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Simultaneously inducing synthesis of semiconductor CdS nanotubes and nanospheres through living bio-membrane bi-template

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Abstract Semiconductor CdS nanotubes with a small ratio of length to diameter and nanospheres were simultaneously synthesized in the light of bio-mineralization process through living bio-membrane bi-template of mungbean sprouts at room temperature. The outside diameter of the nanotube is 220—240 nm and the inner diameter is 200—220 nm, the length is up to 600—700 nm and the ratio of length to diameter is 2∶1. The nanoshpheres are 25 nm in diameter and well distributed. The XRD pattern indicates that these nanocrystals were crystallized in the cubic structure with lattice $a = 5.818$ Å. The optical properties of the products are illustrated, and their possible forming mechanism is explored.

Keywords: cadmium sulfide, nanotube, nanosphere, living bio-membrane, bi-template.

Group II-VI semiconductors, because of its wider band width and nonlinear optical properties, have already shown vital applications in fluorescence probe, sensors, solar battery, photoelectrocatalysis, photoelectricity devices, laser light-emitting diodes[1−3], etc. CdS is one of the most important materials in the group II-VI semiconductors. And its synthesis, assembly and the particles morphology control have received great attention all the time. A number of methods have been developed to synthesize the CdS nanomaterials such as hydrothermal-solvethermal methods[2,4], SBA-15 templates[5], sol-gel methods[6], single-source molecular precursors methods[7], polymethylmethacrylate matrix methods[8], porous alumina template[9], etc. However, so far there has been no report on the synthesis of CdS nanomaterials through living bio-membrane bi-template. Especially, no one has achieved the successful synthesis of different morphologies of CdS nanomaterials simultaneously. In addition, there are many reports about synthesis of CdS nanotubes[10−12], mainly on large L/D nanotubes and there is no report on the synthesis of small L/D nanotubes (L/D=2).

It is well known that there are many active groups and special transport proteins on living bio-membrane, which could transport ions, and induce biological mineralization as well[13−15]. Many living bio-membranes have different structures on the outer and inner surfaces, and there are some active groups on the surface such as hydroxyl, amido, carboxyl and special transport proteins, so it is possible to assemble significant nanomaterials with different morphologies, when the nucleation and growth of molecules are induced through living bio-system.

Mungbean sprout is a simple living bio-membrane material easily available. Its surface is uniform with many shallow channels, and there are many vasculars in its stem (Figs. 1 and 2). And there are great differences in structure between the outer surface of the mungbean sprout and the inner vascular tissue. The inorganic ions could be controlled to enter or exit the organism through the membrane, when the whole mungbean sprout is easily survived and kept fresh in solutions, so it is ideal as a living bio-membrane bi-template. Because of the abundance in the living bio-membrane of plant and animal in the world, the method would be significative not only on materials

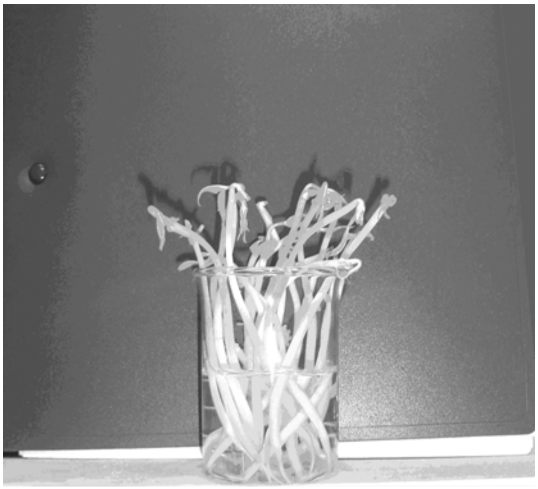

Fig. 1. The whole morphology of mungbean sprout.

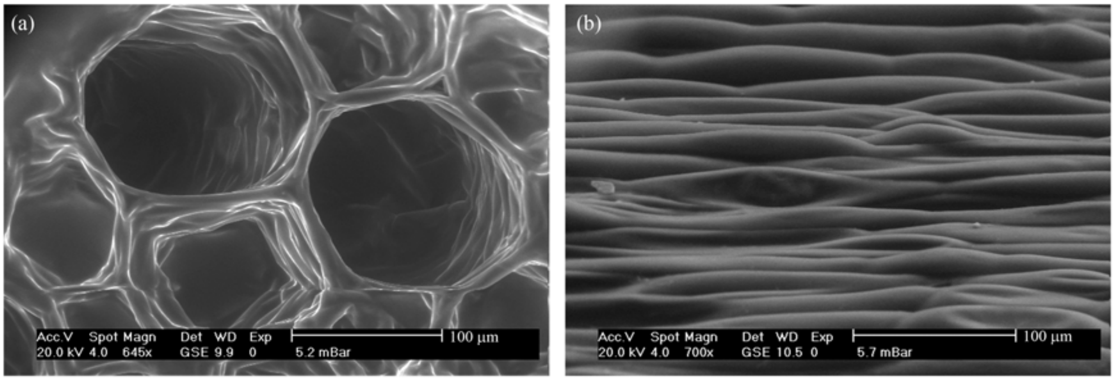

Fig. 2. ESEM pattern of mungbean sprout. (a) The interior of mungbean sprout; (b) surface of mungbean sprout.

science, biology and chemistry, but on the environments.

In this paper, two kinds of semiconductor CdS nanomaterials with different morphologies were synthesized simultaneously through living bio-membrane bi-template for the first time. In them, the nanotube with small L/D is a novel structure and has potential application in the assembly of nanodevice.

1 Experimental

1.1 Reagent and instrument

Chemicals: $Na_2S \cdot 9H_2O$,$CdCl_2 \cdot 2.5H_2O$, carbon disulfide and absolute ethanol (A.R.) (purchased from the Shanghai Chemical Reagent Factory, China). Mungbean sprouts were purchased from the market.

Instruments: TEM images and electron diffraction spectrum were carried out on a Hitachi Model-800 transmission electron microscope. Powder X-ray diffraction (XRD) pattern of sample was measured on 1710 diffraction with Cu Kα radiation (λ=0.15406 nm) (Philips). ESEM images were carried out on XL-30E scanning electron microscope (Philips). Absorption spectrum was recorded on Aligent 8453 UV-Visible spectrophotometer. PL spectra were obtained on a Perkin-Elmer luminescence spectrophotometer (LS-55) (PL, USA).

1.2 Experimental process

(1) Immersing the mungbean sprouts (except laminae) in solution of 0.08 mol/L Na_2S for 12 h.

(2) Taking out the mungbean sprouts and washing them with deionized water. Then immersing them in solution of 0.1 mol/L $CdCl_2$ for 24 h.

(3) Washing the mungbean sprouts with deionized water and ethanol, and transferring the different yellow products into two beakers containing absolute ethanol.

(4) Purifying the products through using carbon disulfide to remove excrescent sulfur.

(5) Taking a small amount of ethanol containing CdS nanomaterials, and dripping one or two drops on the meshwork after ultrasound. Then illustrating the morphology and structure of products through TEM and ED.

2 Results and discussion

2.1 TEM and ED measurements

Fig. 3 shows the TEM micrograph and SAED pattern of the products synthesized through outer template of living bio-membrane bi-template. From the TEM micrograph, it could be concluded that the tubular nanomaterials would emerge through regulating experimental condition. The outside diameter of this nanotube is 200—240 nm and the inner diameter is 200—220 nm, the length is up to 600—700 nm and the length to diameter ratio is 2∶1. Both ends of the nanotubes are opened. The partial magnification image (Fig. 3(c), magnification=8×10^4) of the products demonstrates that the wall is very smooth with thickness being 20—30 nm and minor L/D nanotubes have not been reported up to now.

Fig. 3(c) is the magnification image of single nanotube. Its structure is quite different from the nanorod (Fig. 3(d)), which has solid structure. The fringe color of the nanorod is light but the nanotube is dark. The color of the nanotube middle is light and the structure is hollow. The selected area electron diffraction in Fig. 3(d) shows that these nanotubes are poly-crystalline in structure. The corresponding lattice planes from inner to outer rings are (111), (220), and (311).

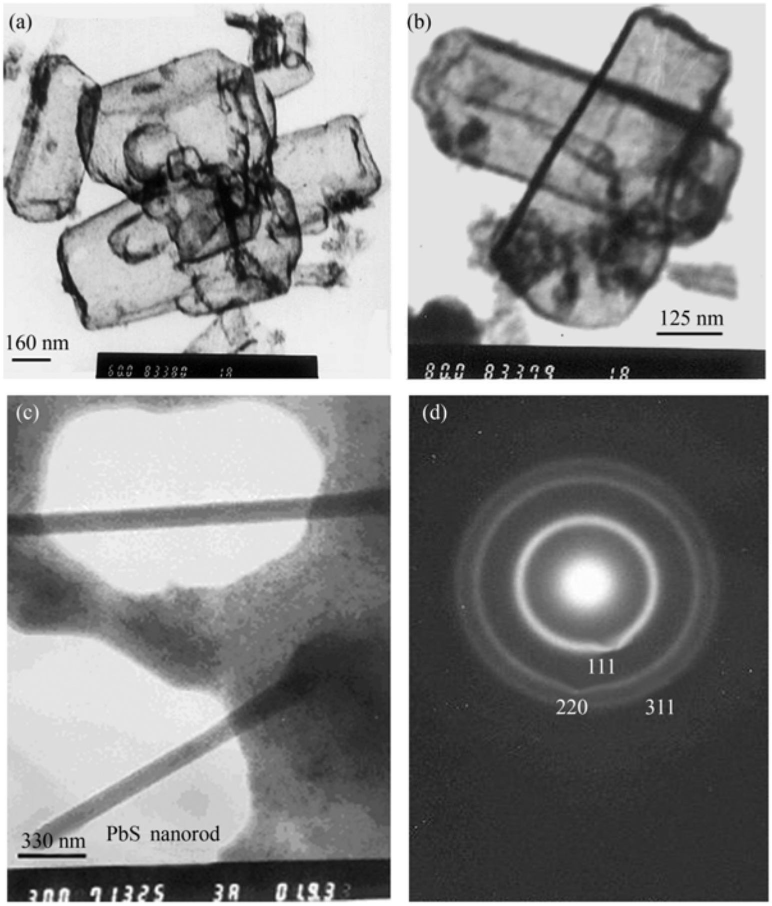

Fig. 3. (a), (b) TEM images of CdS nanotubes (external products); (c) TEM images of nanorod; (d) SAED image of prepared products.

Fig. 4 shows the TEM image and SAED pattern of inner products synthesized through living bio-membrane bi-template. The products are irregular nanospheres and dispersed well, and the dimension of them is 25 nm. The dimensions of the products have been nanosized and this is the key factor of the optics optimization. And because of the spherical morphology of the products, they are useful for the machine lubrication. From the irregular diffraction spots of SAED pattern, it is suggested that they are single-crystalline in structure.

2.2 XRD study

The crystal structure of the semiconductor nanomaterials is very important because the different functions and applications of photochemistry are influenced by the crystal structure. The XRD pattern (Fig. 5) indicates that these nanocrystals of inner and outer products were crystallized in the cubic structure with lattice constants a = 5.818 Å, which is consistent with JC—PDS card No.10-454. And it also shows that there are no mixed peaks and the products are of high purity.

2.3 Choice of experiment conditions

The experiment condition and sequence have certain impact on the growth of CdS nanomaterials. During the experiment, the concentrations of 0.2, 0.1, 0.05 and 0.025 mol/L $CdCl_2$ or Na_2S solution were chosen respectively. When the concentration was too high, it was not a suitable environment for mungbean sprout to live and bulk materials increased gradually. When the concentration was too low, synthetic efficiency would reduce. So the concentrations of 0.1 and 0.08 mol/L were chosen separately for $CdCl_2$ and Na_2S.

In order to eliminate the "toxicity of single salt" caused by the metal ions, the order of metal ions was the S^{2-} and then Cd^{2+}. This is mainly because the absorption and combination of anion and cation was controlled by bio-membrane. If the mungbean sprout was immersed in the solution of Cd^{2+} firstly, it would lose the function of organism and the following reaction

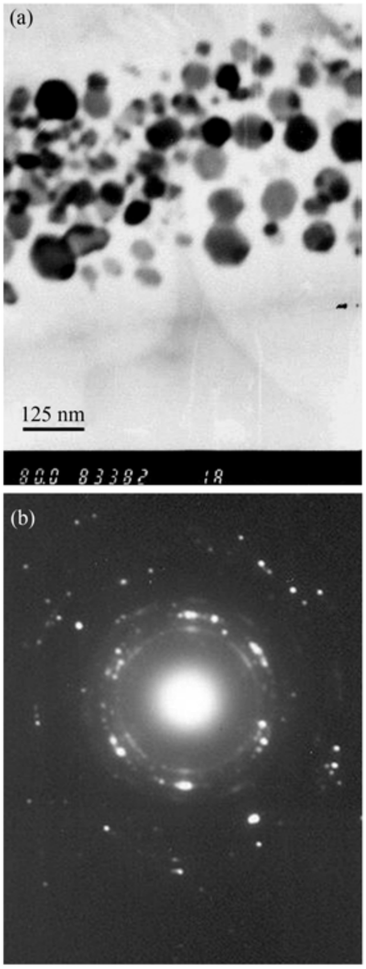

Fig. 4. (a) TEM images of CdS nanospheres; (b) SAED images of CdS nanospheres.

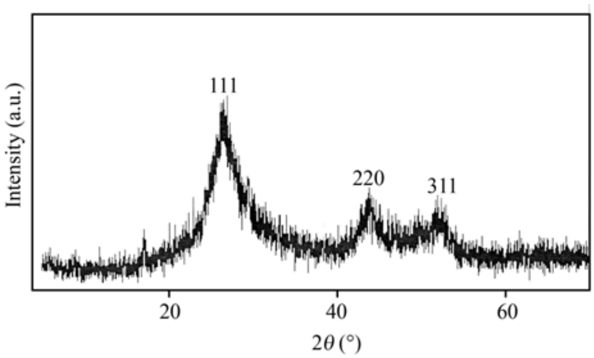

Fig. 5. XRD pattern of CdS nanomaterials.

would not continue. If the mungbean sprouts were immersed in the solution of S^{2-} firstly, it would not only accelerate the synthesis reaction but also offer nutrition to the living bio-membrane.

In addition, when the mungbean sprout was immersed in the solution of S^{2-} and Cd^{2+}, the leaf and the stem were kept fresh. Hence, it is reasonable that the nanomaterials were synthesized through living bio-membrane.

3 Synthetic mechanisms

During the reaction, it was clear that there were some yellow products adhering on the outer bio-membrane. Meanwhile, some other yellow products emerged in the root primarily and then grew up to the stem. After reaction, SEM pattern indicated that there was quantity of CdS nanomaterials on the outer and inner surface of mungbean sprouts. According to the above experiment, the possible formation mechanism of CdS nanomaterials was deduced as follows:

1) When mungbean sprouts were immersed in the solution of S^{2-}, because of the concentration gradient, some S^{2-} ions on the outside of bio-membrane were transferred into the inside of mungbean sprouts by special protein and the other S^{2-} ions were absorbed on the outer membrane.

2) When the mungbean sprouts, which absorbed plenty of S^{2-}, were immersed in solution of Cd^{2+}, some S^{2-} ions in the mungbean sprouts were actively transported to the outer epidermis of mungbean sprouts and at once reacted with Cd^{2+} and produced CdS, while there were other CdS simultaneously formed on its inner surface.

3) With the increase of CdS on outer and inner surface of mungbean sprouts, crystal nucleus of $(CdS)_m$ came into being.

4) Because of the templates operating on the outer and inner surfaces of mungbean sprouts, CdS nuclei were respectively induced to grow into different morphologies of nanotubes and nanospheres.

4 UV optical properties

UV-visible absorption spectra (Fig. 6) of CdS nanomaterials showed a strong absorption peak at about 417 nm and an obvious blue shift was observed comparing with bulk CdS at 515 nm due to size quantization effects. The absorption peak for the products shifted about for 98 nm. And it would have important scientific value on the optical filter, photochemical catalysis and special optical devices if utilizing the optical property of products.

5 Conclusions

In conclusion, two different morphologies of semi-

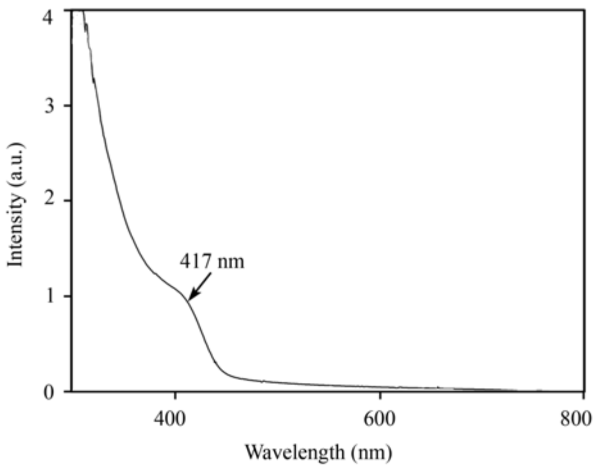

Fig. 6. UV-visible spectrum of prepared CdS nanomaterials.

conductor CdS nanomaterials are successfully synthesized through living bio-membrane bi-template (mungbean sprout) during the growth of plant. This method is easy to generalize, because of its low cost and easily obtained living bio-membranes. Through this method, some new nanomaterials could be synthesized, when many kinds of living bio-membrane bi-templates could be employed. So it offers a new way to synthesize nanomaterials.

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