude of the resonant frequency null.

The simulation and experimental testing results are similar to those published by other authors with comparable meta-atom designs at RF size structures. For example, Pendry et al. show results on the circular split-ring resonator at 8.5 GHz [3]. Smith et al., who followed up with Pendry’s work on split-ring-resonators, experimentally demonstrates the resonant frequencies at 8.5-9.0 GHz [2] and 4.8 GHz [4]. And as a follow-up to the modeling and simulation based on research conducted by Marques et al. we include a comparison to the resonant frequency response described in their papers where they experimentally demonstrate a resonant frequency at 5.45 GHz [8]. The main difference is our designs focuses on using inductance as the attributable factor to shift the resonant frequency response for the meta-atoms.

Conclusion

A Baseline SRR design was modified to increase the overall design inductance and minimize capacitance changes. For the FR4 PCB prototype samples, the Loop A, and Loop B designs changed the initial resonant frequency from 2.68 to 2.37 and 2.18 GHz, respectively resulting in a 0.31, and 0.5 GHz change in resonance, respectively. For the quartz samples, the Loop A, and Loop B designs changed the initial resonant frequency from 2.78 to 2.45 and 2.24 GHz, respectively resulting in a 0.33, and 0.53 GHz change in resonance, respectively. Overall, the theory and simulations of the Loop A and Loop B designs matched the experimental results and varying inductance was shown to be a viable method of varying SRR resonance frequencies.

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Cavity Control of Prefoldin Nano Actuator (PNA) by Temperature and pH

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Abstract: A molecular dynamics study to investigate the cavity control of Prefoldin based bio nano actuator is presented in this paper. Prefoldin is a molecular chaperone with a jellyfish-like structure containing six long coiled-coil tentacles and a large central cavity. We took the temperature and pH of the medium into account, and analyzed the conformational flexibility of the Prefoldin nano actuator in details. Results show that the prefoldin is a very flexible protein, the conformational state of which appears to depend on the temperature and pH values of the medium. In fact, combining these two control parameters, a suitable environment is provided to capture nano cargoes with specific dimensions. These properties of Prefoldin actuator can be used for drug delivery in the body.

Keywords: Prefoldin Nano Actuator (PNA); Cavity control; Molecular Dynamics; GROMACS

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Introduction

Recent advances in the field of nanotechnology have enabled widespread opportunities to investigate and manipulate matter on the nanoscale [1]. The research in nanotechnology, combined with important discoveries in molecular biology, has created a new interest in biomolecular machines and robots [2]. In the field of robotics, new initiatives have been proposed to develop nano-scale actuators, joints, motors, and other machine components. These devices will one day be assembled into functional nanorobots [3]. These devices will have intrinsic mobilities that result in their geometry change and hence enable them to perform specific functions [4].

Just as conventional macro-machines are used to develop forces and motions to accomplish specific tasks, bio-nanomachines can be used to manipulate nano-objects, to assemble and fabricate other machines or products and to perform maintenance, repair and inspection operations [5].

In this way proteins and DNA could act as motors, mechanical joints, transmission elements, or sensors. If all these different components were assembled together they could potentially form nano devices with multiple degrees of freedom, able to apply forces and manipulate objects in the nano scale world, transfer information from the nano to the macro scale world and even travel in a nano scale environment [6].

The most familiar motor is the protein myosin or dynein which moves along filaments, formed through the protein actin, to drive the contraction of muscles. In addition, there are compliance devices such as spring-like proteins called fibronectin, as well as synthetic contractile plant polymers which can act as compliant joints in molecule-size robotic systems [7].

We presented the development of Prefoldin nano actuator (PNA) and their integration in bio nano robotic systems [8]. PNA can be used to manipulate nano-objects.

Prefoldin is a molecular chaperone that is found
in the eukaryotic cytosol and also in archaea [9-10]. Prefoldin captures a protein-folding intermediate and transfers it to a group II chaperonin for correct folding [11]. In fact, the Prefoldin acts as a transporter molecule that transports bound unfolded target proteins to the chaperonin molecule [12].

Unlike many other molecular chaperones, Prefoldin does not use chemical energy, in the form of Adenosine triphosphate (ATP), to promote protein folding in all cells [13]. Recognition mechanism in archaeal Prefoldin is nonspecific, in eukarya however, Prefoldin has acquired a more specific function [14].

In this manner, Prefoldin performs two mechanical works, 1) capture and 2) transfer, and does not need chemical energy. Unlike eukarya Prefoldin, archaeal Prefoldin is nonspecific. This interesting properties cause, we use archaeal Prefoldin to create a novel nano actuator that can be used for nanoscale manipulation [15-17].

Here, we analyze the conformational flexibility of the PNA in detail, and take the temperature and pH of the medium into account. The results provide valuable information on the flexibility of the PNA when compared to the original structure. Temperature and pH are two control parameters to control of cavity of PNA. In this paper, effects of these parameter on PNA are presented.

Archaean prefoldin structure

Crystal structure of Prefoldin has shown that Prefoldin has the appearance of a jellyfish with six long coiled coils protruding from it and a large central cavity [18] (Fig. 1). Biochemical and structural studies indicate that these tentacles bind to substrate proteins in a concerted manner and can move outward for efficient interaction with substrate proteins [19, 20]. Each subunit has a hydrophobic groove at the distal region where an unfolded substrate protein is bound. Each tentacle belongs to one of the six Prefoldin subunits, arranged as two subunits (151 amino acids) located in the center of the structure and four of the homologous subunits (117 amino acids) placed at the periphery [21].

Each coiled-coil tentacle is fully solvated. Its polar and charged side chains are almost exposed to the solvent. On the other hand, hydrophobic residues form a hydrophobic groove between the two α-helical regions in the same subunit. These hydrophobic grooves in the cavity are likely to be responsible for the interaction with the hydrophobic surface of an unfolded protein [18].

Molecular Dynamics Simulation of PNA

In this paper, we investigate the effect of temperature and pH on PNA by molecular dynamics. A variety of simulations were prepared to understand the working of the nano actuator under different temperatures and pH.

All MD simulations were performed with the GROMACS 3.3.3 package in which the equations of motion are solved using a leap-frog integration.

The computational model for MD simulations of the nano actuator was generated starting with the crystal structure of the Prefoldin protein obtained from its PDB file [22]. We used the PDB entry 2ZDI, as source for initial state of the nano actuator. To prepare the initial Prefoldin, the DeepView and Pymol software are used.

For all MD simulations, the water cubic box with periodic binding conditions and minimum distance of 1 nm between the solute and the box and with the Tip3p model for water molecules utilizing force field OPLS-AA/L were used. The starting system consists of a simulation box containing one Prefoldin and 38,000-50,000 water molecules. Energy minimization was performed with steepest descent to release conflicting contacts among residues. The system was equilibrated by 100 ps of MD runs with position restraints on the protein to allow relaxation of the solvent molecules. During the MD simulation, the LINCS algorithm was used to constrain all bonds. A time step of 2 fs was used. The electrostatic interactions were calculated using the particle-mesh Ewald method with a 0.9 nm cutoff. The temperature was kept constant by coupling solute and solvent separately to a thermal bath with a coupling constant dT= 0.1 ps.

Temperature effect on PNA

To investigate the temperature effect on PNA, MD simulation was performed by increasing the temperature gradually from 100 to 330 K to avoid destabilizing the simulated structure. In the Table 1, temperatures and simulation times are presented. Preliminary molec-
Table 1 Temperatures and simulation times of PNA

| Temperature (K) | 100  | 150  | 200  | 250  | 273  | 280  | 290  | 300  | 303  | 306  | 308  | 310  |
|----------------|------|------|------|------|------|------|------|------|------|------|------|------|
| Simulation Time (ps) | 75   | 75   | 75   | 75   | 200  | 500  | 500  | 500  | 200  | 300  | 300  | 300  |

| Temperature (K) | 312  | 314  | 316  | 318  | 320  | 322  | 324  | 326  | 328  | 330  |
|----------------|------|------|------|------|------|------|------|------|------|------|
| Simulation Time (ps) | 300  | 300  | 300  | 300  | 300  | 300  | 300  | 300  | 300  | 300  |

molecular dynamics results indicated that by varying the temperature, the conformation of PNA is changed. Structures of PNA at different temperatures are shown in Fig. 2. As it is expected, at low temperature the variations of PNA are very small. But the positions of the arms (tentacles) have drastically changed at high temperatures. The Pymol software package was used as the visualization software for analyzing trajectories generated by GROMACS.

![Image](image1.png)

Fig. 2 Conformational changes of nano actuator at various temperatures. Green is lower temperature.

It has been shown that, overall structure of Prefoldin is conserved for all temperatures and shape and size of central cavity has only changed. It is very important in practical applications, such as bio nano robotic systems. The resulting conformational change is due to interaction of Prefoldin subunits with each other as well as with solvent.

Comparison of Prefoldin at different temperatures shows the intense changes of coiled coils. This means that the PNA has dexterity. To capture the nano object by nano actuator, this parameter can be very useful.

**pH effect on PNA**

A major goal of the present study is the investigation of the pH-dependent conformational changes in the nano object-binding site of the PNA.

We have carried out MD simulations of the PNA at two different protonation states. These protonation states were correlated with the pH of the system; the starting model for this was the Prefoldin protein at neutral pH at different temperatures.

Of the 20 amino acid residues, Histidine, Glutamic acid, and Asparatic acid are protonated at pH range 3–7.4 (acidic pH) depend on their pKa. Prefoldin has Glutamic acid and Asparatic acid, but it has not Histidine. Glutamic and Asparatic acids are initially

![Image](image2.png)

Fig. 3 pKa of special residues determined by PROPKA server.
negatively charged at neutral pH (≈7.4) and become neutral at lower pH due to the addition of a proton.

At high pH or basic pH (pH range 7.4–13), Lysine and Arginine are unprotonated depend on their pKa. Lysine and Arginine are initially positively charged at neutral pH (≈7.4) and become neutral at higher pH due to the deduction of a proton.

The protonation states of the Prefoldin residues: Asp, Glu, Lys and Arg for the Molecular Dynamics studies were determined in the PROPKA server [23] employing empiric parameters to calculate the pKa of these residues in different environments (Fig. 3).

Fig. 3 shows, All Glutamic acid and Asparatic acid residues are protonated at pH≈3 and all Lysine and Arginine residues are unporotonated at pH≈13. Thus, by the introduction of different Ionizable residues along the peptide chain and varying the pH of the solvent different PNA architectures can be obtained.

To represent a typical biological environment which is electrically neutral, salt (NaCl, 100 mM) was added by placing ions in water to make the system neutral.

In this way, to investigate the pH effect on PNA, 0.5 ns MD simulation was performed. Structures of nano actuator at different pH are shown in Fig. 4.

**Area of cavity of Prefoldin: Effect of control parameters on PNA**

To accurate studying of PNA, we calculate the area of cavity of Prefoldin observed in each of the nano actuator architecture as a function of temperature and pH from the conformational changes result of the MD simulation. The area is measured as the distance between the Cα atoms of end amino acids of arms (Fig. 5). This...
area is a criterion for investigating of cargoes sizes and shapes.

Figure 6(a) and 6(b) show the effect of temperature on this area and change mode of areas, respectively. It is shown that the areas at high temperatures are half of initial area. In fact, as temperature increases, the cavity of PNA becomes closer. This area is also measured for acidic and basic pH (Table 2). These results show, the performance and efficiency of PNA is changed by temperature and pH.

![Graph showing the effect of temperature on area and change mode of areas for PNA.](image)

**Fig. 6** Area of nano actuator at various temperatures.

| pH     | Temperature (K) | Area (nm²) |
|--------|-----------------|------------|
| ~3     | 290             | 23.62      |
| ~7.4   | 300             | 21.77      |
| ~13    | 310             | 22.47      |
|        | 320             | 22.85      |
|        | 330             | 22.92      |

**Table 2** Area of cavity for three different protonation states (Neutral, Acidic and Basic)

The comparison of area of cavity for three different protonation states (Fig. 7) shows, a decrease in pH increases the area of cavity. That is, cavity at acidic pH is more open than neutral pH. At basic pH (high pH), the area of cavity is approximately equal to neutral pH. In other words, increase of pH doesn’t affect the performance of PNA.

![Graph showing the comparison of area of cavity for three different protonation states.](image)

**Fig. 7** Comparison of area of cavity for three different protonation states (Neutral, Acidic and Basic).

**Discussion**

The root-mean-square deviation (RMSD) from the starting structure is an important criterion for the convergence of the system. The RMSDs of the C atoms are shown in Fig. 8, indicating that the whole simulation system appears to have been stable after 300-500 ps of equilibration.

**Flexibility of the PNA arms**

To identify the most flexible parts of the nano actuator, we calculated RMS fluctuations (RMSFs) for individual residues, and compared them with the crystallographic results.

Figure 9 holds the plots of the RMSFs of Prefoldin simulations derived from the MD trajectory at different conditions.

The RMS profiles reveal the most flexible parts of the nano actuator, which are the ends of coiled coil and regions between the α-helical and β-assembly regions. Also, the regions in the middle of α-helical region are flexible.

**The change mode of cavity**

The results show that, increase of temperature causes, distance between β1 and β2' and distance between β2 and β1' are reduced. Distance between β2 and α, and distance between β2' and α', as well as distance between α and α', are approximately constant. Reducing the distance between β1 and α, and distance between β1' and α'a re intense. Although relative distance between β2 and β2' is constant, distance between β1 and β1' is reduced very intense.

These observations show that PNA has a rotational motion during molecular simulations. This result is confirmed by Fig. 6(b). Rotational motion can be very interesting in nano scale systems.
Effect of flexible tentacle on cavity

Any arm of PNA is a coiled coil; therefore Prefoldin consists of six coiled coils which were engineered to obtain an environmentally responsive nano actuator involving the movement of arms towards and away from each other.

One important characteristic observed in this nano actuator is the conserved α-helices of the six coiled coil even in the presence of high temperatures and various pH (Fig. 10). This is due to stabilizing effects of the hydrophobic interactions and hydrogen bonds.

Two elements in flexible arms can change cavity of PNA and adapt it to capture various nano objects (see Fig. 10). The first at the base of each arm serves as a flexible joint and produces large changes. Second ele-
ment is the changes produced in arms themselves, that contains smaller changes and can more accurately adjust nano actuator.

In other words, there are two motions in this nano actuator: large and small motions. The large motions cause to open and close the cavity of nano actuator and the small motions adapt the nano actuator with nano objects accurately. As a result, PNA has several degrees of freedom.

In PNA, it is possible to obtain asymmetric changes, namely if a nano object is non regular, nano actuator is able to adapt itself to capture it.

In fact, this nano actuator has interesting properties. These properties are very useful in bio nano robotic systems, because these various changes empower the nano actuator to capture and transfer the size of different nano objects and nano drugs. A schematic of a PNA, showing the working principle, is presented in Fig. 11.

**Conclusion**

In this study, the dynamics and functions of the PNA is investigated at different temperature and pH with MD simulations. According to the MD trajectories, it is found that PNA is capable of exhibiting largescale conformational changes. Particularly, clear opening–closing motions are observed in Prefoldin simulations. Characterized by their remarkably large flexibilities, it is found that the cavity of PNA can change at different conditions.

In this paper, we focused on the mechanical properties of PNA to change its conformation depending on the temperature and pH of environment. During molecular dynamics simulation, each arm (coiled coil) is highly flexible, enabling it to widen its central cavity and capture various cargoes. Our obtained results show how PNA may well be adapted to interact with many different nano objects. Therefore, PNA has a special structure that it can grasp different cargos.

In fact, combining the two control parameters (temperature and pH), a proper environment is provided to capture nano cargoes with specific dimensions. This renders a set of parameters which can be used to compare different conditions and to select the one with the best possible performance results.

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Micro and Nanotechnology for Intracellular Delivery Therapy Protein

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Abstract: Proteins therapy is of great importance in the treatment of protein deficiency disease. Most human diseases are related to the malfunctioning of one or more proteins. The most effective and direct approach is protein therapy, which delivers the proteins into the target cell to replace the dysfunction protein and maintain the balance of organism. However, clinical application is frequently hampered by various biological barriers to their successful delivery. This review aims to discuss the recent advances about microparticles and nanoparticles fabricated using micro and nanotechnology for intracellular delivery therapy protein and give some suggestions about the promising delivery system.

Keywords: Intracellular delivery; Protein; Nanoparticle

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Introduction

Organisms contain thousands of proteins, which perform a vital role in growth, development, metabolism regulation and disease therapy. These proteins take effect in organism and resist the outside unfavorable factors. Therefore, those specific proteins have shown to be a suitable target for drug research and development (R&D). The Pharmaceutical Research and Manufacturers of America’s (PhRMA) listed 66 protein drugs in 633 new biotechnology medicines relating to more than 100 diseases in 2008, including virus infections, cancer and autoimmune diseases [1]. The drug target for chemical compounds is not currently certain and the non-specific interaction between the compounds and unexpected proteins may cause intense side-effects on patients in clinical trials. Hence, protein therapy is considered as the most effective and direct approach for the dysfunctional protein disease.

Protein drugs gradually become the major in future and thus play a critical role in the process of modern drug design. Although it has a broad application prospect, the protein therapeutic potential and clinical application is frequently hampered by various biological barriers [2].

In contrast to injecting to human body directly, the protein drug must overcome several biological barriers. For example, protein delivery in the bloodstream need avoiding kidney filtration, uptake by phagocytes, aggregation with serum proteins, and degradation by endogenous nucleases [3]. In the bloodstream, phagocytes cells such as monocytes and macrophages remove foreign material from the body to protect against infection by fungi, bacteria and also certain therapeutic protein complexes. Also, it is another challenge that protein drug need get through the bloodstream and the vascular endothelial barriers. Protein drugs can not be allowed the entry the certain tissues including the liver, spleens, and some tumors until they are cleared from the body [4]. Moreover, having been taken up by the target cell, protein drugs must escape from the endosome to cytoplasm immediately in case they may degrade in decreasing pH and various hydrolytic enzymes from lysosome [5]. Finally, protein must be released
from the carrier if formulated with delivery agents.

In order to effective protein therapy, we need an effective delivery system to deliver the protein. And the future delivery system must be safer and can also take account of the barriers in organism. For these reasons above, this review aims to present on-going research on protein drug delivery system and serve to update readers regarding new developments in protein delivery systems while proving suggestions for future advancements.

Drug delivery systems

Single-protein

Although most studies use biocompatible materials to delivery the protein drugs, some researches reported systemic delivery vehicles containing cell-penetrating peptides (CPPs) liked to the target protein for effective transduction. The transactivator of transcription (TAT) was a prototypical example of a cell-penetrating peptide. In 1988, Frankel and Pabo [6] and Green and Lowenstein [7] independently discovered that the transactivator of transcription (TAT) protein separated from the Human Immunodeficiency Virus can penetrate cells and activate the viral genome replication. The protein modified by TAT peptide can enter cells efficiently while non-conjugated proteins were notable in the incubation media rather than in cells [8]. Sun et al (2009) has fused apoptin (a tumor specific killing protein) to the transduction domain named protein transduction domain 4 (PTD4), which is 11-amino acid sequence. It has shown to delivery proteins across the cellular membrane in a very efficient way [9]. The data showed that PTD4-apoptin protein was delivered across cellular membranes and the fused apoptin protein can significantly inhibited tumor growth in vivo [10].

The cell-penetration peptides can also help fusion protein enter into the target cell, mainly due to the specific electrostatic interaction and confirmation. The specific amino acid residues of cell-penetration peptide may interact with the plasma membranes by strongly electric complementation. Substitution of any basic residue of TAT with neutral amino acid may restrain the interaction with membranes, implying the charge of TAT is necessary for cellular uptake [11]. Furthermore, the specific binding receptor on the surface of target cells can also induce membrane deformation for cellular delivery [12].

However, protein native confirmation may change in the process of protein modified and intracorporeal circulation, which may induce the non-specific immunity. So the stability, side effect and nonspecific immunogenicity need to be taken into account for fusion protein therapeutic treatment of human disease.

Microparticles

Generally, microparticles are defined as particles between 1 and 1000 µm. Microparticle vesicles have studies extensively with many different materials and polymers since first designed in the early seventies. These different formulations of microparticles can resist degrading by enzyme and prolong protein’s life in vivo. The following examples present various microparticles designed for protecting the protein drug.

Pol (lactic-co-glycolic acid) (PLGA) can provided sustained delivery of active VGEF (vascular endothelial growth factor) in vivo for more than a month after transplant [13]. One month after treatment an increase in angiogenesis (small caliber caveolin-1 positive vessels) and arteriogenesis (α-SMA-positive vessels) was observed in animals treated with VEGF microparticles, but not in free-VEGF groups. It has demonstrated that the use of microparticles can protect the activity of protein that can be easily and safely deliver to targets. Furthermore, other researchers pay more focus on the sustained-release of microparticles, because sustained-release technology can reduce dosing frequency, maximizing the efficacy and reduce poor patient compliance [14]. Using the 10% PEG with PLGA microparticles (MP), 45% of loading BSA was continuously released during 4 week [15]. Similarly, a new sustained-release amyllopectin microsphere coated with polylyactide-coglycolide can maintain the human growth hormone (hGH) above the baseline for at least 14 days [16]. The data suggest longer-term trials in adults with injection frequencies of no more than once every 2-3 weeks. Moreover, for tissue regeneration therapy, the sustained-release microparticles can precisely regulate the stem cell growth and development. Microparticles, within aggregates of pluripotent stem cell (PSCs), can stably control the spatial differentiation of stem cell [17]. In general, these above strategies of microparticles proved to be of considerable potential values to clinical use.

Unfortunately, although sustained-release microparticles can reduce the dosing frequency and increasing patient compliance, there are very few microparticle delivery formulations approved for clinical use [18]. Several problems such as initial burst release and denaturation of entrapped proteins have prevented the realization of commercially viable products. The microparticles utilize various emulsions in formation processes. Protein may happen to denature after contacting the water/oil interface. So the mostly important issue is that the materials of microparticles need to easily incorporate with protein and maintain the native the confirmation both in preparation and in preserve.

Our lab has invented aqueous-aqueous emulsion formed to encapsulate proteins into dextran microparticles [19-21] and further encapsulated into PLGA mi-
croparticles [21]. Erythropoietin (EPO) is a recombinant protein drug which is used to treat aplastic anemia. But EPO in vivo were likely to aggregate and cause the protein denaturation, which may increase heart problems and even increase mortality in chronic kidney disease patients [22]. But our aqueous-aqueous emulsion can provide friendly environment for protein drug because protein can not contact the hydrophobic interface. The result showed EPO can release from the composite PLGA microspheres with normal biological activity without significant aggregation (<2%). Meanwhile, the near zero-order release without a significant initial burst (<20% at the first day) was achieved using our aqueous-aqueous emulsion.

Looking at the various formulation materials and preparation methods, the design of microparticle DDSs should be considered compatibility with the protein drug as well as the host. To reduce negative side-effects and unwarranted interaction with the host, researchers should also opt for safer materials that can not influence the protein structure, stability and other properties. However, largely-sized microparticles can not be allowed the entry the target cell and also encounter other barriers such as the blood-brain barrier. Thus, nanoparticles might appear to overcome the biological barriers.

Nanoparticles

Nanoparticle(NP) is a rapidly expanding area, including the development of materials in the 5 to 1000 nm size range. The protein is entrapped, encapsulated in the NP depending upon the method of preparation. Owing to submicron in size, NPs are small enough to avoid reticuloendothelial and phagocytic clearance. So they can penetrate deep into tissues through fine capillaries and are easily taken up efficiently by the target cells [23]. Also they can overcome the barriers and have excellent biocompatibility in contrast to larger microparticles.

This review focuses on intracellular delivery of therapeutic agents, so we compare various types of nanoparticles, which have merits and demerits respectively (Table 1). The main reason of demerit is that these formulations do not overcome our biologic barriers totally. The nanoparticles should be designed not only for protein entrapment, but also for good therapeutic effect. So it is extremely necessary to understand more mechanisms of intracellular delivery before designing. Figure 1 shows the steps detailing the endocytosis mechanism. Following their uptake, nanoparticles begin intracellular trafficking. Firstly they are transported to endosomes, which fuse with lysosomes subsequently. After that, nanoparticles release from lysosomes into the cytoplasm, and diffuse to the therapeutic target, such as nucleus and other organelles. In the whole process, the biggest challenge is how nanoparticles escape the endolysomes and enter the cytoplasm. Varkouli reviewed advanced mechanisms of endosomal escape, which included pore formation in the endosomal membrane, pH-buffering effect (the proton sponge effect).

‘Proton- sponge’ is now the most accepted mechanisms [29]. Taking full advantage of the low pH range (pH 4.6-5.0) in endo-lysosomes, many groups focuses on synthetic pH-responsive polymer for protein transduction [30]. Endo-lysosomes are acidified by the ATPase enzymes on the surface that transport protons and counter ions from the cytoplasm into the endolysosomes. The synthetic pH-responsive polymer can combine the protons to prevent acidification, causing the ATPase continuing to transport more protons to reach the desired pH. The accumulations of osmotic pressure by counter ions ultimately trigger swelling and rupture the endosome membrane, while releases the polymer loading protein at the same time [31]. Yan and his colleague report a novel delivery polymer that consists of the neutral monomer (acrylamid) and degradable crosslinker (acid-degradable glycerol dimethacrylate) [32]. The endosomes staining of the cells incubated with rhodamine-B-labelled horseradish peroxidase (HRP) revealed co-localization of the protein with early endosomes, with gradual escaping from endosome to the cytoplasm. Moreover, the released proteins can also execute their own function in cytosol including enhanced green fluorescent protein (EGFP), sueroxide dismutase (SOD) and caspase-3 (CAS).

Table 1 Comparison of various types of therapeutic agents for intracellular delivery

| Therapeutic agent | Advantage | Disadvantage | Reference |
|-------------------|-----------|--------------|-----------|
| Polymeric         | Surface modification provide a wide range of therapeutic agents | Large scale | [22]       |
| Nanoparticle      | Stable over broad range of temperature and pH | Lack of biodegradation, Slow dissolution | [23][24]   |
| Inorganic         | A good biocompatibility | Unstable and low entrapment efficiency | [25][26] |
| Nanoparticle      | Large internal volumes for drug | Debatable toxicity | [27]       |
| Liposome          | Ease of modification and size control | Cytotoxicity, biocompatibility and biodistribution | [28]       |

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Fig. 1 Steps detailing the intracellular delivery of protein drug via nanoparticle carriers. (1) endocytosis of nanoparticles; (2) fusion of endosomes with lysosomes; (3) ‘proton-sponge’ effect; (4) endosomal escape of nanoparticles; (5) degradation of nanoparticle by lysosome; (6) exocytosis of nanoparticles.

Another mechanism of escaping from endo-lysosomes is causing damage and fracture of the endosome membrane. Amphiphilic polymers containing weakly ionizable carboxyl groups and hydrophobic alkyl side chains may respond to acid environment and degrade below their $pK_a$ ranges [33]. The degraded hydrophobic fragment can bind to endosomal membrane because the inner of membrane is hydrophobic fatty acid. Then the additional hydrophobic fragment can interrupt the membrane fluidity, subsequently inducing membrane lysis activity [34]. Liechty et al confirmed the phenylalanine derivatized polymer PP-75 have the ability of endosomal membrane disruption [35,36]. After treatment of Saos-2 cells with MBP-apoptin (a specific tumor killing protein) and PP-75, 30% cells found in the mid-apoptotic state compared with control. This result showed the protein can release successfully from the endo-lysosomes by the destructive hydrophobic polymer [37,38].

Apart from endocytosis, nanoparticles should also meet the various demand of organism in biocompatibility and biodistribution. The barriers should be taken into account seriously for designing a more effective formulation.

Future directions

With the rapid development of molecular biology, more and more are being understood about various proteins and their roles in regulatory networks of human health and disease. Unfortunately, delivery approach remains to be the most significant barrier of widespread use in clinic of protein therapeutics. There is still a lack of good micro- and nano-delivery systems fabricated using micro and nanotechnology for protein available which can overcome all the biological barriers. From discussion above, the on-going research must consider the following: (1) low toxicity of material; (2) nonspecific activation of the immune system; (3) encapsulation efficiency; (4) maintaining the nature confirmation; (5) sustained-release instead of burst release effect; (6) target the diseased tissues or cells; (7) biodegradability; (8) controlled, sustained release of therapeutics. So the future work need focus on develop the safe and effective delivery system to ensure the broadest application of protein therapy in the clinic.

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Development of Inorganic Solar Cells by Nanotechnology

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Abstract: Inorganic solar cells, as durable photovoltaic devices for harvesting electric energy from sun light, have received tremendous attention due to the fear of exhausting the earth’s energy resources and damaging the living environment due to greenhouse gases. Some recent developments in nanotechnology have opened up new avenues for more relevant inorganic solar cells produced by new photovoltaic conversion concepts and effective solar energy harvesting nanostructures. In this review, the multiple exciton generation effect solar cells, hot carrier solar cells, one dimensional material constructed asymmetrical schottky barrier arrays, noble nanoparticle induced plasmonic enhancement, and light trapping nanostructured semiconductor solar cells are highlighted.

Keywords: Inorganic; Solar Cells; Photovoltaic; Nanotechnology

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Introduction

The worldwide demand for energy is causing a dramatic environmental impact on the global climate due to the combustion of fossil fuels. In order to improve the sustainability of our society, photovoltaic solar cells, as a significant device harvesting low-carbon solar energy, have received tremendous attention recently [1,2]. The merits of photovoltaic solar cells are a lot, for example, solar cells provide clean electrical energy by directly converting solar energy into electrical energy without emitting carbon dioxide, besides, the solar energy is not limited, free of charge and distributed uniformly to all human beings. For over the past two decades, all kinds of solar cells have been extensively studied and used for practical terrestrial applications [3-5].

However, high material cost and large amount of energy needed for manufacturing solar cells have made this technology expensive with long energy payback time. This has prevented the PV power generation from rapid commercialization. One important concept to reduce the solar cell cost and to increase the conversion efficiency is to use nanotechnology, i.e., to use the nano-structured materials in solar cell [6-8]. Nanotechnology has achieved rapid development in the area of the specific optical and electrical properties of nanomaterials, assembled functional devices, and so on. Numerous nano-assembly methods can be used to impart a variety of specific optical and electrical properties of nanomaterials in photovoltaic cells [9-12]. Nano-assembly method has many advantages, such as less consumption of materials, using non-vacuum technology and a large area controlled manufacturing.

The aim of this article is to highlight the application of nanostructured materials for inorganic solar energy conversion covering a wide variety of materials. In this

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review, we briefly summarize multiple exciton generation in the semiconductor materials. We emphasize on one dimensional material constructed as asymmetrical schottky barrier arrays, which provides plasmonic light trapping in solar cells. We also highlight the light trapping structure for silicon solar cells.

Multiple exciton generation

Multiple exciton generation (MEG) (Fig. 1), also called carrier multiplication, involves the generation of multiple electron-hole pairs from the absorption of a single photon [13,14]. As early as in 1950s, MEG has been found in the semiconductor bulk materials, known as carrier multiplication effect. However, it is considered less than reasonably useful because of very low efficiency (less than 1%). In 2004, Schaller and Klimov demonstrated for the first time that multiple exciton generation occurred with very high efficiency in semiconductor nanocrystals [15]. Thereby MEG in semiconductor nanostructures has been investigated deeply and extensively. Up to now, MEG has been demonstrated in semiconductor nanostructures (quantum dots) including PbSe, PbS [16], PbTe [17], CdS, CdSe [18], Si [19], InAs [20], and so on. Recently, MEG has also been demonstrated in InP colloidal quantum dots [21]. Beard etc. [19] have confirmed that silicon nanocrystals can exhibit strong MEG in the 0.5-3.5 eV of solar spectral region.

Under normal circumstances, the semiconductor materials can only produce a single exciton after absorbing a photon, and the high excitation energy photon wasted by phonon emission. If a photon can generate multiple excitons, the energy conversion efficiency of nanocrystal based solar cells may be improved significantly. MEG may considerably increase the energy conversion efficiency of nanocrystal based solar cells, though harvesting the energy may be difficult because of the short lifetimes of the multieexcitons [1]. The quantum mechanical origin of MEG is still under debate and several possibilities have been suggested [22]. Among the most credible explanations of the mechanism is considered to be impact ionization.

Currently, the research of MEG in solar cell based on silicon nanostructure has just begun. To our knowledge, in p-i-n solar cell based on QD arrays, the delocalized quantized 3-D miniband states could be expected to slow the carrier cooling and permit the transport and collection of hot carriers at the respective p and n contacts to produce a higher photopotential [1,2]. In the uniform and orderly nano silicon thin films, the electronic coupling in silicon quantum dots can occur very easily, because grain boundary of amorphous silicon is extremely thin (thickness only 2~4 atomic layers).

Solar Energy Research Institute at Shanghai Jiao-tong University not only observed two Gaussian-type photocurrent peaks attributed to transitions from a tail band in the nc-Si:H/ c-Si heterostructure, but also revealed the unique electronic states of the miniband in the nc-Si:H thin film [23]. The results of the investigations of the photocurrent properties of nc-Si:H thin film may help to realize nc-Si:H/c-Si heterostructure-based optoelectronic devices.

Nanostructure-based inorganic solar cells

Hot carrier solar cell

A hot carrier solar cell is a device, which is to slow the rate of photoexcited carrier cooling, caused by phonon interaction in the lattice, to allow time for the carriers to be collected whilst they are still at elevated energies (“hot”), and thus allowing higher voltages to be achieved from the cell [24-27]. The schematic and band diagram of an ideal hot carrier solar cell is shown in Fig. 2.

Unlike a standard cell, which is designed to collect the carriers before the hole and the electron recom-bined, a hot carrier cell has to catch them before the carrier cooling stage. Therefore, carriers either have to traverse the cell very quickly or cooling rates have to be slowed in some way. For the hot carrier cell to be effective, “hot” carriers must be collected from the absorber over a very small energy range. Hence, it is also required that special contacts are used to prevent the
Selective energy contacts
Electron contact  Hot carrier  Hole contact

Fig. 2 Schematic and band diagram of an ideal hot carrier solar cell.

the contacts from cooling the carriers [28]. The limiting efficiency of this approach can reach 86.8% as the same as an infinite tandem cell stack. However, in order to achieve this limiting efficiency, carrier cooling rates should be reduced sufficiently or radiative recombination rates should be sufficiently accelerated, the latter being faster than the former [24].

Despite clear efficiency benefits, no real world device has ever been developed, partly because of the difficulty of a suitable absorber material [29]. Developing a hot carrier absorber material, which exhibits sufficiently slow carrier cooling to maintain a hot carrier population under realistic levels of solar concentration, is a key challenge. A candidate for the absorber material is a Quantum Dot superlattice [30]. InGaAs/GaAsP is proposed as a suitable absorber material and the GaAs surface buffer layer was reduced in thickness to maximize photon absorption in the well region. An enhanced hot carrier effect was observed in the optimized structures [31]. Besides, the hot carrier solar cell with indium nitride (InN) absorber layer, gives a highest efficiency of 37.1%, taking into account the realistic transport properties of energy selective contacts [32]. The efficiency of the hot carrier solar cell, with GaSb-based heterostructures as absorber candidates, is improved significantly compared to a fully thermalized single p-n junction of similar bandgap [33].

SWNTs-based solar cell

The semiconducting single-walled carbon nanotubes (SWNTs) are potentially an attractive material with many unique structural and electrical properties [34-37]. Semiconducting SWNTs bear a wide range of direct bandgaps matching the solar spectrum, and show strong photoabsorption and photoreponse from ultraviolet to infrared, and exhibit high carrier mobility and reduced carrier transport scattering. In addition, like semiconductor NCs, SWNTs exhibit a strong coulomb interaction between electrons and holes, which suggests that SWNTs could also exhibit MEG [38]. They can use the incident photon that other solar cells cannot absorb to generate more electrons. Therefore, Semiconducting SWNTs are nearly ideal materials for PV applications.

In 2008, the research group of Zhang at Shanghai Jiaotong University fabricated SWNT PV solar micro-cells [39], shown in Fig. 3. In this cell, a directed array of monolayer SWNTs was nanowelded onto two asymmetrical metal electrodes with high and low work functions, respectively, resulting in a strong built-in electric field in SWNTs for efficient separation of photogenerated electron–hole pairs. Under solar illumination, the power conversion efficiency can reach 12.6%.

In 2010, a network of SWNTs was directly assembled onto the surface of n-p junction silicon solar cells by Zhang’s group [40], shown in Fig. 4. The SWNTs network not only has high transparency, but also can significantly reduce the electrode resistance of the surface. Therefore, the collection efficiency of the hole was improved, and an enhancement of 3.92% in energy conversion efficiency was typically obtained.

In addition, in 2009 the researchers [41] at Cornell University fabricated photovoltaic cells with CNTs instead of the traditional silicon tube, shown in Fig. 5. The carbon nanotube p-n junction photodiode consist of individual SWNTs in split-gate field-effect geometry. The results clearly confirm that multiple e-h pairs can be generated and collected in a nanotube p-n junction. The e-h pair creation process observed can increase the power conversion efficiency and enhance photocurrent largely.

Cao et al. [42] reported Schottky junction solar cells by coating carbon nanotube films on individual CdSe nanobelts with open-circuit voltages of 0.5 to 0.6 V and modest power-conversion efficiencies (0.45-0.72%). In the planar device structure, the CdSe nanobelt serves as a flat substrate to sustain a network of nanotubes, while the nanotube film forms Shottky junction with the underlying nanobelt at their interface and also makes a
Fig. 3  Structure of the SWNT PV microcells. (a) Schematic diagram of SWNT PV cells. (b) SEM image of SWNT bundle array bridging the Pd and Al electrodes. (c) SEM images of the SWNT bundle ends nanowelded onto the metal electrodes.

Fig. 4  SEM images of SWNT-assembled p-n junction substrate with different densities. (a) 50∼120 tubes µm$^{-2}$, (b) 150∼200 tubes µm$^{-2}$, (c) 300∼400 tubes µm$^{-2}$, (d) Optical transmission of SWNT networks with different density invisible region.

Fig. 5  SWNT p-n junction. (a) p-n junction; (b) Electronic potential energy diagram for the p-n junction with electrons and holes generated at the edges of the junction; (c) I-VSD characteristics for SWNT at various photon energies.
transparent electrode for the device. The nanotube-on-nanobelt solar cells can work either in front (nanotube side) or back (nanobelt side) illumination with stable performance in air.

**Plasmonic nanostructure-based solar cells**

Inspired by optoelectronics, plasmonic nanostructures have recently attracted attention for light trapping in solar cells due to their large resonant scattering cross sections [43]. Metallic nanostructures supporting surface plasmons that excitations of the conduction electrons at the interface between a metal and a dielectric can also achieve light trapping. Metal nanoparticles deposited onto a substrate can increase the coupling of light into a substrate [44, 45]. By proper engineering of these metalloid-electric structures, light can be concentrated and ‘folded’ into a thin semiconductor layer, thereby increasing the absorption. Both localized surface plasmons excited in metal nanoparticles and surface plasmon polaritons (SPPs) propagating at the metal/semiconductor interface are of interest.

Plasmonic structures can offer at least three ways of reducing the physical thickness of the photovoltaic absorber layers while keeping their optical thickness constant [45], shown in Fig. 6.

Light trapping schemes are essential to capture the red and near-infrared portion of the solar spectrum. The metal island films, such as silver-, gold-, copper-island layer, can couple incident light into the waveguide modes of the detector, resulting in increased absorption [46]. Polman et al. [47] studied the light trapping geometries using plasmonic metal nanostructures integrated into coupling of light.

Yu et al. [48] discovered an engineered enhancement of optical absorption and photocurrent in a semiconductor via the excitation of surface plasmon resonances in spherical Au nanoparticles deposited on the semiconductor surface. The surface plasmon resonance wavelength depends on the nanoparticle’s size, shape, and local dielectric environment. Localized surface plasmons on metallic nanoparticles can be surprisingly efficient at coupling light into or out of a silicon waveguide. Catchpole et al. [49] demonstrated a factor of 8 times enhancement in the electroluminescence from a silicon-on-insulator light-emitting diode at 900 nm using silver nanoparticles. Ferry et al. [50] demonstrated that the primary photocurrent enhancement occurs in the spectral range from 550 nm to 800 nm in the ultrathin film a-Si:H solar cell with nanostructured plasmonic back contacts. Derkacs et al. [51] investigated the surface plasmon polariton modes in Au nanoparticles deposited on the amorphous silicon film, and an 8.1% increase in short-circuit current density and an 8.3% increase in energy conversion efficiency are observed.

**Nanostructure-based Thin-film Photovoltaic Cell**

Compared with the traditional monocrystalline silicon solar cell, the important difference of Thin-film Photovoltaic Cell is that the electrode is transparent conductive film instead of conductive metal mesh. The p-type and n-type doping layer, called “dead zone” in Thin-film Silicon Photovoltaic Cell, make no contribution to the photocurrent. In order to increase the conversion efficiency of solar cell, the optical absorption in the doped layer should be reduced as low as possible. Therefore, in addition to reducing the doped layer as low as possible, the wide band gap material is also used as window layer to reduce the optical absorption.

Amorphous silicon solar cell has been especially popular due to its low cost, however, the low photovoltaic conversion efficiency has seriously hampered their wider application. The actual conversion efficiency of amorphous silicon solar modules is only 4.8%-5.0% in industrial production. A series of methods are adopted to improve the conversion efficiency of amorphous silicon solar cell, for example, by using new wide optical band gap and low-resistivity p-type materials as window layer.

![Fig. 6 Plasmonic light-trapping geometries for solar cells.](image-url)
Considering the lattice matching and the impurity diffusion, the amorphous silicon thin-film solar cells use typically silicon thin film as window layer. For example, Haneman et al. [52] employed a-Si:H/SiC layer in p-i-n amorphous silicon solar cells. Kim et al. in Japan [53] adopt p-SiC/graded p-SiC compositional film. Lee and Lim in Korea [54] used a-C:H(B)/a-SiC. Khan et al. in England [55] employed polymeric amorphous carbon as p-type window within amorphous silicon solar cells. Tawada and Hamakawa et al. employed p-type a-SiC:H as window within amorphous silicon thin-film solar cells, the conversion efficiency of single-junction amorphous silicon solar cell achieved significant breakthroughs (7.14%) [56] in 1981, and reached 10.1% [57] in 1987. By 1996, Hamakawa et al. [58] utilized microcrystalline Si(C) as window layer, and the conversion efficiency of 12.5% had been achieved. The p-type μc-SiC:H was used in their work, due to its higher electrical conductivity and higher optical band gap. The role of the carbon is to change and improve the optical band gap of the thin film. The band gap of the thin film carbon can reach as high as 2.8 eV, however, if the content of carbon is too high, the photoconductance will reduce. In μc-Si thin film solar cell, the intrinsic layer is sensitive to the properties of the materials as window layer. If a-SiC: H and a-SiO: H is used directly as window layer, the thick amorphous incubation layer will appear in the intrinsic layer. Huang et al. [59] employed μc-SiC thin film as window layers in n-side illuminated μc-Si:H n-i-p solar cells. High QE current density of 26.7 mA/cm² and conversion efficiency of 9.1% was achieved. It is believed that high conductivity and transmittance of the window layer and the high hole mobility of the intrinsic layer are the key factors affecting the performance of the solar cell. It is reported that the absorption coefficient of c-SiC:H in high-energy section is much less than the absorption coefficient of n-type microcrystalline silicon and amorphous silicon.

The light trapping nanostructured silicon solar cells

The light loss [60,61] of the solar cell comes mainly from the following three aspects: The first is surface reflection; the second is that the incident light is affected by the cover area of the electrode material; the third is that the transmission loss because the thickness of the solar cell is too thin.

In order to maximize absorption of incident sunlight, many optical designs for light trapping have been proposed. For example, 1) To minimize the reflection of the incident light, the most common method is the incorporation of antireflective coatings or surface texturing. 2) To increase the path lengths of the light in the absorbing layer after the light being absorbed. For example, the light without absorption can get a second chance of incidence instead of being lost through increasing the refractive index of the absorbing layer and strengthening the back-reflection. 3) To minimize the cover area of the gate electrode, at the same time, to maximize the photocurrent output.

Most of the solar cells used in the terrestrial applications are bulk-type mono- or multi-crystalline silicon solar cells. The typical cell structure is a thin (less than 1 μm) n-type emitter layer on a thick (about 300 μm) p-type substrate. To achieve full absorption of the solar spectrum, light trapping is required over a broad spectral and angular range. To date, the light trapping method is mainly incorporating antireflective coatings or surface textures. For the antireflective effect, surface texturing is superior to the antireflective coatings, so, surface texture is one of the technologies for enhancing the conversion efficiency of the c-Si solar cells [62]. The most successful optical design for commercial monocrystalline silicon solar cell is probably the anisotropically etched pyramids on single-crystalline silicon (100) surface [63-65]. Sodium hydroxide (NaOH) or potassium hydroxide (KOH) with isopropyl alcohol (IPA) is generally used in industry for the anisotropic etching of monocrystalline silicon. For the large-scale production of polycrystalline silicon cells, antireflective coatings on silicon substrate are only used. The conversion efficiency of polycrystalline silicon cells in laboratory has reached 16.8% or above, however, the technology of surface texturing on polycrystalline silicon has not been applied to the large-scale production. The key point is how to control the interface contact, stability and uniformity of the polycrystalline silicon textured microstructure.

Thin-film structures can reduce the cost of solar cells by using inexpensive substrates and a lower quantity and quality of semiconductor material. However, the resulting short optical path length and minority carrier diffusion length necessitates either a high absorption coefficient or excellent light trapping.

Tao et al. [65] adopted a monolayer of microscale particles to achieve surface texturing. It has been experimentally found that the low reflectance from this coating becomes omnidirectional, and the coating improves the transmittance of a quartz wafer in the spectral range of 400-1100 nm. On this basis, Chen et al. [66] have recently demonstrated that incorporating the microsphere-based textures in the ITO ARC can be used as a novel approach for improving the conversion efficiency of the solar cells. The schematic of the key process steps in the fabrication of the omnidirectional ARC structure is shown in Fig. 7. The conversion efficiency of the solar cell with the ITO+MST structure changes from 7.4% to 13.5% as the incident angle increases from 0° to 60°. This results demonstrate the superior omnidirectional antireflection property of the ITO+MST structure.
Semiconducting nanowire arrays have already been shown to have low reflective losses compared to planar semiconductors. With less reflection and thermalize losses, the light trapping nanowire arrays such as ZnO nanowire arrays (Fig. 8) is an excellent surface layer as the networks. In addition, until now, various technologies for making solar cells from arrays of silicon nanowires [67,68] with radial p-n junctions are used for improving light trapping.

Yang et al. [69] demonstrated that ordered arrays of silicon nanowires (Fig. 9) increased the path length of incident solar radiation by up to a factor of 73. By changing the silicon film thickness and nanowire length, there is a competition between improved absorption and increased surface recombination.

![Fig. 7 Schematic of the key process steps in the omnidirectional ARC structure fabrication.](image)

![Fig. 8 Light trapping nanowire arrays as surface layer.](image)

![Fig. 9 Ordered silicon nanowire array fabrication scheme.](image)
Nanophotonic structures have attracted attention for light trapping in solar cells with the potential to manage and direct light absorption on the nanoscale. While both randomly textured and nanophotonic structures have been investigated, the relationship between photocurrent and the spatial correlations of random or designed surfaces has been unclear. Light-trapping nanostructures allow for nanoscale control of the direction and absorption of light in ultrathin film solar cells.

Numerous methods have been developed to fabricate Si NW arrays, among which metal assisted wet chemical etching of Si substrates is a promising method in combination with nanosphere lithography to synthesize large areas of ordered Si NWs. Fabrication of porous Si by metal assisted chemical etching was first proposed by Li and Bohn [70] in 2000. Mikhael et al. [71] produced Silicon nanowires (SiNWs) by nanosphere lithography and metal assisted chemical etching (Fig. 10). Chim et al. [72] have developed a simple and low-cost method to fabricate high-density and well-aligned Si NWs through metal-assisted chemical etching using metal nanodots as a hard mask (Fig. 11).

![Fig. 10 Schematic diagram showing the overall process to produce Si NW arrays by Au chemical etching combined with nanosphere lithography.](image)

The theory predicts that periodic photonic nanostructures should outperform their random counterparts in trapping light in solar cells. A direct comparison with a cell deposited on the random pyramidal morphology of state-of-the-art zinc oxide electrodes, replicated onto glass using nanoimprint lithography, demonstrates unambiguously that periodic structures rival random textures [73].

**Conclusion**

In this review, we made a brief introduction of multiple exciton generation, and discussed the recent advances on inorganic solar cells by nanotechnology. The inorganic solar cells have achieved exciting development due to the fact that nanomaterials have unique optical and electrical properties. However, the most important challenge regarding nanostructure-based inorganic solar cells is how to enhance the conversion efficiency to achieving the goal of scalable applications and promising market foreground, and there are still difficulties in the development of nanostructure-based inorganic solar cells, particularly on how to take the full advantage of the unique electrical and optical properties of the nanomaterials. Nevertheless, various problems that commonly occur in solar cells might be partially solved in the near future with advances in nanotechnology.
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