Synthesis of solid solutions of Cd$_{1-x}$Zn$_x$S nanocrystals in the channels of mesostructured silica films

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In this contribution, we introduce the use of metal ion (Cd(II) and Zn(II)) modified mesostructured silica as a reaction medium, to produce a solid solution of Cd$_{1-x}$Zn$_x$S nanocrystals as a thin film. With this approach, a true liquid crystalline templating (TLCT) and liquid crystalline mesophase of transition metal salt: oligo(ethylene oxide) non-ionic surfactant ((1-x)[Cd(H$_2$O)$_6$](NO$_3$)$_2$ + x[Zn(H$_2$O)$_6$](NO$_3$)$_2$): CH$_3$(CH$_2$)$_{11}$(OCH$_2$CH$_2$)$_6$OH, (MLC)), systems were collectively used to synthesise mesostructured silica films. The film samples were reacted at room temperature (RT) in an H$_2$S atmosphere to produce zinc blend Cd$_{1-x}$Zn$_x$S nanocrystals in the channels of mesostructured silica. The initial Zn(II) and Cd(II) ion concentrations in the reaction media determine the final composition and band gap of the Cd$_{1-x}$Zn$_x$S nanocrystals. The growth process of the Cd$_{1-x}$Zn$_x$S nanocrystals in the pores is influenced by the silica walls. If the walls are rigid (well polymerized, obtained by aging the samples before H$_2$S treatment), then the Cd$_{1-x}$Zn$_x$S nanoparticles are smaller in size and more uniform in size distribution.

Introduction

The modification of the internal surface of existing mesoporous materials$^1$ and the synthesis of new mesostructured materials with optical, magnetic and catalytic components are emerging fields in materials chemistry.$^2$–$^10$ Mesoporous materials have regular and tunable pores with large surface areas. Modifying the surface with optical, magnetic and catalytic materials will prove beneficial in various applications. There are many methods described in the literature for modifying the surface of mesoporous materials with active materials. Chemical vapor deposition,$^6$ ion-exchange,$^7,8$ impregnation,$^9,10$ true liquid crystalline templating (TLCT),$^{11,12}$ functionalizing the pore walls with organic groups to incorporate various nanocrystals into the pores,$^{13}$ doping mesopores with quantum dots,$^{14}$ etc. are some examples of the methods. Using various approaches, CdS, ZnS, Zn$_{1-x}$Mn$_x$S, and Cd$_{1-x}$Mn$_x$S nanoparticles have also been synthesized in the channels of mesoporous silica.$^7–10,12,15–18$

In this article, we focus on the TLCT approach that uses C$_x$EO$_m$ non-ionic surfactants in a lyotropic liquid crystalline (LLC) mesophase as the templating agent.$^{11}$ A mixture of surfactant, acid (as a catalyst), tetraceneammoniumsalicylate (TMOS, as silica source) and water first produces a liquid mixture that undergoes a transformation, with hydrolysis and condensation, of the silica source to form an LC mesophase and then with further polymerization a solid phase. Mesostructured metal sulfides$^{19–21}$ and metals$^{22,23}$ have also been synthesized using the TLCT approach. As an extension to the use of the LLC mesophase, we have introduced a new metal ion containing liquid crystalline (MLC) mesophase$^{24,25}$ that consists of transition metal salts (TMS) and non-ionic surfactants, C$_x$EO$_m$. The MLC mesophase can be used in the context of TLCT to introduce transition metal ions into mesostructured silica in a one pot synthesis.$^{12}$ The method described here is quite flexible in that more than one type of transition metal ion can be incorporated at once. This is an important step in incorporating optical and magnetic components into wide band gap semiconductors in the channels of the mesostructured materials in one pot. Furthermore, the structure of the MLC mesophase can be controlled using the salt concentration, ionic strength and the type of counter anion in the medium.$^{12,25}$ For example, the nitrate salts of TMS with C$_x$EO$_m$ produce a 2D hexagonal mesophase, however introducing about 10% water changes the structure to a 3D hexagonal mesophase and further increases in the water concentration produce a micelle solution.$^{25}$ The perchlorate salts usually produce cubic mesophases.$^{25}$ Combining the TLCT approach with the MLC mesophase has the advantage in that it enhances the structural and component flexibility of the final materials.

Cd$_{1-x}$Zn$_x$S are direct gap semiconductor materials that are promising for high density optical recording, blue or even UV laser diodes.$^{26,27}$ The solid-solution behavior of Cd$_{1-x}$Zn$_x$S nanocrystals has been observed in various media.$^{28–31}$ The band gap of Cd$_{1-x}$Zn$_x$S has an almost linear dependence on the composition, x, and can be tuned between the band gaps of the CdS and ZnS materials.$^{28,29}$ The particle size also plays an important role in determining the band gap of the final materials due to the quantum confinement effect.$^{32}$

In this contribution, the mesostructured silica materials modified with Cd$_{1-x}$Zn$_x$S nanoparticles were characterized...
using UV-Vis absorption (in transmittance mode), XRD method, POM and TEM microscopy techniques.

**Experimental**

**Synthesis of Cd$_{1-x}$Zn$_x$S in mesostructured silica**

Various amounts, $1 - x$ (0.493 to 0.0 g) and $x$ (0.0 to 0.475 g) of the [Cd(H$_2$O)$_4$](NO$_3$)$_2$ and [Zn(H$_2$O)$_6$](NO$_3$)$_2$ salts, respectively, were dissolved in 3 ml of H$_2$O that was acidified using 0.10 g of concentrated nitric acid (70%). To this mixture, first 1.00 g of C$_{12}$EO$_{10}$ and then 1.60 g of TMOS were added at once. Either gentle heating or simple shaking homogenized the resulting liquid mixture. The film samples were prepared by dip coating with a coating speed of 0.4 mm s$^{-1}$ over glass, quartz and silicon surfaces for various measurements. The Cd$^{2+}$ and Zn$^{2+}$ containing mesostructured materials were prepared by varying the Zn$^{2+}$ mole fraction from 0.0 to 1.0 and with a M$^{2+}$/C$_{12}$EO$_{10}$ (M$^{2+}$ is the total number of Zn$^{2+}$ and Cd$^{2+}$ ions) mole ratio of 1.0. Then, the film samples were reacted in an evacuated reaction chamber under 50–150 Torr of H$_2$S gas. This process usually produces stable transparent nanoCd$_{1-x}$Zn$_x$S-mesoSiO$_2$ composite materials. Some of the film samples were aged before H$_2$S reaction at various temperatures (between RT and 240 °C) by slow heating (for 45 minutes) and heating at the desired temperature for a certain period of time (see Results and discussion).

**Characterization**

Polarized optical microscopy (POM) images were obtained in transmittance mode on a Meije Techno ML9400 series Polarising Microscope with transmitted light illumination, using convergent white light between the parallel and crossed polarizer. X-Ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer using a high power Cu-K$_{α}$ source operating at 30 kV and 15 mA. The XRD patterns were recorded in low and high angle regions to monitor both the mesophase and Cd$_{1-x}$Zn$_x$S nanocrystals, respectively. UV-Vis spectra were recorded using a Varian Cary 5 double beam spectrophotometer with 150 nm min$^{-1}$ speed with a resolution of 2 nm over a wavelength range from 700 to 200 nm in transmittance mode. The UV-Vis absorption spectra were obtained from the film samples of nanoCd$_{1-x}$Zn$_x$S-mesoSiO$_2$ materials. TEM images were recorded on a Hitachi HD-2000 STEM operating at 200 kV and 30 mA and a Philips 430 microscope with an accelerating voltage of 100 kV. The samples were prepared by dispersing the powder/fragments onto a carbon film-supported 200 mesh copper grid or embedded in epoxy resin and microtome. $^{29}$Si MAS-NMR (magic angle spinning nuclear magnetic resonance) proton coupled spectra were recorded using a Bruker DSX 400 spectrometer with a recycle delay time of 100 s. Samples were spun at 5000 Hz, the chemical shift values were reported with respect to tetramethyldisilane.

**Results and discussion**

The hydrolysis and condensation of tetramethyloorthosilicate (TMOS, 1.6 g) in a solution of water, nitric acid and C$_{12}$H$_{25}$(OCH$_2$CH$_2$)$_{10}$OH (denoted C$_n$EO$_m$) with compositions of 3.0 g : 0.1 g : 1.0 g, respectively, produce a liquid crystalline mesophase that transforms to mesostructured silica over time. Adding a certain amount of metal salt into the above mixture does not interrupt the process. However, the salt concentration and salt type influence the structure of the silicatropic LC mesophase (and as a result, the structure of the silica materials). At low salt concentrations (0.0 to 1.0 salt/surfactant mole ratios), the silicatropic LC mesophase (in early stages) and mesostructured silica (after aging the mixture for several hours) have hexagonal structures that change to cubic structures at higher salt concentrations. The same change happens at a much lower concentration of perchlorate salts. Note also that the mesophase is disordered in a [M(H$_2$O)$_6$](NO$_3$) : C$_{12}$EO$_{10}$ system at salt/surfactant mole ratios between 0.0 and 1.0. However, the [M(H$_2$O)$_6$](NO$_3$) : C$_{12}$EO$_{10}$ binary mixtures have a 2D hexagonal mesophase at salt/surfactant mole ratios between 1.2 and 3.2. Therefore, the silica species that is forming in the early stages in the reaction medium behave similarly to the salt ions and organize the surfactant molecules into a LC mesophase and eventually into mesostructured silica materials.

This work focuses on mixed salt systems (where salts are [Cd(H$_2$O)$_4$](NO$_3$)$_2$ and [Zn(H$_2$O)$_6$](NO$_3$)$_2$) with a medium salt concentration (total salt/surfactant mole ratio of 1.0), where the mesostructured silica film is ordered. The film samples (represented as Cd(II)$_{1-x}$Zn(II)$_x$-mesoSiO$_2$) were prepared by varying the Zn$^{2+}$ mole fraction, $x$, between 0.0 and 1.0 with increments of 0.1. Fig. 1 shows a typical POM image of a relatively thick film sample. Note that the film samples in all compositions are birefringent between the crossed polarizers. The POM images display similar schlieren textures, characteristic of the columnar structures (see Fig. 1). Fig. 2 shows a series of XRD patterns recorded from the film samples. All the film samples display similar X-ray diffraction patterns between 1.0 and 5.0° 20, characteristic of oriented mesostructured silica (one very strong line at around 1.77° and a very weak one at 3.50° 20). However, crushed samples obtained from thicker films and/or monoliths display up to 4 diffraction lines at 1.77°, 2.00°, 2.48°, and 2.91° 20.

![Fig. 1 A typical polarized optical microscopy image of a [Cd(H$_2$O)$_4$](NO$_3$)$_2$-mesoSiO$_2$ thick film.](image)
Cared the allowed diffraction planes) in the \( \text{Cmm} \) rectangular structures.\( \text{P} \) and 240 aging of the films was systematically investigated between RT to the desired temperature for 45 minutes and kept at this temperature controlled oven under laboratory conditions from film samples are prepared. The film samples were heated in a hydrothermal treatment of the as-synthesized sample with transformation was observed in the P123 mesostructured silica systems.\( \text{P} \) It appears that in our monoliths we have a mixture of both phases.\( \text{P} \) Note that the \( (h+k) = 2n + 1 \) lines are forbidden \( ((h+k) = 2n \) are the allowed diffraction planes) in the \( \text{C2mm} \) space group.\( \text{P} \) The unit cell parameters \( (a = 88.2 \text{ Å} \) and \( b = 60.3 \text{ Å}, \) with \( ab = 1.4635 \) and the plot of the \( d \)-spacing versus the \( hk \) relation, obtained from \( 1d^2 = k^2a^2 + l^2b^2, \) are consistent with the 2D rectangular structure.\( \text{P} \) Note also that a similar transformation was observed in the P123 mesostructured silica systems.\( \text{P} \) It appears that in our monoliths we have a mixture of both phases.\( \text{P} \) However, the film samples display a very strong diffraction line at around 1.77–20 that is extremely sensitive to aging. The aging of the films was systematically investigated between RT and 240 °C to optimize the conditions in which the transparent film samples are prepared. The film samples were heated in a temperature controlled oven under laboratory conditions from RT to the desired temperature for 45 minutes and kept at this temperature from 30 minutes to 3 days.\( \text{P} \) The aging gradually increases the silica condensation (silanol, –SiOH, groups into –SiOSi–, see NMR section below) and shrinks the silica walls to make the silica walls more rigid. For example, the diffraction line shifts from 1.77 to 1.88 and to 2.38 20 upon aging at 100 °C for 2 hours and at 240 °C for 2 hours, respectively, Fig. 4. Notice also that there is a deviation from the trend of the shifts at 240 °C; this is most likely due to the burning of the surfactant molecules at around 240 °C. Aging the samples at each temperature for a longer duration shifts the diffraction line to an even higher angle at each temperature. For example, this line shifts up to 2.57 20 at 240 °C aging for 1 day. The aging process was also followed using \( ^{29}\text{Si} \) NMR spectroscopy. The \( ^{29}\text{Si} \) MAS-NMR spectra of the samples display 3 peaks at \( \delta = -91, -101, \) and \(-110 \) ppm with respect to tetramethyisilane due to Si(OH)\(_2\)(OSi)\(_2\) (Q\(_2\)), Si(OH)(OSi)\(_3\) (Q\(_3\)) and Si(OSi)\(_4\) (Q\(_4\)) units, respectively.\( \text{P} \) The trend in the spectra shows that the Q\(_2\) band at \(-110 \) ppm increases in intensity with increasing aging temperature, indicating further condensation of the silanol groups.

The fresh and aged samples were exposed to an H\(_2\)S atmosphere in a closed evacuated reaction chamber to convert all Cd(II) and Zn(II) metal ions (Cd(II)\(_{1-x}\).Zn(II)\(_{x}\).mesoSiO\(_2\)) into Cd\(_{1-x}\).Zn\(_x\)S in the silica channels (represented as nanoCd\(_{1-x}\).Zn\(_x\)S–mesoSiO\(_2\)). The EDX elemental analysis of the H\(_2\)S treated samples and their initial salt concentrations in

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**Fig. 2** The XRD patterns of the film samples of a) \([\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2\text{-mesoSiO}_2\), b) \((\text{Cd}(\text{II}))_{0.7}(\text{Zn}(\text{II}))_{0.3}\text{-mesoSiO}_2\), c) \((\text{Cd}(\text{II}))_{0.4}(\text{Zn}(\text{II}))_{0.6}\text{-mesoSiO}_2\) and d) \((\text{Zn}(\text{H}_2\text{O})_6)(\text{NO}_3)_2\text{-mesoSiO}_2\).

**Fig. 3** (A) XRD pattern of a monolith (thicker film) of \([\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2\text{-mesoSiO}_2\) crashed into powder. (B) Plot of \( d \)-spacing obtained from (A) versus \( hk \) relation obtained from \( 1d^2 = k^2a^2 + l^2b^2 \).
the mesostructured silica correlate with each other. The metal ion/sulfur mole ratio after the \( \text{H}_2\text{S} \) reaction is obtained from EDX measurements to be around 1.0 in all samples, also indicating the formation of the \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) particles in the mesostructured silica matrix.

The sharp diffraction line at around 1.77° (49.9 Å) shifts to 1.58° (55.9 Å) and becomes broader in the fresh samples, indicating an enlargement of the silica repeating distances (due to the soft nature of partially polymerized silica walls) and disorder in the pores, and/or the formation of \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) nanoparticles in the channels, respectively, Fig. 5. However, the aged samples do not show any shift or broadening with the \( \text{H}_2\text{S} \) reaction, indicating that the silica walls are quite rigid and limit the growth of the \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) nanoparticles, Fig. 5. Note also that the samples aged at RT for 1 day or more and the samples aged at higher temperatures become resistant to the growth of the \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) nanocrystals.

Fig. 6 and 7 display TEM images of the fresh and aged film samples upon the \( \text{H}_2\text{S} \) reaction. The images show channels in the mesostructured silica and nanocrystals of \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) in the channels after \( \text{H}_2\text{S} \) treatments. The oriented channels and channel dimensions are consistent with the XRD results. Fig. 6(A) shows a dark field image of a portion of a relatively thicker modified silica particle of a fresh 1 : 1 \( \text{Cd(II)} \) and \( \text{Zn(II)} \) sample, which was reacted under \( \text{H}_2\text{S} \) gas, indicating spots (aggregates) of \( \text{Cd}_0.5\text{Zn}_0.5\text{S} \) nanoparticles. The image in Fig. 6(B) clearly shows that these spots consist of ultra-small nanoparticles (see also discussion on UV-Vis absorption spectroscopy and XRD). The changes in the XRD pattern in the small angle regions after the \( \text{H}_2\text{S} \) treatment (Fig. 5) and the TEM image in Fig. 6(A) (aggregation) collectively show that the \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) nanoparticles are forming inside the silica channels and are causing an enlargement of the silica pores in the fresh film samples. However, the aged samples display unaltered, sharp diffraction lines before and after the \( \text{H}_2\text{S} \) reaction. The TEM images in Fig. 7 also show that the nanoparticles are homogeneously distributed with a uniform size distribution in the silica matrix in the aged samples.

The XRD pattern in the high angle region displays changes depending on the \( \text{Zn(II)}/\text{Cd(II)} \) ratios of the [\( \text{M(H}_2\text{O)}_n\](\text{NO}_3)_2 \)-meso\( \text{SiO}_2 \) upon \( \text{H}_2\text{S} \) treatment, Fig. 8(A). The high angle regions of the diffraction patterns were recorded using relatively thicker film samples, which were prepared on silicon wafers to improve the signal to noise ratio. The Si (200) line observed at 32.96° 2\( \theta \) was used as an external reference to obtain the unit cell parameters of the \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) nanocrystals. The (111), (220) and (311) diffraction lines of the zinc blend structure of the \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) nanocrystals are observed at...
around 26.40, 44.00 and 52.60°, respectively, from the nanoCdS–mesoSiO2. These diffraction lines gradually shift to higher angles going from CdS to ZnS in the Cd1–xZnxS nanocrystals, Fig. 8(A). The unit cell parameter, $a$, for the zinc blend structure correlates well with the composition, $x$, Fig. 8(B). The linear dependence of the unit cell parameter on the composition clearly indicates that the nanocrystals are forming a solid solution in the nanoCd1–xZnxS–mesoSiO2 films and monoliths.

The UV-Vis absorption spectra were recorded in transmittance mode for all film samples, Fig. 9(A), to elucidate the electronic properties of the nanocrystallites as well as to characterize them. The low energy absorption edge gradually blue shifts going from nanoCdS–mesoSiO2 to nanoZnS–mesoSiO2 film samples. The band gaps for each sample were evaluated using the linear fit of the absorption edge after plotting the spectra against the direct gap relationship, $(A\hbar^2/n) versus \hbar$ (where $A$ is absorbance and $\hbar$ is the energy in eV). The variation of the band gaps (from 2.63 eV in $x = 0.0$ to 4.05 eV in $x = 1.0$) of nanoCd1–xZnxS–mesoSiO2 with $x$ is shown in Fig. 9(B). Note that the blue shift from the bulk $E_g$ values, by 0.21 and 0.37 eV for the two end compositions CdS and ZnS, respectively, indicates that the particles are smaller at the Zn(II) rich end of the Cd1–xZnxS nanocrystals. This observation is consistent with the XRD patterns, in which the diffraction lines are broader at the Zn(II) rich end of the Cd1–xZnxS nanocrystals.

Recently, Sapra and Sarma37 evaluated the electronic structure of II–VI semiconductor nanocrystals (between 5 and 80 Å) using a modified tight-binding model (TBM), developed by the same group, for bulk II–VI semiconductors.38 The variations in the band gap difference between the nanocrystals and bulk crystals with the diameter of the nanocrystals were best fit to an empirical formula, $\Delta E_g = a_1e^{-d/b_1} + a_2e^{-d/b_2}$ (where $\Delta E_g$ is the difference between the band gaps of nanocrystals and bulk in eV, $d$ is the diameter of nanocrystals in nm and $a_1 = 2.83$ and 7.44, $a_2 = 1.96$ and 3.04, $b_1 = 8.22$ and 2.35, and $b_2 = 18.07$ and 15.30 for CdS and ZnS, respectively).37 Fig. 10(A) displays a plot of $\Delta E_g$ versus $d$ for the CdS and ZnS nanocrystals using the above empirical

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**Fig. 7** The TEM images of the aged (at 100 °C for 2 hours) film samples of nanoCd$_{0.3}$Zn$_{0.7}$S–mesoSiO$_2$: (A) a bright field image of a relatively thick sample and (B) a dark field image of a thinner cross section of another sample prepared under the same conditions.

**Fig. 8** The XRD patterns of nanoCd$_{1-x}$ZnxS–mesoSiO$_2$ of mesostructured silica films, where $x$ is (a) 0.00, (b) 0.25, (c) 0.50, (d) 0.85 and (e) 1.00. The sharp line at 32.96° is from the Si substrate (used as an internal reference). (B) A plot of the unit cell parameter, $a$, of the Cd$_{1-x}$ZnxS nanocrystallites (evaluated from the XRD patterns in (A)) versus composition, $x$, in nanoCd$_{1-x}$ZnxS–mesoSiO$_2$.
Notice that the variations in the band gap with respect to the particle size in both CdS and ZnS, are very similar. We assume that the variation in the nanoCd$_{1-x}$Zn$_x$S will also follow the same trend, given in Fig. 10(A). The size of nanoCd$_{1-x}$Zn$_x$S nanocrystals in mesoSiO$_2$ were evaluated using the plot in Fig. 10(A) and the $\Delta E_g$ was evaluated using the plots in Fig. 9(B). Fig. 10(B) displays the variation in the particle size of the nanoCd$_{1-x}$Zn$_x$S–mesoSiO$_2$ with $x$. Note that the variation in the particle size of our nanocrystals correlates with the observed deviation in the $E_g$ versus $x$ plots in Fig. 9(B). The CdS and ZnS nanoparticles are smaller but all the intermediate compositions have similar particle size, Fig. 10(B). Note also that the band gaps of the nanocrystals with intermediate compositions display an almost linear dependence (Vegard type plot) on the composition, indicating solid-solution behavior in nanoCd$_{1-x}$Zn$_x$S–mesoSiO$_2$.

The particle size of the nanocrystals were also evaluated using Scherrer’s formula ($D = 0.9 \lambda / B \cos \theta$, where $D$ is the diameter of the particles in Å, $\lambda$ is the wavelength of the X-ray source, 1.54078 Å, $B$ is the corrected full width at half maximum in radians and $\theta$ is half of the angle of diffraction of the (111) plane) and the XRD patterns of thicker film samples of nanoCd$_{1-x}$Zn$_x$S–mesoSiO$_2$. The particle sizes of Cd$_{1-x}$Zn$_x$S nanocrystals, obtained from Scherrer’s formula, are around 4.0 nm, consistent with the values obtained from the band gap (using the relation obtained from TBM). The findings from the UV-Vis absorption spectroscopy, TEM and XRD techniques collectively show that a solid solution is forming in the nanocrystals of Cd$_{1-x}$Zn$_x$S inside the channels of mesostructured silica.

The effect of aging the film samples was also investigated using UV-Vis spectroscopy after H$_2$S reaction. Trends in the UV-Vis absorption spectra of these samples also fall into two categories, fresh and aged. Fig. 11 displays UV-Vis absorption spectra of a fresh sample (aged for 15 minutes before the H$_2$S reaction) and two aged (one aged for 3 days at RT and another aged further at 240 °C for 45 minutes before H$_2$S reaction) samples after the H$_2$S reaction of the

![Graph](https://example.com/graph.png)

**Fig. 9** (A) UV-Vis absorption spectra of Cd$_{1-x}$Zn$_x$S nanocrystals in the mesostructured silica films (low energy end is pure CdS, high energy end is pure ZnS, the spectra in between the spectra of CdS and ZnS are from the Cd$_{1-x}$Zn$_x$S nanocrystals, where $x$ is increasing from 0.1 to 0.9 with an increment of 0.1 going from left to right). (B) Plots of band gap ($E_g$) versus $x$ of (a) nanoCd$_{1-x}$Zn$_x$S–mesoSiO$_2$; and (b) bulk materials obtained from empirical formula given in reference 36.

![Graph](https://example.com/graph.png)

**Fig. 10** (A) Plot of band gap shift ($\Delta E_g$) of CdS and ZnS obtained from an empirical formula ($\Delta E_g = a_1 e^{-d b_1} + a_2 e^{-d b_2}$, where $\Delta E_g$ is the difference between the band gaps of nanocrystals and bulk in eV, $d$ is the diameter of nanocrystals in nm and $a_1 = 2.83$ and 7.44, $a_2 = 1.96$ and 3.04, $b_1 = 8.22$ and 2.35, and $b_2 = 18.07$ and 15.30 for CdS and ZnS, respectively). The inset is the same plot showing the regions used in this work. (B) Plot of particle size evaluated from the plot in (A) versus $x$ in nanoCd$_{1-x}$Zn$_x$S–mesoSiO$_2$. 

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Fig. 11 The UV-Vis absorption spectra of H2S treated films of [Cd(H2O)4](NO3)2–mesoSiO2 (Cd2+/C12EO10 ratio is 1.0 in all samples): (a) a relatively fresh film sample (aged for only 1 hour), (b) sample aged for 3 days, and (c) the 3 days aged sample after further aging at 240 °C. The inset is a plot of (Absorbance × Energy (eV))² vs. Energy (eV) of the three samples in (a), (b) and (c).

[Cd(H2O)4](NO3)2–mesoSiO2. The optical band gaps of the nanoCdS–mesoSiO2 shift from 2.63 eV (at RT) to 2.78 eV (at 240 °C), respectively, corresponding to 4.3 nm and 3.3 nm CdS nanoparticles, see inset in Fig. 11. Fig. 12 shows a series of absorption spectra recorded from the film samples aged at RT and 100 °C for different periods of time. In addition to a blue shift in the absorption edge, the spectrum of the aged sample displays a relatively sharp absorption edge with some structure (discrete like energy levels), indicating smaller particles and a uniform size distribution of the CdS nanoparticles in the aged silica channels. Notice that the prolonged heating at 100 °C causes broadening on the absorption edge, Fig. 12. The blue shift on the absorption edge, and the shift of the X-ray diffraction line with aging at RT and higher temperatures are consistent with each other, see Fig. 12 and 4, respectively. Therefore, the rigidity of the silica walls is important in the growth process and the size distribution of the Cd1−xZn,S nanoparticles in the channels of the mesostructured silica films. Both XRD patterns and UV-Vis absorption spectra indicate that the nanoparticles are relatively smaller in the aged matrix and have a more uniform size distribution. We are currently investigating the matrix effect of the growth, particle size and size distribution in a much softer environment, such as an LC mesophases of salt : CnEOm systems.21

Conclusion

In this work, we have developed a new and simple method to produce Cd1−xZn,S nanocrystals in the channels of mesostructured silica. The Cd(II) and Zn(II) ions can be homogeneously incorporated into the channels of mesostructured silica thin films using the TLCT approach with the help of the MLC mesophase. Simply, preparing MLC mesophases with compositions of (1 − x)[Cd(H2O)4](NO3)2 to x[Zn(H2O)6](NO3)2 mole ratio enables us to control: i) the homogeneous distribution of Cd2+ and Zn2+ ions in channels of the mesostructured silica films, ii) the composition of the Cd1−xZn,S nanoparticles after exposing the silica films to H2S gas, and iii) tuning the optical band gap of the Cd1−xZn,S nanocrystals between 2.63 and 4.05 eV. Aging of the film samples has a strong impact on the growth process and size distribution of the nanocrystals. For example, the band gap of CdS nanoparticles can also be tuned between 2.63 and 2.78 eV by controlling the aging temperature and aging period of the [Cd(H2O)4](NO3)2–mesoSiO2 film samples. Rigid silica walls of mesopores limit or stop the growth of the Cd1−xZn,S nanoparticles in the channels of mesostructured silica. The method described above could also be used to produce other alloy metal sulfides and metal selenides.

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