

Developing a coordination chemistry of intact quantum dots: The preparation of novel nanocomposites of PbS with CdS or CdSe

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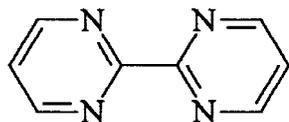
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In this communication a new kind of nanocomposite is reported in which a bridging coordination ligand, 2,2'-bipyrimidine, is used to bind quantum dots of CdS or CdSe (4–6 nm) to larger PbS nanoparticles.

There are several reports of nanostructures consisting of more than one semiconducting phase in which a quantum dot of one material is coated with a shell of another semiconductor.^{1–5} Another kind of nanostructure can be built from extended arrays of spheres of a semiconductor⁶ and the linking of similar quantum dots by thiolates has been reported.⁷ In this communication we report a novel approach to the synthesis of nanostructures comprising two different semiconducting phases in which a molecular bridging ligand is used to support the composite. The bridging ligand 2,2'-bipyrimidine (BPM; Scheme 1) has been used to promote binding between intact nanocrystallites of PbS and CdE (E = S, Se).



SCHEME 1.

Nanodispersed tri-n-octylphosphine oxide (TOPO)-passivated CdS or CdSe (40–60 Å) were prepared by the thermolysis of mixed alkyl cadmium dichalcogenocarbamates in TOPO, as described previously.^{8,9} Nanoparticles of PbS were prepared by the thermolysis of dithiocarbamate lead (II) compounds in TOPO.¹⁰ The novel nanocomposites were prepared by mixing nanodispersed CdE and PbS, in toluene, in the presence of an excess of BPM and stirring for 24 h.

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The CdE/BPM/PbS nanocomposites were synthesized using CdE and PbS nanocrystallites that had distinct and different morphologies. The CdE nanoparticulates used are close to spherical (4–6 nm) whereas the PbS nanoparticulates had larger dimensions and cubic particles predominated. A typical high-resolution electron microscopy (HREM) image of the CdS/BPM/PbS nanocomposite is shown in Fig. 1; many such images were analyzed in the course of the study. The larger PbS nanocrystals were always observed to be surrounded by smaller nanocrystallites of CdS. The latter were somewhat obscured by a cloudy and noncrystalline background (distinct from the graphite background), which is probably associated with the presence of BPM in the final nanocomposite. Several images showed large dark squares of PbS in which lattice fringes were not easily observed, probably due to BPM surrounding the nanocrystallites. It is hard to observe in the same HREM images the smaller CdS and the larger PbS nanocrystallites. However, elemental detection by analytical x-ray (EDAX) measurements (Fig. 1, inset on the right) performed at the border of the larger particles showed the peaks for cadmium, sulfur, and only a weak signal for lead (NB a weak copper signal is observed from the grid). Phosphorus was also detected, confirming also the presence of TOPO molecules in the final material. EDAX performed on centers of the large cubes (PbS) did not show cadmium.

It was not possible to obtain an electron-diffraction pattern for the CdS nanocrystallites when an area containing both semiconducting phases was analyzed, e.g., at the borders of the PbS nanocrystallites. However, electron diffraction of the PbS nanocrystallites showed a well-defined spot electron-diffraction pattern (inset on

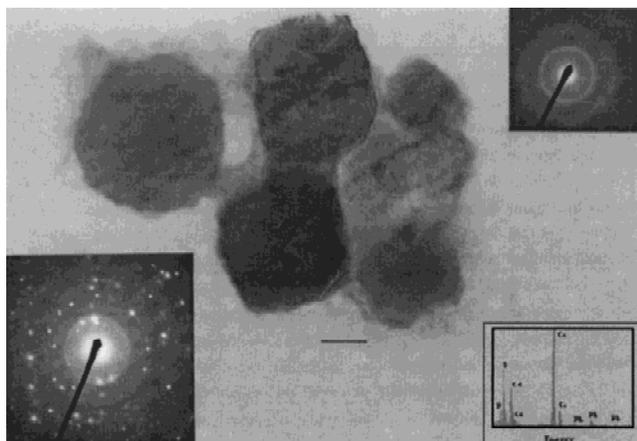


FIG. 1. HREM image of CdS/BPM/PbS nanocomposite (bar = 50 nm) showing (right inset) electron-diffraction pattern of the smaller CdS nanocrystallites and an EDAX performed at the border of a square particle (PbS); and (left inset): electron-diffraction pattern of PbS nanocrystallites.

the left), which was clearly assigned to cubic PbS (rock-salt type). The other electron-diffraction pattern shown in Fig. 1 (inset on the right) was obtained from analysis of the area of small nanocrystallites around the PbS particles, confirming this part of the material to be mainly of CdS. The electron-diffraction pattern shows continuous diffuse rings due to the small particle size and is similar to those for the nanocrystalline CdS used as starting material. The similar electron-diffraction patterns for cubic and hexagonal CdS makes difficult a clear distinction between these polymorphs. However, we suggest that the first strong ring is a set of diffuse features corresponding to the 100, 002, and 101 planes of hexagonal CdS, the commoner phase in such materials. The other diffuse rings at $d(\text{\AA})$ 2.10, 1.90 and 1.67, may then be indexed as the 110, 103 and 201 planes for the same CdS phase.

The presence of BPM in the final nanocomposite was confirmed by infrared spectroscopy. [Infrared data (cm^{-1} , relative intensity): BPM: 1562, very strong; 1555, very strong; 1430, strong; 1401, very strong; CdS/BPM/PbS: 1625, strong; 1570, very strong; 1560, very strong; 1466, medium; 1453, medium; 1406, very strong; CdSe/BPM/PbS: 1624, medium; 1585, medium; 1569, strong; 1559, strong; 1449, weak; 1406, very strong.] The shifts observed to higher frequencies in the BPM vibrational modes are probably associated with the coordination of the BPM to the surface of the nanoparticulates. Similar shifts in the bands position were found for nanocomposites of CdE with BPM.⁹

The optical spectra in Fig. 2 are typical of semiconductors showing quantum-size effects; e.g., the presence of an excitonic peak that is blue shifted in relation to the bulk optical band gap wavelength of the semiconductor.¹ The optical absorption spectra of the new nanocomposites (Fig. 2) may be regarded as the sum of the optical

spectra of the nanodispersed materials from which they were made, i.e., of CdE and PbS (Fig. 2, inset). Although the first excitonic peak (581 nm) of CdSe is not clear in the spectrum of the CdSe/BPM/PbS nanocomposite, expansion of the spectrum revealed a slight shoulder at a red-shifted wavelength (602 nm), which suggests that dispersion on the particle-size distribution has probably occurred in the final nanocomposite. This was not the case of the CdS/BPM/PbS nanocomposite, which still showed a sharp excitonic peak of nanocrystalline CdS at ~ 420 nm.

There are no significant differences between the optical properties of the individual components (PbS, CdE) and the final nanocomposites. Luminescence measurements performed in pyridine solutions containing CdE/BPM/PbS showed band-edge emission typical of CdE; emission that could be assigned to PbS was not detected ($\lambda_{\text{exc}} = 300$ nm). These initial results do not preclude the synthesis of similar materials with interesting optical or electronic properties. We believe that the nanostructure shown in Fig. 1 is a novel class of material that effectively may be regarded as a coordination complex structure of quantum dots. The use of electronic active bridging ligands should enable the evolution of a new class of electrically active materials of this type.

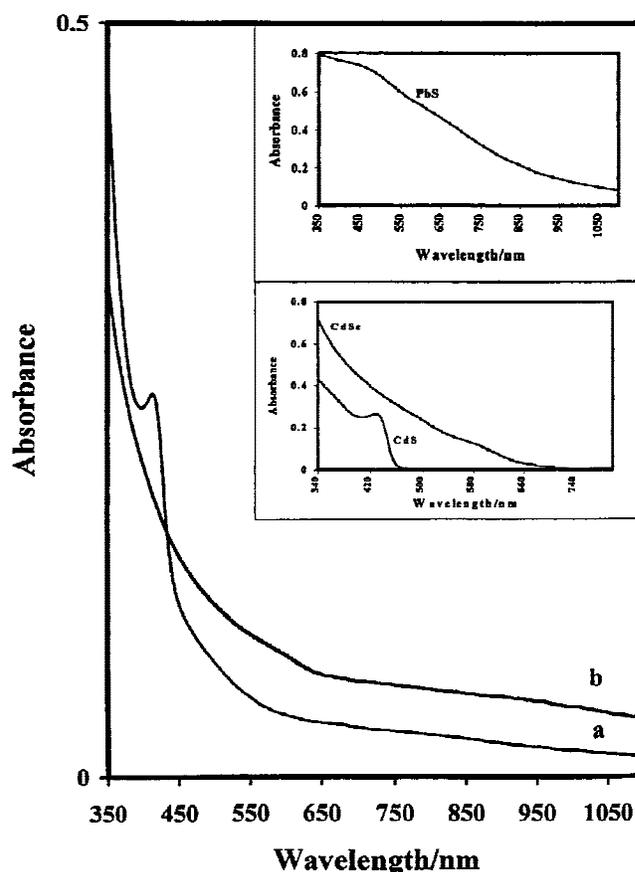


FIG. 2. Optical absorption spectra of nanodispersed materials: (a) CdS/BPM/PbS, and (b) CdSe/BPM/PbS, in pyridine, Inset shows the optical absorption spectra of the starting nanodispersed materials.

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