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Synthesis of MS/TiO_2 (M = Pb, Zn, Cd) nanocomposites through a mild sol–gel process

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In a sol–gel process, metal acetates reacted with thioacetamide to form the corresponding metal sulfides homogeneously dispersed in a colloid. The as-prepared dry gels were decomposed by heat treatment at 120 °C to form MS/TiO_2 (M = Pb, Zn, Cd) nanocomposites. The products were analyzed by infrared spectroscopy, X-ray powder diffraction, transmission electron microscopy, elemental analysis, UV-Vis absorption, and photoluminescence. The final nanocomposites consisted of amorphous titanium dioxide nanoparticles and nanocrystalline metal sulfides. Nanocrystalline PbS in the gel had fine optical properties and showed obvious quantum confinement effects.

Introduction

Quantum states in the nanocrystalline sulfides of many transition or post-transition metals are size-dependent, leading to new electronic, optical, magnetic, mechanical, and catalytic properties.[1–5] The areas of application, which can be foreseen to benefit from the small size and organization of nanocrystallites, include nanoelectronics, non-linear optics, catalysis, high-density information storage, and hybrid materials.[6–9] Studies relating to these well-defined inorganic particles have brought about not only a deep understanding of quantum confinement effects but also the development of new and useful spectroscopic methods and detection technologies.[10,11]

Nanocomposite techniques provide convenient routes to improve the processability and stability of nanocrystals with intriguing novel electronic, optical, and magnetic capacities.[12,13] Recently, special attention has concentrated on developing methods for assembling nanoscale building blocks.[14,15] These methods usually rely on both building block components and assembly strategies. For example, a variety of methods have been developed for preparing monodispersed samples of CdS, CdSe, and Au particles with diameters ranging from 1 to 40 nm.[7,16–19] The general principle in the construction of nanocomposites involves the intimate mixing of nanocrystallites with procurable matrices. The nanoscale matrices usually provide spatially localized sites for nucleation, which minimizes the degree of particle aggregation and imposes an upper limit on the size.[20–22] In the view of materials science, nanocomposites are usually valuable materials, for example the coupled semiconductors CdS/TiO_2 are potentially useful in improving the photocatalytic conversion efficiency of photoelectrochemical systems.[23] These properties are largely determined by matrix materials and the size of metallic or semiconducting nanocrystallites within the matrices. Therefore, it will be significant to select suitable reaction routes to obtain worthwhile matrix materials and control the size of nanocrystallites within the matrices. It is well known that nanoscaled metal oxides have potential or demonstrated applications in many technologies, such as solar energy conversion, batteries, catalysis, and ductile ceramics.[24–30] Furthermore, the sol–gel technique has been widely adopted to prepare metal oxide nanomaterials, including TiO_2,[31] employing hydrolysis of metal alkoxides or halides. The advantage of this method is the intimate molecular-scale mixing of all components. By controlling the sol–gel process, the reactions can proceed smoothly and the products can disperse homogeneously in a colloidal solution. Therefore, this technique can be applied to prepare nanocomposites with TiO_2 nanoparticles as the matrix with small-sized nanocrystallites dispersing in the matrix. In this work, nanocrystalline metal sulfides were formed by the reactions of metal acetates with thioacetamide in a sol–gel process. By a simple heat treatment of the as-prepared gel, MS/TiO_2 nanocomposites were obtained, with nanocrystalline metal sulfides dispersed homogeneously in a TiO_2 amorphous matrix. Here the gel system consisted of tetrabutyl titanate, acetic acid, ethanol, and glycerol.

Experimental

Analytical grade reagents were purchased from Shanghai Chemistry Co. Ltd. As a typical example, we mainly present the synthesis and characterization of nanocomposites of PbS/TiO_2. 5 mmol hydrous lead acetate was dissolved in a solution of 20 ml acetic acid and 25 ml ethanol. 3 ml Tetrabutyl titanate, the appropriate amount of glycerol, and an excess of thioacetamide were subsequently added into the solution, which was then stirred for 2 h and left for one day under ambient conditions to form a homogeneous gel. Dark gray PbS/TiO_2 nanocomposites were obtained by drying the gel under vacuum at room temperature for about 20 h, and heating the dry gel in air at 160 °C for 4 h. Similar processes were carried out to obtain white ZnS/TiO_2 and bright yellow CdS/TiO_2 nanocomposites.

The infrared spectra were recorded in the wavenumber range 4000–400 cm^{-1} with a Nicolet Model 759 Fourier transform infrared (FTIR) spectrometer, using a KBr wafer. X-Ray powder diffraction (XRD) analyses were carried out on a Japan Rigaku D/max-rA rotation anode X-ray diffractometer equipped with graphite monochromatized high-intensity Cu-Kα radiation ($\lambda = 1.54178$ Å). The accelerating voltage was set at 50 kV, with a 100 mA flux at a scanning rate of $0.05^\circ\ s^{-1}$ in the 2θ range from 10 to 70°. Transmission electron microscopy (TEM) images were taken with a Hitachi Model H-800 transmission electron microscope with a tungsten filament, using an accelerating voltage of 200 kV. Elemental analyses were carried out by atomic absorption spectroscopy using a Perkin-Elmer 1100B atomic absorption spectrophotometer.

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UV-Vis absorption spectra of the gel for the PbS/TiO_2 nanocomposites were collected at room temperature on a SPECORD 200 UV-Vis spectrophotometer. The sample was prepared by dispersing the gel in alcohol. The photoluminescence (PL) experiment was carried out on a Hitachi 850 fluorescence spectrometer with a Xe lamp at room temperature.

Results and discussion

Fig. 1(a) is the IR spectrum of as-prepared dry gel for PbS/TiO_2 nanocomposites, which is similar to the standard infrared spectrum of the corresponding ethanol and acetic acid solution, indicating that there was residual acetic acid and ethanol in the dry gel. There are no characteric peaks for thioacetamide, probably because thioacetamide was decomposed to gaseous products. The vibration absorption peaks of the Pb–S bond were also not observed, since they are weaker and covered by the peaks from the gel.[32,33] Fig. 1(b) is the corresponding IR spectrum of the final product in which the dry gel was heated at 120 °C for 2 h. We can see that there are two weak peaks at 556 and 465 cm^{-1}, corresponding to the vibration absorption peaks of the Ti–O bond. The absorption peaks of the Pb–S bond do not appear, since they are usually weak.

The XRD pattern of the final product is shown in Fig. 2(a). We can see that there are many amorphous components and all the diffraction peaks can be indexed as cubic PbS, with the corresponding lattice parameter $a = 5.94$ Å.[34] The average size of the nanocrystalline PbS formed, calculated from the half-width of the (200) diffraction peak using the Scherrer formula,[35] is 9.8 nm. In Fig. 2(b) and Fig. 2(c), the diffraction peaks can be indexed as cubic ZnS and hexagonal CdS, respectively.[34] From the TEM image shown in Fig. 3(a), the final nanocomposites consist of quasi-spherical PbS nanoparticles with an average size of about 10 nm and sheet matrix particles with an average size of 15 nm. The TEM images in Fig. 3(b) and Fig. 3(c) also showed quasi-spherical ZnS particles with the average size of 9 nm, and short 40 nm × 8 nm rod-like CdS, respectively. Elemental analysis showed that the content of PbS was 58%, 33% for ZnS and 44% for CdS, respectively. The atom ratios were calculated and showed that the nanocomposites consisted of MS and TiO_2 according to the mole ratio MS : $TiO_2 = 1 : 2$. No other elements were detected.

Here, thioacetamide was an important sulfur source and according to the literature,[36] thiourea reacts with water to produce gaseous NH_3, H_2S, and CO_2:

$$NH_2CSNH_2 + 2H_2O \rightarrow 2NH_3(g) + H_2S(g) + CO_2(g) \quad (1)$$

Similarly, when thioacetamide was selected as the sulfur source, an analogous reaction could occur between thioacetamide and trace water coming from the system and the air to produce H_2S:

$$CH_3CSNH_2 + 2H_2O \rightarrow CH_3COONH_4 + H_2S(g) \quad (2)$$

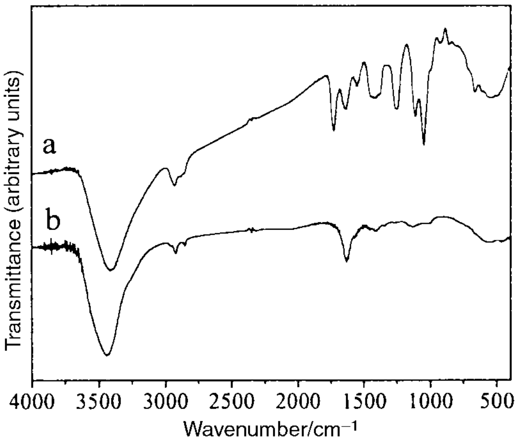

Fig. 1 IR spectra of the products: (a) the dry gel for PbS/TiO_2 and (b) the nanocomposites PbS/TiO_2.

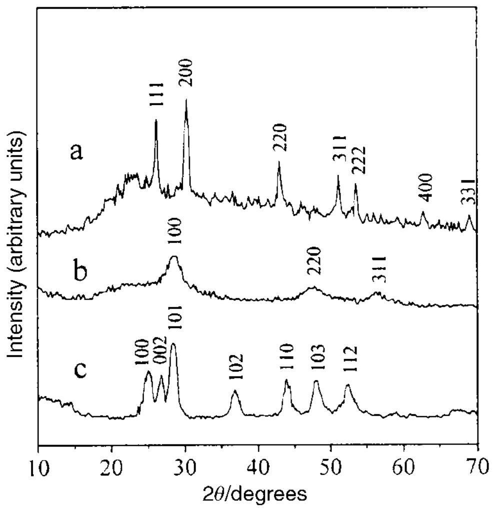

Fig. 2 XRD patterns of the obtained nanocomposites: (a) PbS/TiO_2, (b) ZnS/TiO_2, and (c) CdS/TiO_2.

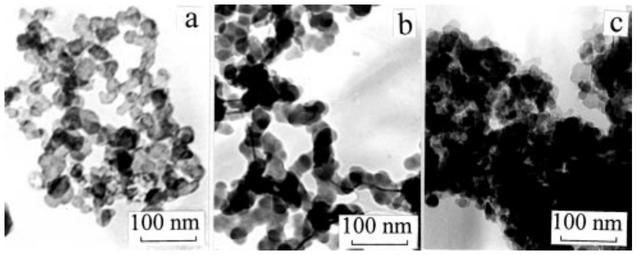

Fig. 3 The TEM images of the nanocomposites: (a) PbS/TiO_2, (b) ZnS/TiO_2, and (c) CdS/TiO_2.

The H_2S produced could then react with Pb^{2+} to form PbS:

$$Pb^{2+} + H_2S \rightarrow PbS + 2H^+ \quad (3)$$

In addition, the sol–gel process also played a critical role in controlling the reaction velocity, confining the growth and aggregation of the nanoparticles, and obtaining the homogeneous PbS/TiO_2 nanocomposites. In the whole process, all components including thioacetamide formed a homogeneous sol. Since the system mostly consisted of acetic acid and ethanol, the formation of H_2S was confined, which confined the formation velocity of lead sulfide. On the other hand, due to the hydrolysis of tetrabutyl titanate, the system constantly absorbed water from the air so that the liquid sol converted to a solid gel. The lead sulfide particles produced were suspended in the gel, which limited their aggregation. In addition, it was very important to control the formation velocity of the gel, which depended on the composition of the sol system. Only when the formation velocity of the gel was close to or slightly faster than that of lead sulfide, could the produced lead sulfide disperse homogeneously into the colloid solution. When heated, the formed gel decomposed and amorphous TiO_2 was obtained, the final product was a homogeneous mixture of PbS nanocrystallites and amorphous TiO_2 nanoparticles.

The nanocrystalline nature of the product PbS/TiO_2 was also reflected by its optical properties. In nanosized semiconductors, the de Broglie wavelength of electrons (or holes) becomes comparable to the crystallite size. The charge carriers have to be treated quantum mechanically as "particles in a box", where the size of the box is given by the dimensions of the crystallites. The spacing between these energy levels and band gaps strongly

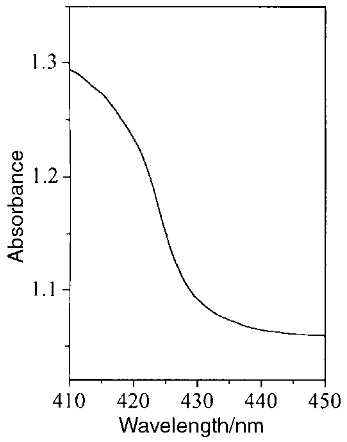

Fig. 4 The UV-Vis absorption spectrum of the obtained nanocomposites PbS/TiO_2.

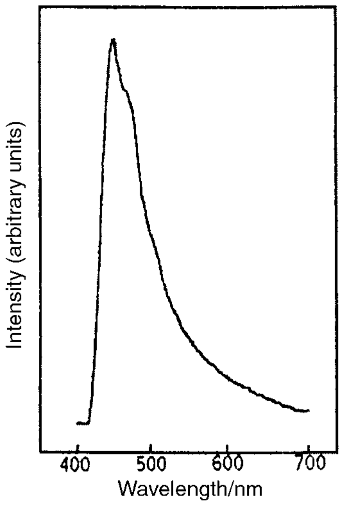

Fig. 5 PL spectrum of the nanocomposites PbS/TiO_2.

depends on the sizes of the nanocrystallites. The optical absorption peak shifts towards higher energies as the crystallite size approaches a value comparable with or below its exciton size, indicating a quantum size effect. The UV-Vis absorption spectrum of the gel for PbS/TiO_2 nanocomposites is shown in Fig. 4. We can see that the absorption edge is at approximately 440 nm and it is clearly blue-shifted. The same size-tunable phenomenon is also observed in the PL spectrum shown in Fig. 5, with an excitation wavelength of 380 nm and a 430 nm filter. It is noteworthy that the PL spectrum shows an intense PL peak centered at 447 nm. The corresponding energy gap is 2.77 eV, which is higher than the 2.66 eV value reported for 10.4 nm PbS nanoparticles,[37] indicating that the size of the PbS nanoparticles is below 10 nm. This result accords well with the XRD and TEM results for the particle diameter. The nanocrystalline PbS in the gel exhibits a blue shift in UV-Vis and PL spectra, compared with its bulk counterpart, obviously showing the quantum size effect.

Conclusion

In summary, a mild sol–gel process was successfully developed for the synthesis of MS/TiO_2 nanocomposites ($M = Pb, Zn, Cd$) in an ethanol–acetic acid media. The sulfur source thioacetamide and the sol–gel system had a significant influence on the formation of high-quality MS/TiO_2 nanocomposites. The present synthesis process provides a favorable low-temperature reaction pathway for the preparation of other nanocomposites.

Acknowledgements

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References

1 J. H. Fendler and F. C. Meldrum, *Adv. Mater.*, 1995, **7**, 607.
2 Y. Wang, *Adv. Photochem.*, 1995, **19**, 179.
3 B. O. Dabbousi, C. B. Murray, M. F. Rubner and M. G. Bawendi, *Chem. Mater.*, 1994, **6**, 216.
4 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
5 G. A. Ozin, *Adv. Mater.*, 1992, **4**, 612.
6 A. P. Alivisatos, *Science*, 1996, **271**, 933.
7 H. Weller, *Adv. Mater.*, 1993, **5**, 88.
8 Y. Wang and N. Herron, *J. Phys. Chem.*, 1991, **95**, 525.
9 L. Brus, *J. Phys. Chem.*, 1986, **90**, 2555.
10 R. S. Kane and R. E. Cohen, *Chem. Mater.*, 1999, **11**, 90.
11 R. N. Bhargava, D. Gallagher, X. Hong and A. Nurmikko, *Phys. Rev. Lett.*, 1994, **72**, 416.
12 D. Wang, Y. Cao, X. Zhang, Z. Liu, X. Qian, X. Ai, F. Liu, D. Wang, Y. Bai, T. Li and X. Tang, *Chem. Mater.*, 1999, **11**, 392.
13 L. L. Beecroft and C. K. Ober, *Chem. Mater.*, 1997, **9**, 1302.
14 L. C. Brousseau, Q. Zhao, D. A. Shultz and D. L. Feldheim, *J. Am. Chem. Soc.*, 1998, **120**, 7645.
15 J. J. Storhoff, R. C. Mucic and C. A. Mirkin, *J. Cluster Sci.*, 1997, **8**, 179.
16 K. C. Grabar, R. G. Freeman, M. B. Hommer and M. Natan, *J. Anal. Chem.*, 1995, **67**, 735.
17 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
18 H. Weller, *Angew Chem., Int. Ed. Engl.*, 1993, **32**, 41.
19 M. A. Hayat, in *Colloidal Gold: Principles, Methods, and Applications*, Academic Press, San Diego, CA, 1991
20 V. Sankaran, T. Yue, R. E. Cohen, R. R. Schrock and R. S. Sillbey, *Chem. Mater.*, 1993, **5**, 1133.
21 C. C. Cummins, R. R. Schrock and R. E. Cohen, *Chem. Mater.*, 1992, **4**, 27.
22 V. Sankara, C. C. Cummins, R. R. Schrock, R. E. Cohen and R. J. Silbey, *J. Am. Chem. Soc.*, 1990, **112**, 6858.
23 K. R. Gopidas, M. Bohorquez and P. V. Kamat, *J. Phys. Chem.*, 1990, **96**, 6435.
24 W. Li, H. Osora, L. Otero, D. C. Duncan and M. A. Fox, *J. Phys. Chem. A*, 1998, **102**, 5333.
25 L. Bedja, P. V. Kamat, A. G. Lapin and S. Hotchandani, *Langmuir*, 1997, **13**, 2398.
26 A. Hagfeldt and M. Gratzel, *Chem. Rev.*, 1995, **95**, 49.
27 L. Kavan, K. Kratochvilova and M. Grätzel, *J. Electroanal. Chem.*, 1995, **394**, 93.
28 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
29 M. J. Mayo, R. W. Siegel, A. Narayanasamy and W. D. Nix, *J. Mater. Res.*, 1990, **5**, 1073.
30 J. Karch, R. Birringer and H. Gleiter, *Nature*, 1987, **330**, 556.
31 T. J. Trentler, T. E. Denler, J. F. Bertone, A. Agrawal and V. L. Colvin, *J. Am. Chem. Soc.*, 1999, **121**, 1613.
32 N. N. Parvathy, G. M. Pajonk and A. V. Rao, *J. Cryst. Growth*, 1997, **179**, 249.
33 T. P. Martin and H. Schaber, *Spectrochim. Acta, Part A*, 1982, **38**, 655.
34 Joint Committee on Powder Diffraction Standards (JCPDS), File No. 5-592 for PbS, 5-566 for ZnS, and 41-1049 for CdS.
35 C. N. J. Wagner and E. N. Aqua, *Adv. X-Ray Anal*, 1964, **7**, 46.
36 S. H. Yu, Z. H. Han, J. Yang, H. Q. Zhao, R. Y. Yang, Y. Xie and Y. T. Qian, *Chem. Mater.*, 1999, **11**, 193.
37 L. Spanhel and M. A. Anderson, *J. Am. Chem. Soc.*, 1990, **112**, 2278.