

The Synthesis of SiO₂@CdS Nanocomposites Using Single-Molecule Precursors

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A chemical method for preparing cadmium sulfide nanocrystals over silica surfaces is reported. This is a one-step synthetic method involving the chemical degradation of alkylthiocarbamate complexes of cadmium in the presence of submicrometric SiO₂ particles. The X-ray powder diffraction patterns of the SiO₂@CdS nanocomposites show diffraction peaks consistent with the presence of hexagonal CdS. Visible spectroscopy and scanning and transmission electron microscopy indicate that an inorganic composite formed by islands of CdS nanocrystals at the SiO₂ surfaces. The SiO₂@CdS nanocomposites can, in turn, be capped with a protective layer of SiO₂ using the Stöber method.

Introduction

Composite nanostructures have been the subject of intense research during the past few years.^{1–3} A number of reports on the synthesis of inorganic nanocomposites can be found in the literature, including CdS@Cd(OH)₂,⁴ CdS@SiO₂,⁵ SiO₂@ZnS,⁶ CdSe@CdS,⁷ CdS@PbS,⁸ CdS@ZnS,⁹ ZnS@CdSe,¹⁰ and CdSe@ZnS.^{11,12} Here, the terminology proposed¹ for the designation of C1@C2 inorganic nanocomposites is followed: a C2 phase (shell) is covering a C1 phase (core). The synthesis of C1@C2 nanocomposites has been accomplished using distinct chemical methods, including epitaxial growth of semiconducting phases,¹³ nucleation and growth inside inverse micelles,¹⁰ reaction of molecular precursors,¹¹ ultrasonic irradiation of colloidal solutions,⁶ and electroless deposition.¹⁴ Other chemical routes are yet to

be developed to allow for the preparation of a wider range of nanocomposites with controlled chemical compositions and well-defined morphological characteristics.

Single-molecule precursors have been investigated as an alternative approach to the production of a range of semiconducting materials either as thin films^{15,16} or, more recently, as nanocrystalline materials.^{17,18} The single-source approach to the production of nanocomposite systems has not been investigated as thoroughly, although the thermalysis of mixed single-molecule precursors has been reported.¹⁹ It will be shown here that, under mild conditions, metal dithiocarbamate complexes can be used to prepare nanocomposite particles such as SiO₂@CdS. This method clearly yields materials with properties distinct from those prepared by coprecipitation methods or by the thermalysis of molecular precursors in high-boiling-point solvents. For the SiO₂@CdS nanocomposites in particular, which could find use in photoelectrochemical cells or in luminescent devices, the use of a nanocrystalline semiconducting phase over SiO₂ leads to a less expensive product and makes these materials technologically more interesting.

Experimental Section

All chemicals were supplied by Aldrich, except ethanol (Merck), and were used as received.

Preparation of SiO₂ Particles. The silica particles were prepared using the Stöber method reported in the literature:²⁰ 0.73 g of tetraethoxysilane (TEOS) was added to 5 mL of absolute ethanol containing 0.06 g of distilled water, and the mixture was allowed to stand for 30 min. Subsequently, 2 mL of NH₄OH solution (25%) was added, and the solution was left to stand for 30 min. The SiO₂ colloid formed was filtered

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(1) Mulvaney, P.; Liz-Marzán, L. M.; Giersig, M.; Ung, T. *J. Mater. Chem.* **2000**, *10*, 1259.

(2) Ishida, H.; Campbell, S.; Blackwell, J. *Chem. Mater.* **2000**, *12*, 1260.

(3) Beecroft, L. L.; Ober, C. K. *Chem. Mater.* **1997**, *9*, 1302.

(4) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649.

(5) Chang, S.; Liu, L.; Asher, S. A. *J. Am. Chem. Soc.* **1994**, *116*, 6739.

(6) Dhas, N. A.; Zaban, A.; Gedanken, A. *Chem. Mater.* **1999**, *11*, 806.

(7) Hao, E.; Sun, H.; Zhou, Z.; Liu, J.; Yang, B.; Shen, J. *Chem. Mater.* **1999**, *11*, 3096.

(8) Zhou, H. S.; Honma, I.; Komiyama, H.; Haus, J. W. *J. Phys. Chem.* **1993**, *97*, 895.

(9) Youn, H.; Baral, S.; Fendler, J. H. *J. Phys. Chem.* **1988**, *92*, 6320.

(10) Kortan, A. R.; Hull, R.; Opila, R. L.; Bawendi, M. G.; Steigerwald, M. L.; Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1990**, *112*, 1327.

(11) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem. B* **1997**, *101*, 9463.

(12) Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *Nano Lett.* **2001**, *1*, 207.

(13) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997**, *119*, 7019.

(14) Kobayashi, Y.; Salgueiriño-Maceira, V.; Liz-Marzán, L. M. *Chem. Mater.* **2001**, *13*, 1630.

(15) O'Brien, P.; Nomura, R. *J. Mater. Chem.* **1995**, *5*, 1761.

(16) Bochmann, M. *Chem. Vap. Deposition* **1996**, *2*, 85.

(17) Trindade, T.; O'Brien, P.; Zhang, X. *Chem. Mater.* **1997**, *9*, 523.

(18) Monteiro, O. C.; Nogueira, H. I. S.; Trindade, T.; Motevalli, M. *Chem. Mater.* **2001**, *13*, 2103.

(19) Ravaprasadu, N.; Malik, M. A.; O'Brien, P.; Wakefield, G. *Chem. Commun.* **1999**, 1573.

(20) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

and washed thoroughly with water and ethanol. The SiO₂ particles were used as prepared (untreated SiO₂) or after thermal treatment at 700 °C for 4 h (treated SiO₂). This thermal treatment increased the degree of dehydroxylation of the silica surface.

Synthesis of Dialkyldithiocarbamate Cadmium Complexes Cd[S₂CNRR']₂. The precursors for CdS were prepared as reported previously.¹⁷ (CAUTION: Because of cadmium toxicity, wear protective gloves when manipulating Cd-containing compounds.) Typically, 20 mmol of the secondary amine (diethylamine or *n*-hexylmethylamine) and 1.1 mL (13.5 mmol) of CS₂ were added to a dispersion containing 1.42 g (10 mmol) of Cd(OH)₂ in ethanol (50 mL). The mixture was stirred for 2 h, and the solid obtained was isolated by filtration and washed with ethanol. The cadmium complexes were identified by IR and ¹H NMR spectroscopies.

Preparation of SiO₂@CdS Nanocomposites. The nanocomposite particles were prepared by adding ethylenediamine (2.5 mL) dropwise to an acetone solution (47.5 mL) containing 0.25 mmol of the cadmium alkyldithiocarbamate and 0.25 g of SiO₂ particles. The suspension was then refluxed with stirring for a certain period of time under a N₂ stream inside a well-ventilated fume hood. The bright yellow solid obtained was collected by centrifugation and washed thoroughly with acetone. The powder obtained was dried at room temperature in a desiccator over silica gel.

Instrumentation. Spectroscopic Methods. Diffuse reflectance spectra of the SiO₂@CdS powders, obtained as described above, were recorded on a Jasco V-560 UV/vis spectrophotometer using MgO as the reference. NMR spectra were recorded on a Bruker AMX 300 spectrometer using acetone-*d*⁶ as the solvent. Infrared spectra were recorded on a Matson 700 FTIR spectrometer using dry CsI disks. Photoluminescence (PL) measurements obtained at room temperature (RT) were carried out with a 325-nm CW He–Cd laser. The luminescence was dispersed by a Spex 1704 monochromator (1 m, 1200/mm) and detected with a Hamamatsu R928 photomultiplier. X-ray photoelectron spectra (XPS) were measured using an LAS ESCALAB 200A instrument, using the Al K α line as the X-ray source on powders dispersed on carbon tape.

Powder Diffraction and Electron Microscopy Techniques. X-ray powder diffraction (XRD) was performed using a Philips instrument operating with Cu K α radiation (λ = 1.541 78 Å) at 40 kV and 50 mA.

Transmission electron microscopy (TEM) was carried out on a Hitachi H-9000 microscope operating at 300 kV. The samples were prepared as follows: an aliquot containing the nanocomposite dispersed in acetone was placed on a copper grid coated with an amorphous carbon film, and then the solvent was evaporated.

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDAX) were performed using a FEG-SEM Hitachi S4100 microscope operating at 25 kV. The samples were prepared by depositing an aliquot of the suspension of the nanocomposite in acetone onto aluminum pieces and then coating them with Au/Pd or evaporated carbon.

Results and Discussion

Cadmium dithiocarbamate complexes have been investigated as suitable single sources for the preparation of CdS nanocrystals.¹⁷ A possible approach described in the literature involves thermal decomposition of the precursor in a high-boiling-point coordinating solvent such as tri-*n*-octylphosphine oxide (TOPO).¹⁷ Using this method, high-quality nanocrystals showing a passivated surface with TOPO molecules have been obtained. To prepare SiO₂@CdS nanocomposite particles, thermal decomposition of a single-molecule precursor in the presence of SiO₂ particles and TOPO was first attempted. However, our preliminary experiments showed that a mixture of segregated SiO₂ and CdS phases was

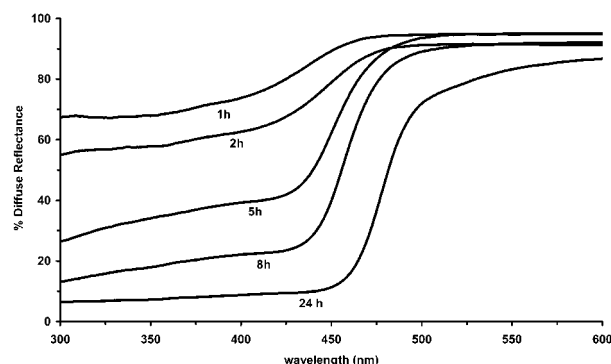


Figure 1. Diffuse reflectance spectra of SiO₂@CdS nanocomposites collected at different reaction times.

obtained, along with the desired product SiO₂@CdS.²¹ The preparation of SiO₂@CdS particles using cadmium dithiocarbamates was then investigated by an alternative method in which lower temperatures were used. In this method, well-defined synthetic SiO₂ particles act as substrates favoring the formation of morphologically uniform particles of the nanocomposite. This mild-temperature deposition method involves the chemical degradation of the precursor in the presence of ethylenediamine, possibly mediated by the formation of a cadmium coordination compound containing the dithiocarbamate and ethylenediamine ligands.²²

In the work reported here, the compounds Cd[S₂CN(CH₃)(C₆H₁₃)₂] and Cd[S₂CN(C₂H₅)₂]₂ were used as single sources for the deposition of CdS onto SiO₂. The two precursors yielded nanocomposites with similar optical and morphological properties. The results presented refer to the use of Cd[S₂CN(CH₃)(C₆H₁₃)₂] as a single-molecule precursor. It was found that the time and temperature of the reaction had a strong influence on the optical and morphological properties of the final SiO₂@CdS particles. This is clearly shown in Figure 1, which presents the diffuse reflectance spectra of the powders collected at different reaction times. For the short reaction times, the optical band gap of the CdS phase is blue-shifted from the typical E_g at 2.5 eV (512 nm) of the semiconductor. A result consistent with the presence of quantum-sized CdS at the surface of the SiO₂ particles. As the reaction time increases, the band edge (Figure 1) approaches the typical E_g value of macrocrystalline CdS. This is in agreement with a process in which the CdS nanoparticles located at the SiO₂ surfaces grow into crystallites of larger dimensions as the reaction proceeds. For samples collected at various times (Figure 1), the percentage of reflectance observed within the 300–500 nm region decreases for longer reaction times, as expected for an increasing amount of CdS covering the SiO₂ surfaces.

Figure 2 shows the XRD patterns for a typical SiO₂@CdS nanocomposite sample. The XRD performed on the SiO₂@CdS nanocomposites showed broad features at 2θ values of 27°, 35°, 44°, 48°, and 52°, consistent with the presence of hexagonal CdS as the predominant crystalline phase.²³ Because of the small

(21) Monteiro, O. C.; Esteves, A. C. C.; Trindade, T. Presented at the 1st COST D19 Workshop on Nanomaterials, Coimbra, Portugal, Sep 21–22, 2001.

(22) Glinskaya, L. A.; Zemskova, S. M.; Klevtsova, R. F.; Larionov, S. V.; Gromilov, S. A. *Polyhedron* **1992**, *11*, 2951.

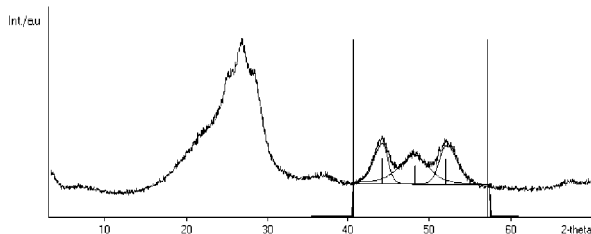


Figure 2. Typical XRD patterns of a SiO_2 @CdS nanocomposite.

particle size, band broadening is observed, precluding a definite conclusion regarding the presence of vestigial cubic CdS. The SiO_2 particles also contribute to the peak broadness observed at lower diffraction angles. The crystalline phase present in the SiO_2 @CdS samples was confirmed by selected area transmission electron diffraction performed on the nanocomposites. The SiO_2 @CdS electron diffraction patterns, typical of hexagonal CdS, appeared as diffuse rings, as expected for a sample consisting of particles of nanometric dimensions. EDAX measurements performed at the surface of the particles showed peaks for Cd and S, as well as Si from the substrate.

In a control experiment, it was found that the nanocomposites showed distinct optical properties and different diffraction patterns from the powders obtained by the direct precipitation of CdS over SiO_2 using Cd^{2+} and S^{2-} solutions. This distinction was immediately obvious by visual inspection of the final powders, in which the latter material showed a pale orange color, instead of the bright yellow appearance of the SiO_2 @CdS nanocomposites prepared by the single-source method. Also, the X-ray diffraction patterns of the materials obtained from the direct precipitation of CdS over SiO_2 particles is consistent with the presence of a mixture of CdSiO_4 and CdS phases. Asher et al. reported⁵ the preparation of cubic CdS/ SiO_2 nanocomposites of diverse morphologies using microemulsions as templates. It is interesting to note that the method reported here yields SiO_2 nanocomposites containing hexagonal CdS, thus allowing for the preparation of nanocomposites containing a CdS polymorph distinct from that present in the materials described by Asher.⁵ The domain size for nanocrystalline CdS obtained here was estimated by applying the Scherrer formula to the 44° and 52° 2θ reflections in the XRD patterns for samples collected at reaction times of 24, 48, and 60 h (i.e., 1, 2, and 5 days). The particle dimensions estimated by this method range from 37 to 42 Å in diameter. This result agrees with the presence of nanocrystalline CdS, for which quantum size effects are expected.^{4,17} In this case, the size domain for the CdS particles should be carefully considered, although it is clearly within the nanometric range. In fact, the XRD particle size analysis is based on the crystalline domains; hence, CdS particles with an incomplete band structure do not contribute significantly to the X-ray diffraction pattern. A more detailed morphological analysis was performed on the SiO_2 @CdS samples using SEM and TEM techniques.

Figure 3a shows a SEM image of a thermally treated SiO_2 particle. The SEM images of SiO_2 @CdS nanocom-

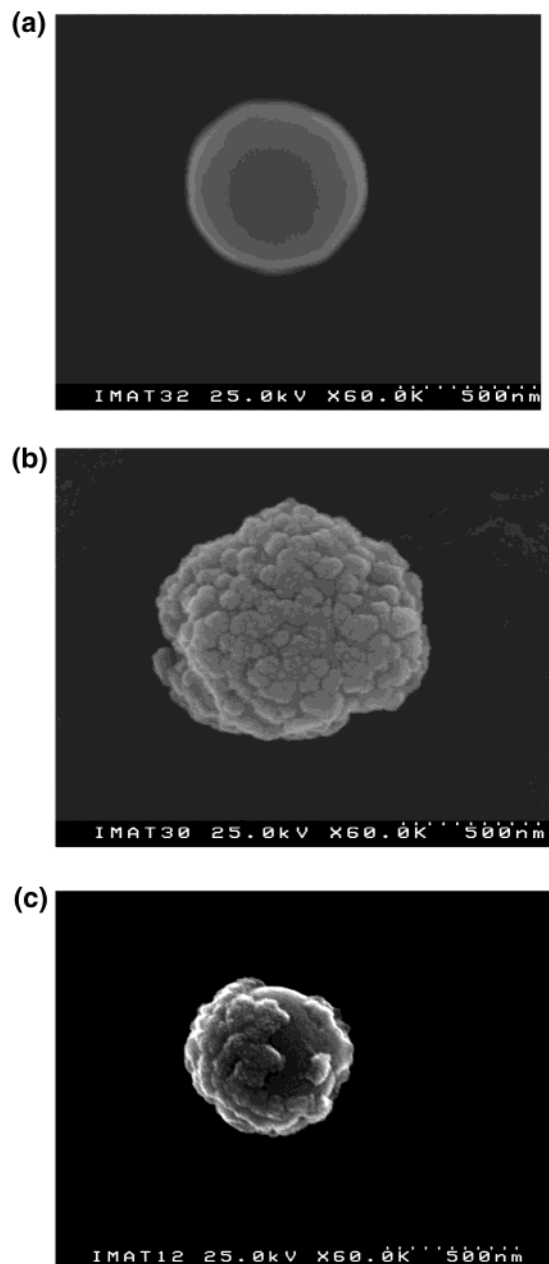


Figure 3. SEM images of SiO_2 @CdS nanocomposites collected at different reaction times: (a) $t = 0$ h, (b) $t = 8$ h (using thermally treated SiO_2), (c) $t = 48$ h (using untreated SiO_2).

posites prepared at different reaction times, using treated SiO_2 or untreated SiO_2 , are shown in Figure 3b,c, respectively. The nanocomposite particles prepared for 8 h using thermally treated SiO_2 particles are completely coated with CdS. The SEM images (Figure 3b,c) suggest that the outer layer is formed of CdS islands, ca. 50 nm in size, at the surface of the SiO_2 particles. This is a size domain for which quantum size effects would not be expected (for nanocrystalline CdS) because it is considerably larger than the Bohr radius of the bulk exciton for the semiconductor. However, it is clear from Figure 1 that the SiO_2 @CdS nanocomposites show quantum size effects in their optical spectra; also, the domain sizes estimated from the Scherrer formula are within the quantum size regime for CdS. Moreover, preliminary photoluminescence studies performed for the SiO_2 @CdS nanocomposites showed a

(23) JCPDS Powder Diffraction File (Inorganic), File No. 41-1049, ICDD.

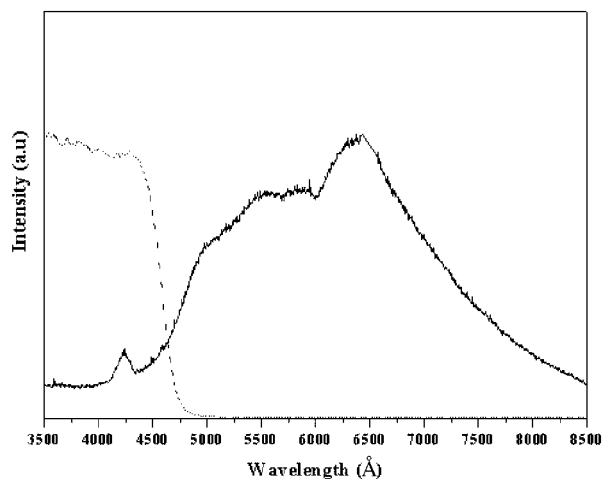


Figure 4. Visible diffuse reflectance (dashed line) and photoluminescence (solid line) spectra of $\text{SiO}_2\text{@CdS}$ nanocomposites.

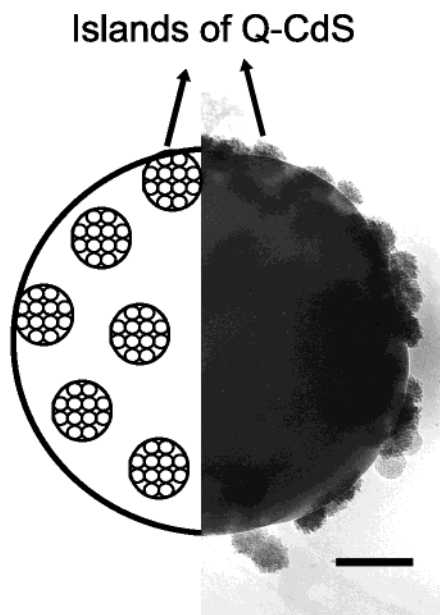


Figure 5. TEM image (bar = 140 nm) and diagrammatic picture of a $\text{SiO}_2\text{@CdS}$ nanocomposite particle showing nano-sized CdS forming islands at the SiO_2 surface.

structured band emission distinct from the bulk CdS emission that is slightly red-shifted from the optical band gap of the same sample (Figure 4). This result is consistent with the presence of CdS nanocrystals.^{24,25} The experimental evidence for the presence of CdS nanocrystals smaller than the islands indicates that the CdS nanocrystals might cluster and form the islands observed by SEM. The morphological nature of the CdS layer was further investigated by a close inspection of the CdS formed at the SiO_2 surfaces using TEM. Figure 5 shows the TEM image of a $\text{SiO}_2\text{@CdS}$ nanocomposite particle formed by clustered CdS nanocrystals at the SiO_2 surface. This result is in agreement with the relatively broad emission band observed in Figure 4.^{24,25}

Although detailed mechanistic studies are beyond the scope of this work, the $\text{SiO}_2\text{@CdS}$ nanocomposites might

result from CdS nanocrystals acting as nuclei for further growth of the CdS phase at the SiO_2 surface. An island growth mechanism could explain the formation of the CdS phase. In agreement with this process, the number density of CdS islands at the SiO_2 surfaces increased with reaction time, i.e., as the molecular precursor is consumed. For longer reaction times, the SiO_2 particles became completely coated with CdS (Figure 3b). Coating SiO_2 substrates using metals or semiconductors has been reported to involve migration and coalescence of nanoparticles following an island growth process.²⁶ This mechanism seems to apply not only to large substrates but also to submicron-sized SiO_2 particles, as suggested here and recently in the sonochemical preparation of $\text{SiO}_2\text{@ZnS}$ nanocomposites.⁶

It is not clear whether the nanocrystals start to nucleate at the surface of the SiO_2 microparticles or are formed in solution and then migrate to the SiO_2 surface. The first event, corresponding to a heterogeneous nucleation process, is well-known to be more favorable than a homogeneous nucleation process (corresponding to the latter event). However, this distinction applied to the system under study is not straightforward, because other processes can be important. For example, small CdS nuclei could be formed at the SiO_2 surface and then migrate to the solution, where an Ostwald mechanism would generate larger particles. The fact that encapsulation of the thermally treated SiO_2 particles (at 700 °C during 4 h) was more effective than that of the untreated counterparts, as shown in Figure 3b and c, led us to conclude that a surface-nucleated process is predominant for the formation of the CdS nanocrystals.

It was found that the $\text{SiO}_2\text{@CdS}$ particles can be covered by a SiO_2 shell simply by using the Stöber method employed to obtain the SiO_2 spheres. The coating process of $\text{SiO}_2\text{@CdS}$ was monitored using XPS measurements (Figure 6). As expected, the Cd and S peaks assigned to the CdS phase are present in the $\text{SiO}_2\text{@CdS}$ nanocomposites (Figure 6b) as compared to the naked SiO_2 particles (Figure 6a). The XPS measurements performed for $\text{SiO}_2\text{@CdS}$ particles covered with a SiO_2 layer showed Cd and S peaks that were considerably less intense when compared with the Si peak (Figure 6c). This SiO_2 coating was confirmed by TEM measurements, although aggregation of the particles also occurred to some extent by applying directly the Stöber method to the "as-prepared" $\text{SiO}_2\text{@CdS}$ nanocomposites. The previous chemical surface treatment of the $\text{SiO}_2\text{@CdS}$ nanocomposites might improve their final morphological properties, following similar procedures described in the literature.²⁷ Moreover, surface treatment using the appropriate capping molecules would make these nanocomposites compatible with organic matrices. The silica encapsulation of semiconductors and metal nanocrystals has recently been reviewed.¹ The importance of silica encapsulation of inorganic particles has been long recognized. For example, in the pigments industry, some inorganic pigments require a stabilization step, consisting of coating of the pigment using a robust chemical material such as SiO_2 or

(24) Chestnoy, N.; Harris, T. D.; Hull, R.; Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 3393.

(25) Liu, B.; Xu, G. Q.; Gan, L. M.; Chew, C. H. *J. Appl. Phys.* **2001**, *89*, 1059.

(26) Shirakawa, H.; Komiyama, H. *J. Nanopart. Res.* **1999**, *1*, 17.

(27) Correa-Duarte, M. A.; Giersig, M.; Liz-Marzán, L. M. *Chem. Phys. Lett.* **1998**, *286*, 497.

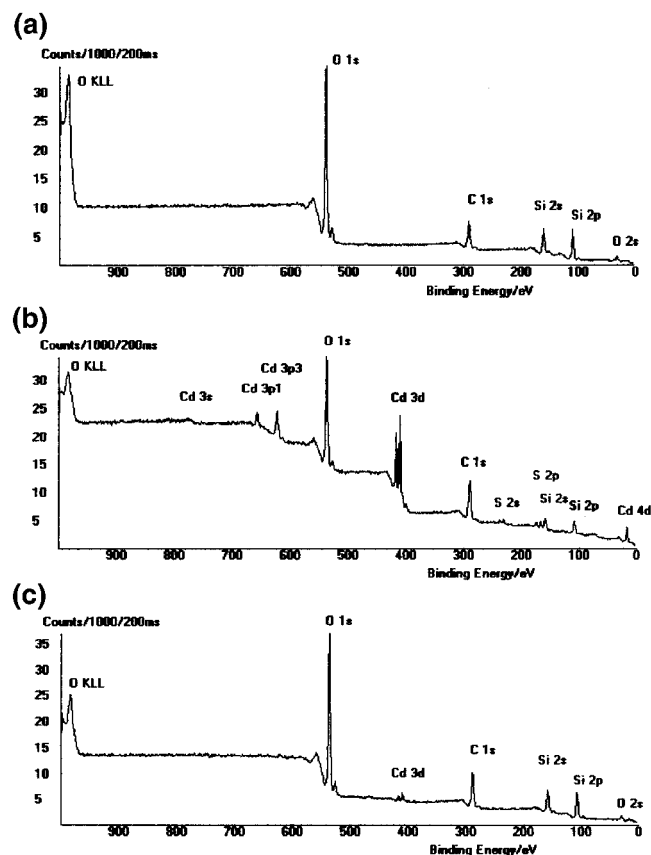


Figure 6. XPS spectra: (a) SiO_2 , (b) $\text{SiO}_2\text{@CdS}$, and (c) SiO_2 -coated $\text{SiO}_2\text{@CdS}$.

Al_2O_3 .²⁸ There are obvious reasons for producing coated pigment particles, such as chemical protection of the core or improvement of its thermal stability. In the particular case of the $\text{SiO}_2\text{@CdS}$ materials reported here, there are additional advantages. In fact, the disordered surface of the semiconductor is passivated

by amorphous phase-filling surface defects, hence promoting the optical properties of the material²⁹ and enhancing its photochemical stability.²⁷ Also, the toxic CdS phase is not available for direct contact with biological systems.

Conclusions

In summary, $\text{SiO}_2\text{@CdS}$ nanocomposites can be prepared using a single-source method under mild conditions. This method establishes an alternative route for the preparation of nanocomposites based on a semiconducting phase on submicrometric SiO_2 particles. Moreover, it was observed that the nanocomposites obtained by this method show properties distinct from those of the analogues prepared by traditional synthetic routes such as coprecipitation. Mechanistic studies using these types of systems would be of great interest from both technological and purely academic perspectives. In fact, the mechanism involved would probably make use of our actual knowledge of the reactivity of soluble molecular species at the surfaces of a heterogeneous system to form a crystalline solid phase. The mild temperatures employed in the synthetic method reported here are compatible with the preparation of inorganic/organic hybrid materials, for example, by blending the capped $\text{SiO}_2\text{@CdS}$ particles with polymers.

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CM011257E

(28) *Industrial Inorganic Pigments*, 2nd ed.; Buxbaum, G., Ed.; Wiley-VCH: New York, 1998.

(29) Bruchez, M., Jr.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013.