JOURNAL OF
Materials
CHEMISTRY
Communication

Metal chalcogenide–organic nanostructured composites from self-assembled organic amine templates

Neeraj and C. N. R. Rao*

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur Post, Bangalore 560 064, India

Hexagonal and lamellar nanostructured organic–metal chalcogenide composites have been prepared by the reaction of metal salt aliphatic-amine nanostructured adducts with Na_2S or Na_2Se solution; nanostructured composites of CdS, SnS_2, Sb_2S_3 and CdSe with long-chain aliphatic amines obtained in this manner have been characterized.

Braun *et al.*[1] have recently described semiconductor–organic nanostructured composites of hexagonal symmetry based on cadmium sulfide obtained by using non-ionic amphiphiles such as poly(ethylene oxide). Such nanocomposites have been prepared by starting with different cadmium salts.[2] By employing hydrated polyol amphiphiles, Osenar *et al.*[3] have obtained lamellar, nanostructured cadmium sulfide. In all these preparations, the nanostructured adduct of a cadmium salt with the amphiphiles was treated with H_2S gas. Since the preparation of the chalcogenide nanocomposites using amphiphiles involves methods akin to those employed in the synthesis of mesoporous metal oxides,[4–6] we considered it important to evolve a general method for the synthesis of mesostructured semiconductor chalcogenide–organic nanostructures and characterize the materials suitably. By employing long-chain amines as the amphiphiles,[7] we have prepared both hexagonal and lamellar nanostructures of CdS, SnS_2, Sb_2S_3 and CdSe.

The general procedure for the synthesis employed by us is as follows: to an aqueous solution of cadmium acetate (5 mmol) was added an alcoholic solution of the amphiphilic amine (5 mmol) and the mixture was stirred to obtain a gel. The gel was aged at ambient temperature for 18 h and dried. X-Ray diffraction (XRD) patterns of the gel indicated that nanostructured mesophases of the amine and $Cd(CH_3CO_2)_2$ had indeed formed. To the gel, a concentrated aqueous solution of sodium sulfide was slowly added and the pH adjusted to 9.0–9.5. The resulting product was aged at 333 K for 18 h. The product thus obtained was washed first with water, followed by a ethanol–diethyl ether (50:50) mixture and dried at 333 K. The X-ray diffraction pattern of the product was then recorded. Fig. 1(*a*) and (*b*) show the XRD patterns of the mesophases obtained with dodecylamine (DA) and stearylamine (SA), respectively. The diffraction patterns are characteristic of a hexagonal mesophase with d_{100} values of 4.1 and 5.5 nm, respectively, for DA and SA. EDX analysis of these products gave a Cd:S ratio of 1:1 (see inset of Fig. 1) showing that the sulfide had the expected composition. Thermogravimetry (TG) showed that the amine template was completely removed below 573 K while the water of hydration, if any, was removed at 393 K. TG gave the compositions of the chalcogenide amine adducts as 3CdS·DA and $7CdS{\cdot}6SA{\cdot}9H_2O$ for DA and SA, respectively. The hexagonal nature of the CdS–amine adducts was also confirmed by recording transmission electron microscope (TEM) images. The TEM image of the adduct of CdS with DA shown in Fig. 2(*a*) suggests that the mesophase has a hexagonal structure consistent with the XRD pattern in Fig. 1(*a*). The image shows the wall thickness to be *ca.* 2.0 nm, however, there is considerable disorder.

When we employed a $Cd(CH_3CO_2)_2$:amine ratio of 1:2 instead of 1:1, we obtained a lamellar structure as evident from the XRD pattern of an adduct with SA shown in Fig. 1(*c*) with *d*-values of 5.0, 2.5 and 1.64 nm corresponding to the (001), (002) and (003) reflections, respectively. TG showed that the amine was completely removed at 623 K and the water removed at 393 K. The composition of the chalcogenide–SA adduct from TG gave the composition $9CdS{\cdot}8SA{\cdot}3.5H_2O$. A typical TEM image of the lamellar mesophase is shown in Fig. 2(*b*) which shows a well defined striped pattern with a periodicity of *ca.* 5 nm. No change was observed on tilting the particle perpendicular to the stripes, confirming the lamellar morphology. When we employed thiourea instead of Na_2S as the sulfiding agent, we obtained a lamellar nanostructure of CdS with DA of composition 4CdS·3DA. The XRD pattern of this adduct is shown in Fig. 1(*d*), with *d* values of 3.53, 1.74, 1.17, 0.88 and 0.7 nm, respectively, due to (001), (002), (003), (004) and (005) reflections. We also obtained excellent lamellar mesophases by using long-chain thiols with $Cd(CH_3CO_2)_2$. For example, the adduct with dodecanethiol (DT) had the composition $3Cd(CH_3CO_2)_2{\cdot}4DT$. However, on heating this adduct we could not obtain pure CdS.

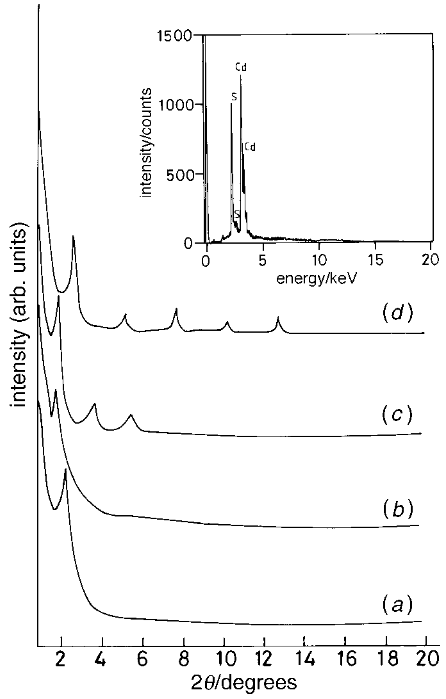

Fig. 1 X-Ray diffraction patterns of (Cu-Kα radiation) CdS–amine nanostructures. Hexagonal phases obtained with (*a*) dodecylamine and (*b*) stearylamine. Lamellar phases obtained with (*c*) stearylamine and (*d*) using thiourea as the sulfiding agent. Inset shows EDX of an adduct with dodecylamine.

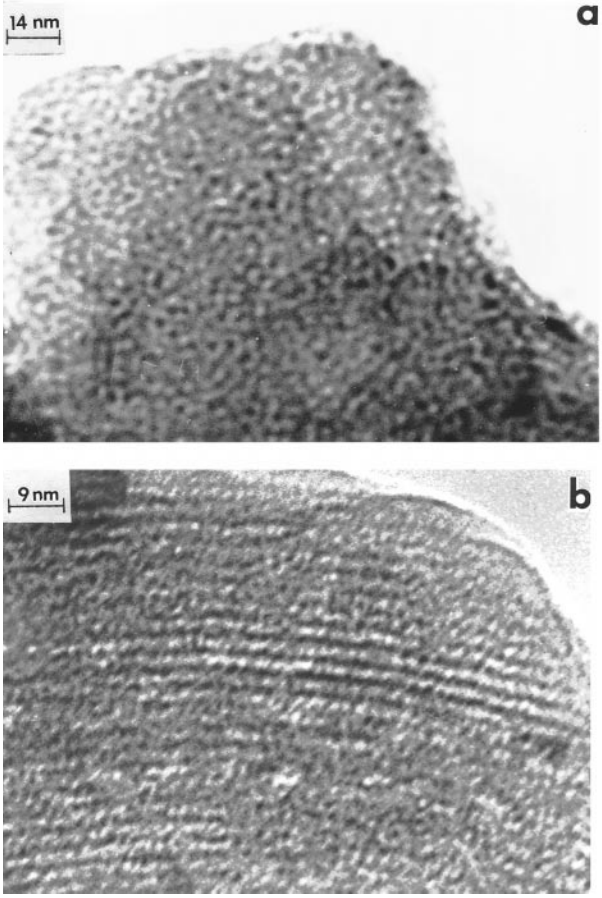

Fig. 2 TEM images of CdS–amine nanostructures: (*a*) hexagonal phase with dodecylamine, (*b*) lamellar phase with stearylamine

On heating the hexagonal CdS adduct with DA at 473 K for 2 h, the mesostructure collapsed, but the resulting sulfide exhibited high surface area (90 $m^2 g^{-1}$). We have been able to remove amine partly from the hexagonal phase of the CdS adduct with SA by heating it slowly at 448 K for 2 h. The XRD pattern of the product showed a feature corresponding to a d_{100} value of *ca.* 5.5 nm, although somewhat weaker in intensity compared to the adduct.

We have also been able to synthesize metal sulfide–organic amphiphile nanostructures of tin and antimony by starting from $SnCl_4 \cdot 2H_2O$ and $SbCl_3 \cdot 5H_2O$, respectively, and keeping the metal salt : amine ratio at 1 : 1. XRD patterns of the hexagonal mesophases of the adducts of SnS_2 and Sb_2S_3 with DA are shown in Fig. 3(*a*) and (*b*), respectively, with d_{100} values of 3.12 and 3.57 nm. The d_{110} and d_{200} reflections are also observed at larger angles. The composition of the sulfides was confirmed by EDX analysis (see insets of Fig. 3). TG indicated the adduct compositions to be $2SnS_2 \cdot 3DA \cdot H_2O$ and $5Sb_2S_3 \cdot 7DA \cdot H_2O$. TEM images showed that the adducts possessed disordered hexagonal structures.

In order to prepare CdSe–amine nanostructures, we employed a procedure similar to that with CdS, except that an aqueous solution of Na_2Se was reacted with the $Cd(CH_3CO_2)_2$–amine gel. Fig. 3(*c*) shows the XRD pattern of the hexagonal mesophase of the CdSe–DA adduct with *d* values of 3.66, 1.9 and 1.75 nm for the (100), (110) and (200) reflections, respectively. The adduct had the composition 9CdSe·4DA and the amine could be removed completely at 573 K. We have also been able to obtain CdSe–amine nanostructures by employing sodium selenosulfate as a seleniding agent instead of Na_2Se; Na_2Se however appears to be a better seleniding agent.

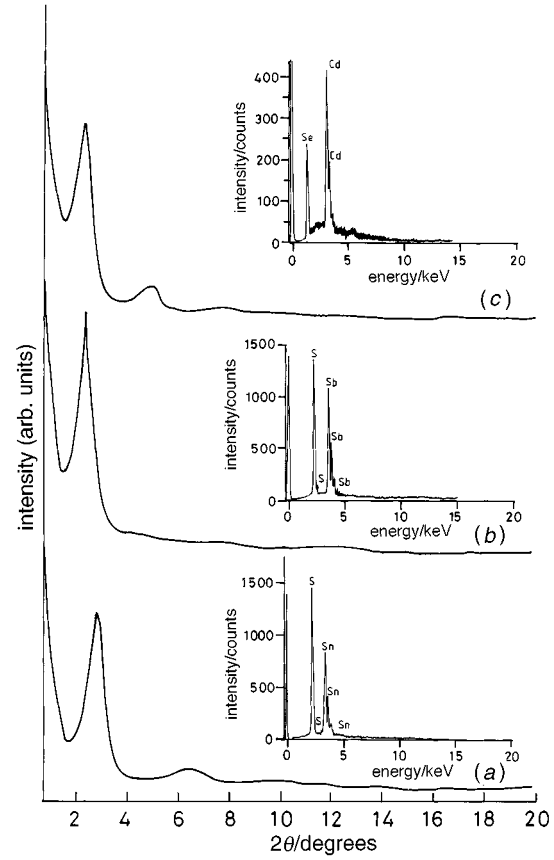

Fig. 3 X-Ray diffraction patterns of metal chalcogenide–amine nanostructures: (*a*) SnS_2–dodecylamine, (*b*) Sb_2S_3–dodecylamine, (*c*) CdSe–dodecylamine. The EDX results are shown alongside the XRD patterns.

References

1 P. V. Braun, P. Osenar and S. I. Stupp, *Nature* (*London*), 1996, **380**, 325.

2 V. Tohver, P. V. Braun, M. U. Pralle and S. I. Stupp, *Chem. Mater.*, 1997, **9**, 1495.

3 P. Osenar, P. V. Braun and S. I. Stupp, *Adv. Mater.*, 1996, **8**, 1022.

4 J. S. Beck and J. C. Vartuli, *Curr. Opinion Solid State Mater. Sci.*, 1996, **1**, 76.

5 P. Behrens, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 515.

6 S. Ayyappan and C. N. R. Rao, *Chem. Commun.*, 1997, 575.

7 P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 365.

8 N. Ulagappan, Neeraj, B. V. N. Raju and C. N. R. Rao, *Chem. Commun.*, 1996, 2243.

Communication 7/07690H; *Received* 24*th October*, 1997