

SiO₂/PE/Bi₂S₃ 核壳结构纳米颗粒的合成与性能

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摘要: 以多层电解质作为微型反应器,制备了 SiO₂/Polyelectrolyte(PE)/Bi₂S₃ 核壳纳米粒子。XRD 结果表明 Bi₂S₃ 颗粒属于正交晶系。由透射电镜和场发射扫描电镜照片可知,在直径为 640 nm 左右的 SiO₂ 表面覆盖了厚度 35 nm 的 Bi₂S₃ 壳层。红外光谱分析结果表明硅烷网络在结构上发生了变化(SiO₂ 表面的硅烷醇键沉积在 Bi₂S₃ 的表面)。SiO₂ 核和 SiO₂/PE/Bi₂S₃ 的紫外-可见吸收光谱显示在 900 nm 存在典型吸收边。

关键词: 纳米粒子; 核壳结构; 聚电解质; 微型反应器

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SiO₂/Polyelectrolyte(PE)/Bi₂S₃ Core-shell Nanoparticles: Synthesis and Properties

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Abstract: SiO₂/Polyelectrolyte(PE)/Bi₂S₃ composite nanoparticles were prepared by a polyelectrolyte(PE) multilayer as microreactor. Bi₂S₃ particles were shown by XRD to be with an orthorhombic uniform structure. The surfaces of SiO₂ (about 640 nm) particles were covered by thin layers (35 nm) of Bi₂S₃ consisted of 32 nm particles as evidenced by TEM and field emission scanning electron microscopic studies. The structural changes occurred in the siloxane network and surface silanol groups of SiO₂ upon the deposition of Bi₂S₃. The UV-Visible spectra of SiO₂ core and SiO₂/PE/Bi₂S₃ show typical absorption band onset (900 nm).

Key words: nanoparticles; core-shell structure; polyelectrolyte; microreactor

0 Introduction

Semiconductor nanoparticles have been the subject of intense research during the past few years because of their potential applications in solar energy conversion, photocatalysis and the optoelectronic industry^[1-5]. Many synthetic routes have been developed so far to control the size and distribution of semiconductor nanoparticles. One of the most advanced and intriguing developments in the area of nanoparticles is the coating of semiconductor nanoparticles on a solid support to synthesize core/shell nanocomposites with

unique optical, electronic, magnetic and catalytic properties. Although the technique for coating the nanoparticles on rather large substrates is well established, coating on very small substrates, such as sub-micron-sized particles, remains a technical challenge. The coating of semiconductor nanoparticles on sub-micro-sized particles has been accomplished by using distinct chemical methods, including epitaxial growth of semiconducting phase^[4], nucleation and growth inside inverse micelles^[5], reaction of molecular precursors^[6], ultrasonic irradiation of colloidal solutions^[7] and electroless deposition^[8]. Other methods are also used for

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the preparation of a wide range of core-shell structure with controlled chemical compositions and well-defined morphological characteristics.

Nanocomposite multilayers can also be assembled on particle surface by using the layer-by-layer method based on colloidal templates. Eswarnand and Pradeep have reported a method of synthesis for zirconia coated silver clusters using self-assembled monolayers as templates^[9]. Keller and Johnson et al. have prepared alternating composite multilayers of exfoliated zirconium phosphate sheets and charged redox polymers on (3-aminopropyl) triethoxysilane-modified silica particles^[10]. Olinda and co-workers have synthesized SiO_2 / Bi_2S_3 nanocomposites using single-molecule precursors^[11]. Sonochemistry is also an alternative technique for the production of coated particles. Dhas and co-workers have reported the synthesis of ZnS semiconductor nanoparticles on submicron-sized silica by ultrasound irradiation near room temperature^[7]. Recently, Christina and Alfons have reported a new approach for the synthesis of colloidal gold shell particles with a dielectric core, small gold nanoclusters being attached to the functionalized surface of colloidal silica particles^[12]. In the past, efforts had been made to bind semiconductor nanoclusters to metal or inorganic surfaces using a self-assembled monolayer approach. Pastoriza-Santos and Koktysh et al. have synthesized Ag/ TiO_2 core-shell nanoparticles with the layer-by-layer assembly method^[13].

Recently, polyelectrolyte multiplayer shells have intrigued widespread interest as novel types of carriers and microreactors with designed properties because they exhibit controllable permeability and surface functionality^[14-16]. They have many applications in drug delivery, food and cosmetic industries or biotechnology. Shchukin and co-workers have recently synthesized smart inorganic/organic nanocomposite hollow microcapsules^[17]. In this paper we report the surface synthesis of Bi_2S_3 semiconductor nanoparticles on submicron-sized SiO_2 by the polyelectrolyte microreactor on the surface of SiO_2 colloids.

1 Experimental

1.1 Materials

Bismuth chloride, tetraethoxysilane (TEOS), ammonium hydroxide, thioacetamide (TAA), and ethanol

were purchased from Shanghai Chemical Reagent Company and used without further purification. Poly (doallyldimethylammonium chloride) (PDA), $M_w=200\,000\sim370\,000$, Poly (sodium 4-styrenesulfonate) (PSS), $M_w=70\,000$, purchased from Aldrich. Doubly distilled water was used for the process.

Monodispersed silica spheres were prepared according to the procedure by Stöber et al.^[19], i.e., hydrolysis of TEOS in an ethanol solution containing water and ammonia. In a typical experiment, 2.00 g of the TEOS was added to 15 mL of absolute ethanol containing 0.16 g of distilled water, and the mixture was allowed to stand for 30 minutes. Then 5 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$ solution (25%) was added, and the mixture was left to stand for 30 minutes. The SiO_2 colloid formed was centrifuged and washed thoroughly with water and ethanol.

The synthesized SiO_2 suspension (2 mL) was mixed with a solution of citric acid (20 mL, 0.001 mol). Then an aqueous solution of PDA (1 mL, $1\text{ mg}\cdot\text{mL}^{-1}$) was added under stirring, to form a water-insoluble PDA/citrate complex on the surface of SiO_2 particles. The deposition of the first PDA/citrate layer was followed by layer-by-layer assembly of polyelectrolyte PDA/PSS multiplayer using PDA (10 mL, $1\text{ mg}\cdot\text{mL}^{-1}$) and PSS (10 mL, $1\text{ mg}\cdot\text{mL}^{-1}$) solutions. After the formation of PDA/PSS shells, the positive charge of the inner PDA layer, covered by the outer PDA/PSS shell was compensated by negatively charged citrate ions, resulting in a stable PDA/citrate complex. Exposure of PDA/citrate-PDA/PSS- SiO_2 composite particles to a solution containing $0.1\text{ mol}\cdot\text{L}^{-1}$ NaOH would result in the rapid substitution of citrate ions to OH^- and the formation of PDA/ OH^- -PDA/PSS- SiO_2 microreactors. The products was collected by centrifugation and washed with absolute ethanol.

The $\text{Bi}(\text{OH})_3$ nanoparticles were prepared by adding 25 mL ethanol solution of BiCl_3 to 50 mL above ethanol solution of PDA/citrate-PDA/PSS- SiO_2 , 30 minutes later, the white solid was collected by centrifugation and washed thoroughly with ethanol. The white powder obtained was dried at room temperature.

Typically 0.025 g thioacetamide and 20 mL of absolute ethanol were added to a 100 mL round-bottom flask. The solution was agitated in the sonic bath

until all the thioacetamide was dissolved. Then an aliquot of white powder prepared above was added and agitated for five minutes. Then the flask was immersed in a sonic bath for several hours. The brown powders were recovered by centrifugation, washed repeatedly with absolute ethanol, and dried in vacuum.

1.2 Characterization

The phase composition of the as-prepared samples were determined by X-ray diffraction, on a Rigaku (Japan) D/max-rA X-ray diffractionmeter equipped with graphite monochromatized Cu K α radiation ($\lambda=0.154\ 06\ \text{nm}$). The overall morphologies of SiO₂ and SiO₂/Bi₂S₃ were obtained by Transmission electron microscopy (TEM) using a Hitachi H-800 Transmission electron microscope (accelerating voltage =200 kV) and field emission scanning electron microscopy (FESEM) were performed on JEOL JSM-6700F. Samples for the Transmission electron microscopic measurements were obtained by placing a drop of sample suspension in absolute ethanol on a Formvar copper grid, followed by air drying period to re-

move the solvent. For the field emission scanning electron microscopic measurements, a few drops of sample suspension were placed on aluminum foil. Infrared spectra were recorded using EQUINOX 55 FTIR spectrometer, using KBr transparent pellets. KBr was used as the background file. The optical properties of SiO₂/PE/Bi₂S₃ were measured on a SHIMADZU UV-2401PC recording spectrophotometer.

2 Results and Discussion

In Fig.1, the X-ray diffraction pattern of a typical sample shows the presence of sharp peaks, corresponding to the Bi₂S₃ crystal structure. The X-ray diffraction profile of SiO₂/Bi₂S₃ shows weak in intensity Bi₂S₃ peaks intensity, due to a small amount of Bi₂S₃. The strong background in the lower angle side is due to the presence of the SiO₂ core. The average particle sizes, calculated by the diameter of Bi₂S₃ grain t , was 32 nm at $2\theta=46.85^\circ$ ((115) peak) using the Debye-Scherrer formula $t=0.89\lambda/(\beta\cos\theta)$.

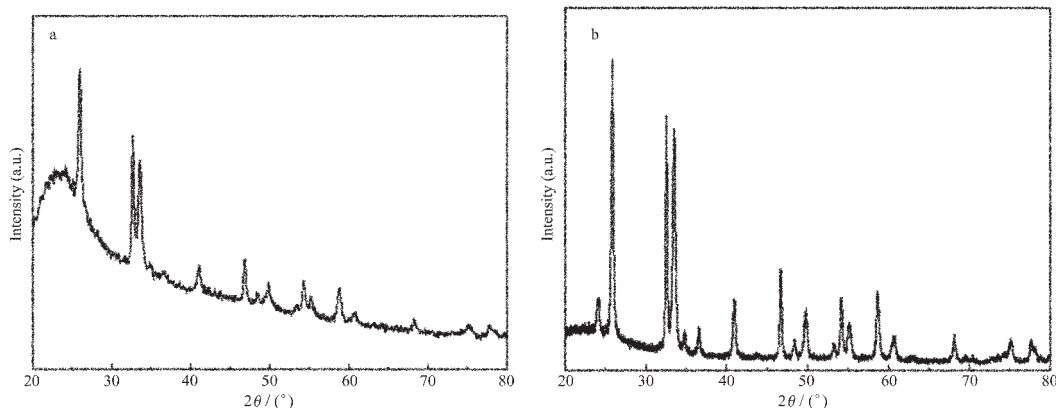


Fig.1 X-ray diffraction patterns of (a) SiO₂/PE/Bi₂S₃ and (b) Bi₂S₃

Compared to the bare SiO₂ (Fig.2a), TEM images of SiO₂/Bi₂S₃ reveal the coating feature of the Bi₂S₃ particles. It can be seen that Bi₂S₃ is coated on the surface of SiO₂ as a thin layer. In Fig.2b, 2c, the central SiO₂ core is coated with a Bi₂S₃ layer with an average thickness about 30~35 nm, almost without any free bare zones. From the FESEM images (Fig.3a,b), we can see that the final products have high yield (Fig.3a) and perfect spherical morphology (Fig.3b).

Infrared (IR) spectra of SiO₂ and SiO₂/Bi₂S₃ clearly show the formation of an interfacial bond between SiO₂ and Bi₂S₃. The spectrum of SiO₂ shows three absorption bands in the region from 1 600 cm⁻¹

to 4 00 cm⁻¹, characteristic of the siloxane links. The absorption band at 460 cm⁻¹ corresponds to the rocking mode, while the band at 810 cm⁻¹ is due to the symmetric stretching of the Si-O-Si group. The observed broad doublet band in the wavenumber region of 1 300~1 000 cm⁻¹ corresponds to the asymmetric stretching vibrational mode of the Si-O-Si bridge of the siloxane link. The sharp band at 1 060 cm⁻¹ corresponds to the characteristic oxygen asymmetric stretching mode. The splitting of the asymmetric stretching mode is probably due to the presence of strained siloxane links and surface silanols (disorder-induced coupling). The IR spectrum of SiO₂/Bi₂S₃ (Fig.4b) shows a sig-

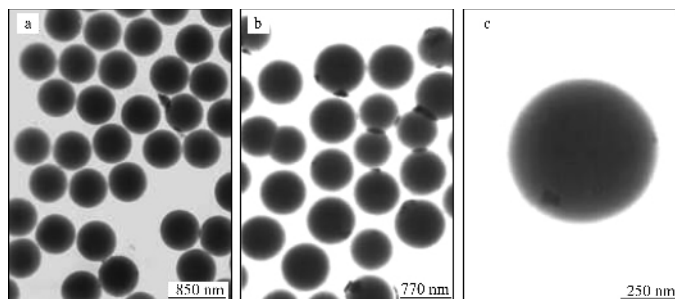
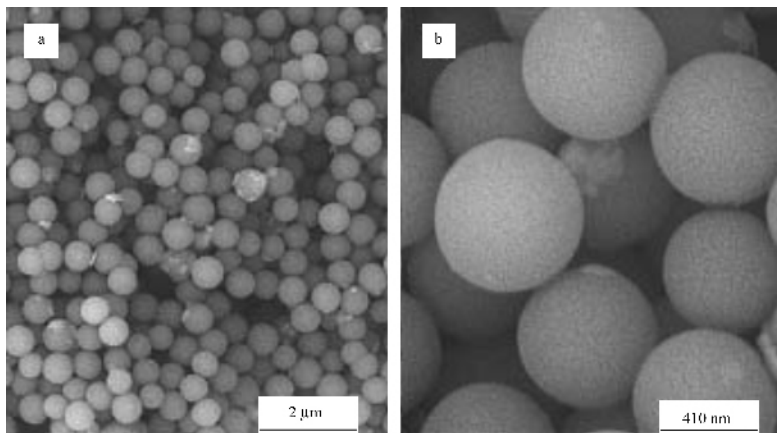


Fig.2 TEM micrographs

(a) SiO_2 , (b) $\text{SiO}_2/\text{PDA}/\text{Bi}_2\text{S}_3/\text{PSS}$, (c) $\text{SiO}_2/\text{PDA}/\text{Bi}_2\text{S}_3/\text{PSS}$. (b) and (c) are lower and higher magnification.

Fig.3 Field emission scanning electron microscope micrographs of $\text{SiO}_2/\text{PE}/\text{Bi}_2\text{S}_3$ composite nanoparticles

(a) lower magnification and (b) higher magnification.

nificant change in the asymmetric stretching mode of the SiO_2 core. The doublet of the SiO_2 asymmetric stretching band is replaced by a sharp band near 1114 cm^{-1} , corresponding to the asymmetric stretching mode and indicating a surface modification by the Bi_2S_3 coating. A 30 cm^{-1} shift to a higher frequency is observed for the asymmetric stretching mode upon coating, probably associated with the bonding change around the $[\text{SiO}_4]$ tetrahedral.

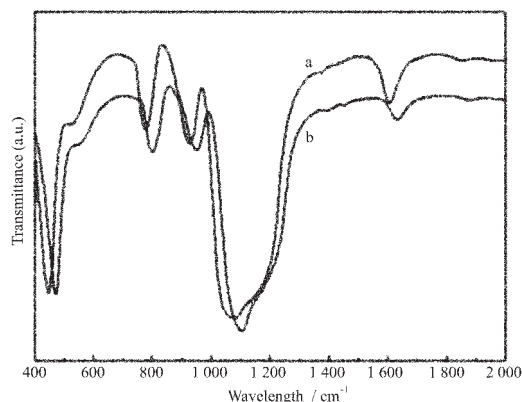
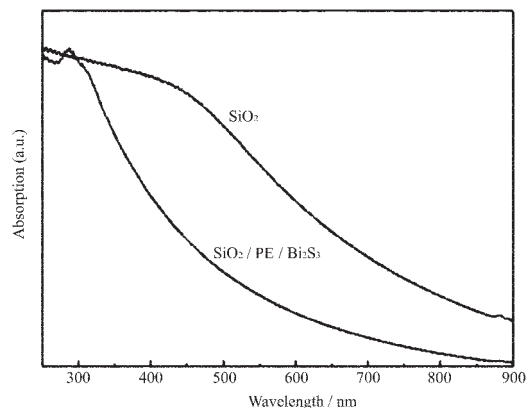
Fig.4 FTIR Spectra of (a) SiO_2 and (b) $\text{SiO}_2/\text{PE}/\text{Bi}_2\text{S}_3$

Fig.5 shows the UV-Visible spectra of the starting SiO_2/PE core and the final products $\text{SiO}_2/\text{PE}/$

Bi_2S_3 aqueous colloids. The absorption spectra of both samples are characteristic of colloidal Bi_2S_3 nanoparticles the absorption band onset is closed to 900 nm , *i.e.*, slightly blue-shifted in relation to the typical bulk E_g of this semiconductor ($E_g=954\text{ nm}$), and extends all the way to the UV region. It is clear that the SiO_2 core was covered by Bi_2S_3 . The UV-Visible spectrum closed to 900 nm , means that Bi_2S_3 nanoparticles has been synthesized in PE microreactor.

Fig.5 UV-Visible spectra of ethanol dispersions of SiO_2 and $\text{SiO}_2/\text{PE}/\text{Bi}_2\text{S}_3$

The formation of composite can be visualized be-

low, as illustrated in Fig.6: The surface of the silica particles is predominantly covered by PDA/OH⁻-PDA/PSS polyelectrolyte microreactor, when the Bi³⁺ ions was added to the system, Bi(OH)₃ was formed in the microreactor, then the Bi(OH)₃ can react with TAA under the ultrasonic irradiation and form Bi₂S₃. It is reasonable to attribute the success of our preparation to the proper deposition of polyelectrolyte layers on the surface of SiO₂ and proper anions we chose. Some other anions were used to replace the citrate acid, but cannot get desired product. The key factor is that the anions can be rapidly substituted by OH⁻. This method could be used to synthesize other new core-shell composite materials.

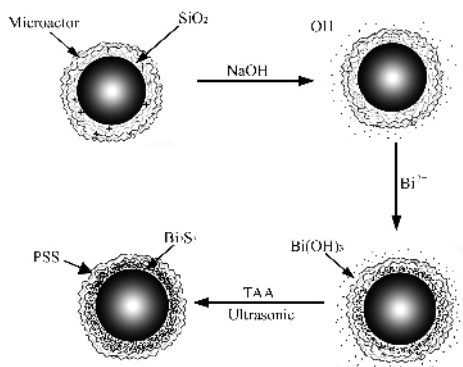


Fig.6 Schematic illustration for the formation of SiO₂/PE/Bi₂S₃ composite nanoparticles

3 Conclusions

In summary, A new approach, using the polyelectrolyte microreactor synthesis of Bi₂S₃ nanoparticles on the surface of SiO₂ colloids is suggested to construct SiO₂/PE/Bi₂S₃ core-shell particles with Bi₂S₃ composite shell with defined thickness. The Bi₂S₃ nanoparticles synthesized are about 32 nm in diameter. Because the coating process is the key factor and dependent on the polyelectrolyte charge and ions exchange, the shell thickness can be tuned by altering the num-

ber of polyelectrolyte layer deposited. Studies are in progress using the polyelectrolyte microreactor for preparing colloids coated with a variety of different properties and functions.

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