Synthesis and characterization of a sol-gel derived ureasilicate hybrid organic-inorganic matrix containing CdS colloidal particles.

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Abstract

A hybrid organic-inorganic material filled with *in situ* generated inorganic particles has been synthesised by the homogeneous precipitation of CdS from aqueous solutions of $Cd(NO_3)_2$ and CH_3CSNH_2 . These highly transparent, homogeneous and flexible CdS doped xerogels were prepared by the sol-gel technique using, as precursors, organically modified silicon alkoxide (3-isocyanatepropyltriethoxysilane) and a di-amine functionalized oligopolyoxyethylene (Jeffamine ED-600), which by subsequent hydrolysis and condensation processes formed a solid 3-D network. TEM studies indicate the presence of round nanoparticles around 20 nm in diameter dispersed in a homogeneous amorphous matrix. The samples were also characterized by spectroscopic (UV-visible and photoluminescence) and XRD techniques.

Keywords; CdS, Nanoparticles, Sol-gel, Ureasilicate, Photoluminescence

1. Introduction

Typical sol-gel derived organic/silica hybrids exhibit a combination of organic and inorganic components on a molecular scale. In contrast to conventional polymers, the formation of covalently bonded hybrid organic-inorganic polymeric materials requires the presence of functionalised reactive precursors. Chemical interaction between organically modified siloxanes containing an isocyanate (-NCO) group with amphiphilic polyether diols or polyether diamines give rise to transparent, rubber-like ureasilicate/urethanesil xerogels also known as ORMOSIL´s (organically modified silicates). During the last decade doping (during synthesis) with rare earth and

transition-metal ions to modify the thermal, magnetic, electrical and photoluminescence properties has been extensively studied [3-6].

Incorporation of semiconductor nanoparticles in transparent glassy-like matrix is of important due to their non-linear optical properties [7], i.e. use as non-linear optical filters, wave guides and optical limiters. However, attention must be paid to their stabilization, as nanosized materials possess a large specific surface area and can spontaneously aggregate due to Van der Waals interaction. To this end, inorganic glasses, polymers and zeolites have been used as stabilizing media [8-10] and semiconductor silicate glasses, produced by the low-temperature sol-gel technique, have been fabricated [11]. Only a few papers, however, have considered the doping of semiconductor nanoparticles in hybrid organic-inorganic matrices [12-14]. In this work CdS nanoparticles were synthesised by the homogeneous precipitation process and immobilized in a hybrid organic-inorganic host medium. The synthesis involved the formation of CdS nanoparticles *in situ* in the ureasilicate sol and the subsequent densification to provide a protecting medium, preventing the aggregation and oxidation of the particles.

2. Experimental procedures

The precursors, O,O´-bis(2-aminopropyl)-polyethylene glycol-500 (Jeffamine ED-600, Fluka) and 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich) were dried under dynamic vacuum before use. Tetrahydrofuran (THF, Merck), cadmium nitrate tetrahydrate (Riedel-deHaën), thioacetamide (TAA, Fluka) and concentrated ammonia solution (25 % w/w, Pronalab) were used as received. Synthesis involved a stoichiometric proportion of 1 mole of Jeffamine ED-600 (500 µL, 0.875 mmol) to 2 moles of ICPTES (435 µL, 1.76 mmol) mixed, together with 0.5 mL of THF, in a closed glass flask under stirring (300 rpm) at room temperature, until a transparent and homogeneous solution was obtained.

Aqueous solutions of $Cd(NO_3)_2.4H_2O$ and thioacetamide of differing concentrations (described in Table 1) were freshly prepared using high purity water. A mixture of 500 µL of thioacetamide solution and 250 µL of ammonia solution was added drop-wise. The mixture initially showed a high turbidity and gradually became transparent and homogeneous. At this point 500 µL of cadmium solution was slowly added. The solution aspect changed instantaneously, from pale yellow and transparent to bright yellow and turbid (depending on the quantity of reactants), indicating the

formation of CdS particles. This mixture was then poured into Teflon moulds, covered with Parafilm and kept at 8C for a week. Flat and uniformly transparent/translucent disks of *ca.* 1 mm thickness and a diameter of 25 mm were obtained. Disks without cadmium sulphide were prepared by the same procedure. Samples containing TAA or U(600)TAA were obtained by adding 500 μL of TAA, 250 μL of ammonia solution and 500 μL of water to the ureasilicate sol. Pure samples or U(600) were prepared by adding 1 mL of water and 250 μL of ammonia solution to the sol. The sample composition (shown in Table 1) are described by the $U(600)_nCdS$ empirical formula, where *n* represents the mole ratio between ureasilicate and cadmium nitrate. Powdered CdS was precipitated from a water-THF mixture with the same cadmium nitrate, TAA and ammonia solutions used for the preparation of sample (III) and collected on a 0.45 μm porosity cellulose acetate filter.

INSERT TABLE 1

Characterization involved a Philips CM20 Transmission Electron Microscope (point resolution 0.26 nm) with the samples for the TEM first milled to a fine powder, mixed with butanol and treated in ultra sonic bath. A drop of this suspension was placed on a metal grid supported by Formvar film, which was then placed in the microscope. X-ray diffraction patterns were obtained with a Philips Analyzer X-ray PW 171, at counting time of 10 sec per 0.04º, using Cu-α radiation. Absorption (UV-Vis) and luminescence spectra were recorded, at room temperature, on a Shimadzu UV-2501 PC and Spex Fluorolog spectrophotometers respectively. The latter were done using a 420 nm excitation wavelength, front face geometry and a bandpass of 1.7 nm. The spectra were corrected for photomultiplier response.

3. Results and discussion

Figure 1 shows XRD patterns of CdS doped ureasilicate matrices and precipitated CdS. The diffraction spectrum of CdS powder was performed for comparison purposes and displays a broad peak around 26.7º relating to (100), (002) and (101) crystal plane reflections. These were found by deconvolution of overlapping peaks using a pseudo-Voigt function (also shown in the figure). These planes are assigned to the hexagonal modification of CdS (α-CdS), although some lines can be attributed to cubic

modification (β-CdS), which does not exclude the existence of both crystalline structures in the precipitate.

INSERT FIGURE 1

The XRD patterns of CdS free samples U(600) and U(600)TAA exhibit a broad halo at *ca.* 21.2º, confirming an amorphous character. The spectra of the doped ureasilicate matrices with lower CdS content (samples (I) (II) and (III)) do not show any peaks that could be assigned to microcrystalline CdS, although a large sample thickness and XRD time exposition were used. This behaviour indicates that the CdS particles are predominately amorphous, but further studies are necessary to elucidate this aspect. Samples (IV) and (V), with higher CdS content, present some features of a crystalline phase, as expressed by the changes of the shape of the halo at angles coincident with that observed for CdS powder.

INSERT FIGURE 2

The TEM image of the ureasilicate sample with the lowest CdS content (sample I) is shown in Figure 2. Particles with a round shape and mean diameter between 20-25 nm are clearly seen and are interpreted as colloidal CdS. TEM analysis data shows that the particle size distribution and morphology of CdS depends on the initial cadmium nitrate and TAA concentrations. We found that, after investigation of samples I and III (not shown) increasing these concentrations makes the particles exhibit a polygonal shape, with a size range from 20 to 50 nm.

INSERT FIGURE 3

The measurements of the absorption spectra are depicted in Figure 3, where absorbance has been normalized to sample thickness. The pure matrix of U(600) is transparent in the visible range, but the matrices with TAA and U(600)TAA show a strong absorption edge around 300 nm, resulting from non hydrolyzed thioacetamide. Samples (I), (II) and (III) display well defined absorption onsets and good transparency in lower energy range, where a gradual increase is seen with CdS fraction. The absorption onset of the CdS doped samples is situated near 495 nm, but no evidence of

size quantisation is observed, as the absorption edge is close to that of CdS [15]. Samples (IV) and (V) exhibit a significant degree of scatter, which increases with CdS concentration, accompanied by a small apparent shift of the absorption band towards higher wavelength. The basic difference between these two sets of samples arises from the increasing number of CdS particles formed, with the possibility of a larger size range, from the possible formation of aggregates. Separation of the CdS fraction as a discrete phase in the matrix has also been visually observed under these experimental conditions. This is not surprising, because from Smoluchowski's work [16] stable sols require the mixing of dilute solutions.

The photoluminescence (PL) spectra of the U(600)TAA and CdS doped ureasilicate samples, excited at 420 nm, are shown in Figure 4. The pure matrix and the matrix with TAA exhibit a similar broad (lower wavelength) emission peak, centred at 480 nm, which coincides with the peak emission of pure Jeffamine and is due to the lone pair electrons on the NH- groups [17].

INSERT FIGURE 4

Two emission bands can be identified in the samples containing CdS particles, while the PL emission from the CdS powder (not shown) was found to be negligible. Samples (I), (II) and (III) show a broad emission band at 730 nm and pronounced Stokes' shift with respect to the absorption edge. The emission band in the lower wavelength region clearly originates from the matrix and exhibits a substantial decrease in intensity and an apparent red shift with the increase in CdS fraction. This can be explained by the increase in absorption which acts as a filter to the luminescence (inner filter effect), although the front face geometry should help minimise this artefact. The PL data of the last two samples (IV and V) are not included in the plot because of this distortion caused by their high absorption. Unfortunately, because of the sample geometry and high values of absorption, a realistic correction for the inner filter effect [18] and hence quantitative analysis was not possible, but (for (I), (II) and (III)) its influence should only be present in the lower wavelength (matrix emission) region where there is an overlap of the PL with the absorption spectrum.

The 730 nm emission of CdS nanoparticles has been related to a recombination mechanism involving trapped electron/holes at surface defects [19], which originates from the sulphur vacancies (uncompensated cadmium atoms). The substantial decrease

in the 730 nm band with increase of the CdS concentration seen in Figure 4 may be explained by protection given by the matrix and for the lower concentrations used in this study it is an effective barrier against aggregation. However with the higher concentrations the particles can associate, which leads to larger dispersion in their size and shape and an apparent decrease in PL efficiency. The high-energy band to band transition, which is sharp and is located near the absorption edge of the semiconductor material, is not observed because of the low degree of crystallinity of the particles. The position of the native emission of the ureasilicate matrix could be another obstacle this peak to be detected.

4. Conclusion

A hybrid organic-inorganic ureasilicate matrix was doped, *in situ,* with CdS nanoparticles prepared by homogeneous precipitation. Characterisation of the final solid host confirmed the presence of homogeneously distributed CdS particles. The matrix exhibited the ability to prevent (up to a reasonably high concentration) the colloidal CdS phase from undergoing further aggregation and sedimentation. This methodology is adept for the fabrication of clear, high transparent and flexible samples with potential application as flexible cut-off filters in the visible range of the spectrum. The same approach can be adapted for use with other low solubility metal chalcogenide salts.

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Table and Figure captions

Table 1. Concentration of stock solution and sample composition.

Figure 1. X-ray diffraction patterns of the ureasilicate matrix with different CdS concentration and the pure CdS powder, with deconvoluted peak around 26.7°. Hexagonal structure (solid arrows), cubic structure (dotted arrows).

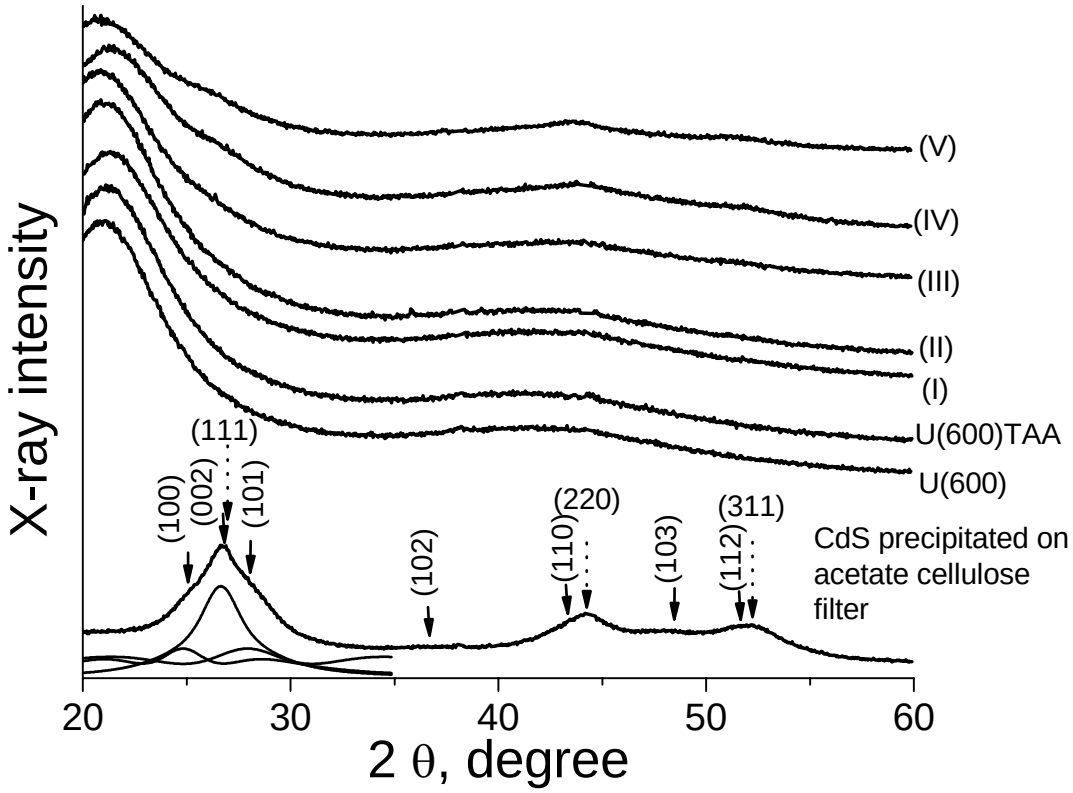
Figure 2. TEM photograph of the sample (I), $U(600)_{175}CdS$. The void can relate to the procedure for producing the TEM sample.

Figure 3. UV-vis absorption spectra of CdS doped (I to V) and undoped samples (U(600) and U(600)TAA).

Figure 4. PL spectra of CdS doped (I to III) and an undoped sample, U(600)TAA. Excitation was at 420 nm.

Table 1. Concentration of stock solution and composition of prepared samples.

Sample	[Cd^{2+}] (mol L^{-1})	[TAA] (mol L^{-1})	Empirical formula
pure matrix	-	-	U(600)
TAA doped matrix	-	0.100	U(600)TAA
I	0.010	0.010	$U(600)_{175}CdS$
II	0.025	0.025	$U(600)_{70}CdS$
III	0.050	0.050	$U(600)_{35}CdS$
IV	0.075	0.075	$U(600)_{23}CdS$
V	0.100	0.100	$U(600)_{18}CdS$



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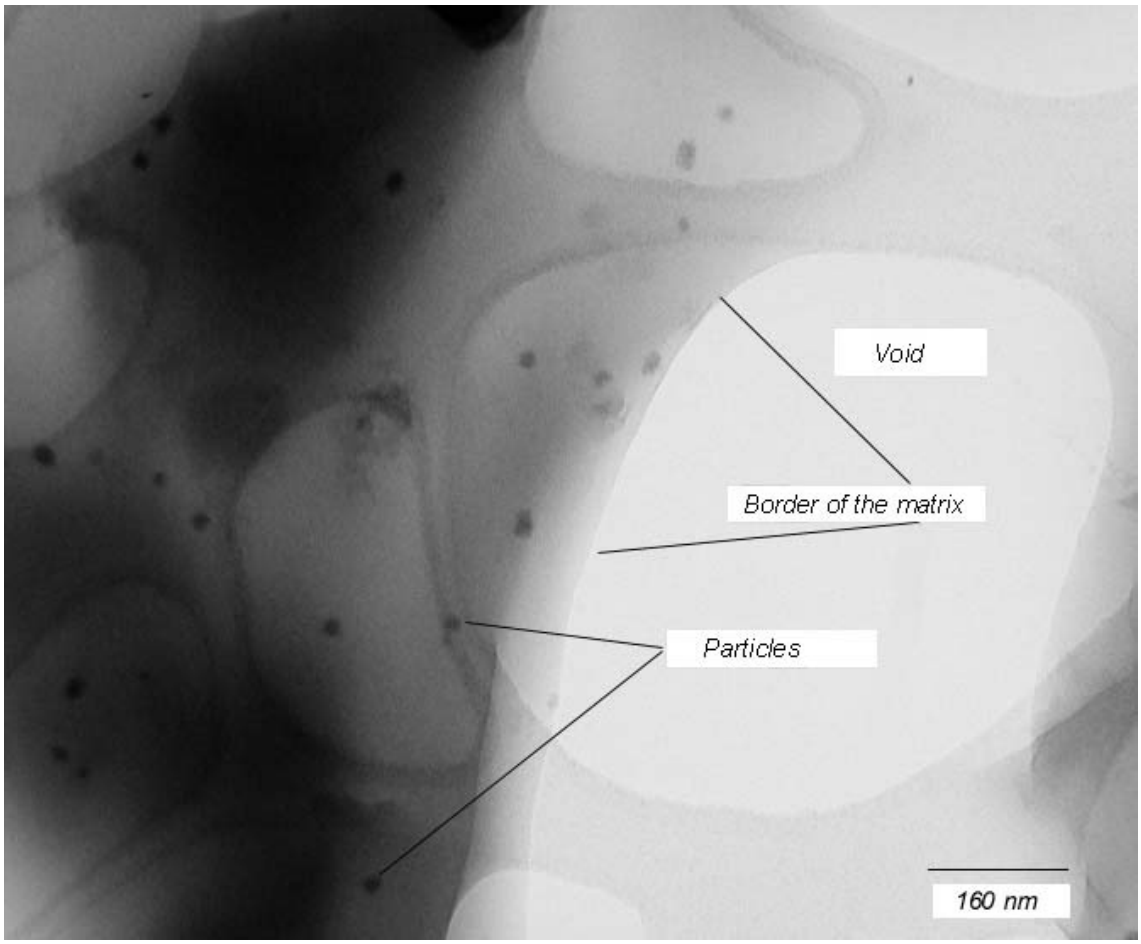

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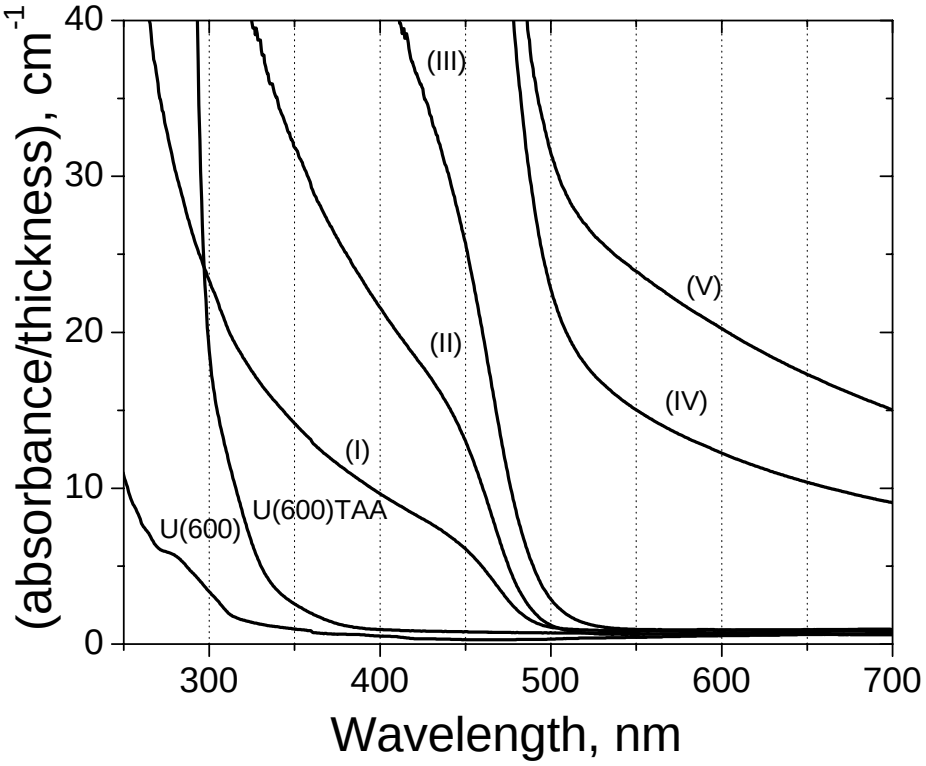

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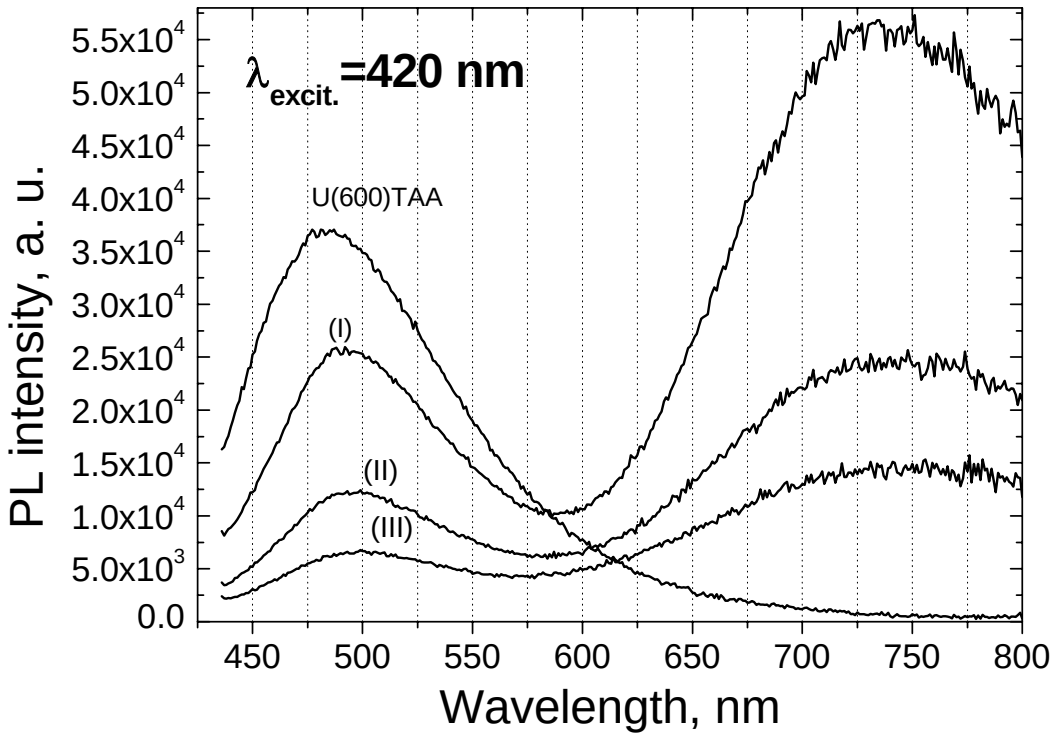

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