Cd(II) ions can be incorporated into the channels of mesostructured titania films, using the evaporation-induced self-assembly (EISA) approach, up to a record high Cd/Ti mole ratio of 25%. The film samples were obtained by spin or dip coating from a mixture of 1-butanol, [Cd(H2O)4][NO3]2, HNO3, and Ti(OC4H9)4 and then aging the samples under 50% humidity at 30 °C for a few hours before H2S (or H2Se) reaction. This step removes about 90% of the nitrate ions, eliminates the nitric acid production step, and stabilizes the CdS nanoparticles on the surface and/or walls of the pores of the coupled semiconductor films, denoted as meso-x-CdS-TiO2. However, the H2Se reaction, additionally, needs to be carried at lower H2Se pressures in an N2 atmosphere to produce stable CdSe nanoparticles on the surface and/or walls of the pores of the films, denoted as meso-x-CdSe-TiO2. Otherwise, an excessive number of Se8 particles form in the film samples.

**Introduction**

After the first synthesis of mesostructured titania in 1995, the field progressed very slowly until 2004.2-8 The major problem is the difficulty in controlling the hydrolysis and condensation of titania precursors. However, the use of 1-butanol as a solvent can produce ordered transparent titania films.9 However, the method requires large quantities of hydrochloric acid, which causes the contamination of the mesostructured titania films with Cl ions as charge-balancing counterions on the titania surface. Notice also that the evaporation process leaves the inorganic ingredients in the film samples as impurities. It is necessary to remove these ions from the mesostructured titania for many applications. The Cl− ions can be removed from the mesostructured titania films by heating the samples to over 200 °C. At this temperature, the surfactant molecules also burn and cause further contamination in the samples. Therefore, it may be necessary to use an acid source that either does not contaminate the film samples (this is very unlikely) or decomposes at lower temperatures. Note also that the P123 molecules start decomposing from propoxides as low as 150 °C and calcination is complete at around 300 °C. The nitrate ion is a good candidate because (i) it has a low decomposition (or removal) temperature, (ii) it plays a useful role in the self-assembly of organic (surfactant) and inorganic ingredients, and (iii) the transition-metal nitrate salts have higher solubility in the reaction media and in the as-synthesized mesostructured materials.

Large quantities of the metal nitrate salts can be dissolved in the hydrophilic domains of a salt-pluronic lyotropic liquid-crystalline mesophase and in solid media such as in the mesostructured silica film. However, the transition-metal chloride salts have limited solubility under typical mesostructured titania synthesis conditions. Therefore, it is important to change the salt and acid sources to metal nitrates and nitric acid, respectively. The nitrate ions play important roles in the self-assembly process by coordinating to the metal ion as a mono- or bidentate ligand via coordination with the coordinated water molecules. Coordination of the nitrate ion to the metal centers reduces the charge and ion densities of the self-assembling media, which enhances the solubility of the nitrate salts. The ligand-exchange reaction can be monitored best using FTIR and Raman techniques.
The doubly degenerate asymmetric stretching mode of the free nitrate ion, which is observed at around 1360 cm\(^{-1}\), splits into two modes, observed in the 1280–1600 cm\(^{-1}\) region. The splitting energy between these two modes is 120–160 cm\(^{-1}\) in the monodentate, 160–210 cm\(^{-1}\) in the bidentate, and above 210 cm\(^{-1}\) in the bridged coordinated nitrate ions.\(^{19}\) The symmetric stretching mode, which is Raman-active, is shifted from 1050 cm\(^{-1}\) in the 1010–1030 cm\(^{-1}\) range, which also becomes IR-active upon coordination.

The synthesis of stable CdS and CdSe nanoparticles on the channel surface or pore walls of mesostructured/mesoporous titania and CdSe-TiO\(_2\) nanocomposites is important for many applications in fields such as efficient solar energy conversion and photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis (the CdS and CdSe nanoparticles can function as an efficient sensitizer for the large band gap semiconductor photocatalysis). Therefore, the maximum amount of Cd(II) ion that can be incorporated using this approach is around 10 mol %\(^{26}\). The other group incorporated the presynthesized 4.2 nm CdSe nanoparticles with very low density, only 3 mol % (Cd/Ti), into the pores using a rapid immobilization method\(^{26}\). The metal sulfide or metal selenide nanoparticles can also be produced by first impregnating the metal ions into the pores and then reacting them with H\(_2\)S or H\(_2\)Se. However, this process also yields an extensive amount of acid that decomposes the nanoparticles. Note also that both impregnation (ions) and/or immobilization (nanoparticles) strategies yield nonuniform particle distributions in the channels. However, the transition-metal nitrate salts can be dissolved at relatively higher concentrations in the hydrophilic domains of the liquid-crystalline phase and remain solvated in the mesostructured film samples after the film becomes a rigid solid.\(^{11}\) This is important in order to process a larger number of metal ions into the mesostructures to produce other metals, metal oxides, metal sulfides, and metal selenides on the pore walls of mesoporous materials.

In this contribution, we have investigated the role of nitrate ions in the assembly of Cd(II), Ti(IV), P123, 1-butanol, and Cd(II)/P123 and Ti(IV)/P123 mol ratios. Each film sample was exposed and kept under 200 Torr of H\(_2\)S for 5 min three times or under atmospheric pressure of 5–20% H\(_2\)Se in N\(_2\) for 1 min in separate evacuated vacuum chambers. Upon completion of the reactions, the reaction cell was first evacuated into a trap with Cu(II)-loaded mesoporous silica to deposit unreacted H\(_2\)S or H\(_2\)Se as CuS or CuSe, respectively, for 2 min. The reaction chambers were then evacuated by pumping, using a rotary pump, for 5 min before removing the samples from the reaction chambers. The samples were labeled as meso-xCd(II)-yTiO\(_2\), where x and y are the initial Cd(II)/P123 and Ti(IV)/P123 molar ratios.

Instrumentation

The X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex diffractometer using a Cu K\(_\alpha\) source operating at 30 kV/15 mA (generating 1.5405 Å X-rays) and a Scintillator NaI(Tl) detector with a Be window. All of the XRD measurements were recorded using thin film samples on microscope slides. The FTIR spectra were recorded using a Bruker Tensor 27 FTIR spectrometer. A high-sensitivity DIALTGS-detector with a resolution of 4 cm\(^{-1}\) was used, and the spectra were collected from 128 scans. The FTIR spectra were recorded as thin films on a Si(100) wafer. The micro-Raman spectra were recorded on a LabRam confocal Raman microscope with a 300 mm focal length. The spectrometer is equipped with a Ventus LP 532 50 mW, diode-pumped, solid-state laser operated at 20 mW with a polarization ratio of 100:1 and a wavelength of a 532.1 nm and a 1024 element \(\times\) 256 element CCD camera. The collected signal was transmitted via a fiber optic cable into a spectrometer with a 600 groove/mm grating. The Raman spectra were collected by manually placing the probe tip near the desired point of the sample on a silicon wafer. The UV–visible absorption spectra were recorded using a Varian Cary 5 double-beam spectrophotometer with a speed of 200 nm/min and a resolution of 2 nm over a wavelength range from 800 to 200 nm in transmittance mode.
The UV regions were collected using film samples coated on quartz slides. The SEM images and the EDS data were obtained using a Zeiss EVO-40 SEM operating at 15 kV and a Bruker AXS XFlash detector 4010 attached to the same microscope using the same samples. The samples were prepared on silicon wafers that were attached to aluminum sample holders using conductive carbon adhesive tabs. The TEM images were collected using an FEI Tecnai G2 F30, operated at 200 kV. The film samples, first calcined at 250, 300, and 350 °C and then collected from the substrate, were finely ground in a mortar and then dispersed into ethanol. A drop of the above dispersed ethanol solution was dried on a TEM grid for the TEM measurement.

Results and Discussion

A homogeneous, aged 1-butanol solution of Cd(II), Ti(IV), HNO₃, and P123 can be spin or dip coated onto various substrates, following an aging step, first under 50% humidity for 12 h at 30 °C and then at 130 °C for 4 h to produce well-ordered, transparent mesostructured titania films. The nitric acid and P123 content of the above solutions was kept the same in all 18 samples, which have been separately used for the H₂S and H₂Se reactions. The nitric acid concentration was optimized to determine the minimum amount of nitric acid necessary to prepare well-diffracting samples. The Ti(IV)/P123 mol ratios were kept at 40, 60, and 80 by changing the Cd(II)/P123 mol ratios from 0 to 15 to prepare the 18 film samples. The aging steps are critical to obtaining well-ordered film samples. No decomposition of the surfactant molecules is observed at 130 °C. The treatment of the film samples with a 200 Torr H₂S and 700 Torr 20% H₂Se/N₂ mixture, in a vacuum chamber, ensures the synthesis of stable CdS and CdSe nanoparticles, respectively, on the channel surface and pore walls of the transparent mesostructured titania films.

The film samples were further analyzed using TEM, XRD, EDS, UV–vis absorption, FTIR, and Raman techniques at each stage of the film preparation to characterize the films structurally and to resolve the stability problems of the CdS and CdSe nanoparticles in the film samples. Note that the CdS or CdSe nanoparticles that are synthesized using fresh film samples, without the 130 °C aging step, decompose back to Cd(II) and H₂S or H₂Se, respectively. The CdS/TiO₂ and CdSe/TiO₂ w/w percentages in the stable, well-ordered mesostructured film samples can be increased up to 37 and 44% (equivalent to 25 mol %), respectively, using this approach. These are record high concentrations for both CdS and CdSe using a one-pot synthesis approach. Recall that the highest CdS/TiO₂ quantity was only 10% in the literature.

Figure 2 shows a series of XRD patterns of oriented meso-xCd(II)-60TiO₂ (where x is 0, 2, 5, 10, and 13) films of as-prepared (fresh), aged (at 130 °C for 4 h), and after-H₂S-treatment samples. The structure remained at each stage in the above processes with some alteration in the unit cell and structural order. Each diffraction line gradually shifts to a higher angle; typically the small-angle line at 0.95° (92.9 Å d spacing) shifts to 1.22° (72.4 Å d spacing), 2θ upon aging, and shifts slightly to a lower angle or remains the same after H₂S (or H₂Se) treatment. This behavior indicates that the structure contracts as a result of further condensation of the titania walls and likely the formation of some Cd(OH)₂ and/or CdO species and then expands as a result of the formation of CdS (or CdSe) nanoparticles in the walls. The integrity of the film samples remains unaltered after all of the treatments. The TEM images show well-ordered channels oriented parallel to the film surface with curling channel patterns.
The TEM images were collected using the samples that are calcined at 250, 300, and 350 °C because the fresh samples and the samples treated at up to 130 °C are damaged under the electron beam in the TEM. The samples calcined at over 300 °C display crystalline walls. The spacing between the repeating features in the TEM images have a 7.3 nm spacing, corresponding (100) planes of the mesostructured samples (Figure 3). The observed distances in the images and the (100) diffraction line are consistent with each other. Figure 3a shows a TEM image of the film sample before the H$_2$S treatment, and all other images are obtained from the same sample after the H$_2$S reaction. It is difficult to collect HR-TEM images of the samples for better resolution because the samples are very sensitive to the electron beam. However, the images collected over 1.0 s clearly display the mesostructures and crystalline domains on the walls. The titania walls are amorphous at 250 °C. Note also that the wide-angle XRD patterns of relatively thicker film samples show only broad diffraction lines due to nanocrystalline CdS. Therefore, the crystalline parts of the walls must be CdS nanoparticles. Similar images were also obtained from the meso-CdSe-TiO$_2$ film samples.

It is important to note that the CdS and CdSe nanoparticles undergo decomposition upon reaction with nitric acid, both in the mesostructured silica and titania. Notice that the H$_2$S or H$_2$Se and nitrate ion reaction produces excessive amounts of nitric acid in the media. There are two nitrate ion sources, namely, the nitric acid (used to stabilize titania species in the solution phase) and cadmium nitrate (used as a Cd(II) ion source) in the reaction mixture. Therefore, the nitrate ions, which are important during the assembly of mesostructured films, need to be removed from the media before or right after the H$_2$S reaction. We have solved this problem in the case of silica by washing the samples and interacts with the metal centers through coordination as monodentate, bidentate, and/or bridged ligands. The asymmetric stretching mode of the nitrate ion, which is doubly degenerate in the free ion, splits into two peaks in the 1290–1600 cm$^{-1}$ region. Figure 4 shows FTIR spectra of three samples, which were prepared using HCl (as the acid source, labeled as meso-TiO$_2$) and HNO$_3$ with a Cd(II)/P123 mol ratio of 2 and Cd(II)/P123 mol ratio of 60 with increasing Cd(II) in the samples (meso-xCd(II)-60TiO$_2$, where $x$ is 2, 10, and 13). It is clear from the trend
in the spectra that the intensity of the nitrate ions coordinated to Ti(IV) does not change; however, the peaks at 1290 and 1475 cm\(^{-1}\) gradually increase with increasing Cd(II) content of the samples, indicating that these two peaks belong to nitrate ions coordinated to Cd(II) sites. The schematic representation of those coordinative interactions of the nitrate ions with Cd(II) and titania is also shown in the insets in Figures 4 and 5. Note also that the nitrate ions undergo a ligand exchange with coordinated water molecules of the Cd(II) ions and display peaks at 1290 and 1475 cm\(^{-1}\) in the [Cd(H\(_2\)O)\(_2\)](NO\(_3\))\(_2\)/P123 liquid-crystalline mesophases.\(^{18}\) Therefore, there is no ambiguity in the above assignments, and they can be used to monitor the aging and H\(_2\)S (or H\(_2\)Se) reaction processes. Similarly, the titania surface and walls, under acidic conditions, consist of coordinated water molecules (protonated Ti=OH sites, Ti=OH\(_2\)) that also undergo ligand exchange with the nitrate ions.

Both sets of peaks, due to the Cd(II)-(O\(_2\)NO) and Ti(IV)-(O\(_2\)NO) species, lose intensity upon aging the samples at 130 °C (Figure 6). A majority of the nitrate signals disappear upon heating the samples at 130 °C for 4 h without losing the mesostructured integrity of the film samples. The aging step was also repeated for the cadmium nitrate free samples in which the behavior of the nitrate signals is very similar, indicating that nitrate removal is carried out over the titania sides.

The condensation of the titania species is obvious from the changes in the broad peaks at around 580 cm\(^{-1}\) (gradually increases) and 830 cm\(^{-1}\) (gradually decreases, which is due to the \(\Delta TiOH\) deformation mode) upon aging. Notice also that aging influences the interaction of the surfactant molecules with the metal ion species. The peak at 1080 cm\(^{-1}\) due to \(\nu\)-CO of the ethylene oxide shifts to 1105 cm\(^{-1}\) upon aging and CdSe (or H\(_2\)Se) reactions. The original shift of this peak from 1105 cm\(^{-1}\) (for pure P123) to 1080 cm\(^{-1}\) (after mixing with cadmium nitrate salt) is due to the hydrogen bonding interaction of the ethylene oxide and coordinated water (Cd-OH\(_2\)) that seems to be completely removed by aging at 130 °C (most likely due to formation of cadmium-oxy-hydroxy species) and H\(_2\)S or H\(_2\)Se treatment (due to the formation of CdS or CdSe nanoparticles).

The H\(_2\)S reaction with meso-Cd(II)-TiO\(_2\) films produces CdS nanoparticles independently of the amount of H\(_2\)S and the duration of H\(_2\)S exposure, but the H\(_2\)Se reaction produces an extensive number of Se species if the H\(_2\)Se concentration is high (greater than 120 Torr) and if the samples are kept under H\(_2\)Se far too long. The Raman spectra of the samples that are kept at over 100 Torr of H\(_2\)Se display a peak at 252 cm\(^{-1}\) due to the polymeric Se chain.\(^{27}\) The EDS data also show a higher Se/Cd ratio, between 2 and 30, compared to the bulk ratio, 1.28 in the CdSe. Figure 7a shows an SEM image with selected area EDS data of a sample carried out under high humidity, the removal of the nitrate ions is faster. However, it is difficult to remove all nitrate ions from the media. The remaining small number of nitrate ions coordinates to the titania surface sides upon H\(_2\)S (or H\(_2\)Se) reaction. Notice that the peak intensity at 1290 cm\(^{-1}\), which is common for both nitrates, remains unaltered but the peak at 1475 cm\(^{-1}\) due to the Cd-O\(_2\)NO sides completely disappears and the peak at 1540 cm\(^{-1}\) due to nitrates on the titania sides is almost completely recovered upon H\(_2\)S reaction (Figure 6). These observations indicate that the nitrate ions coordinated to the Cd(II) are replaced by Cd=S bonds and the liberated nitrate ions coordinate to the titania surface. Possible reaction mechanisms during aging and the H\(_2\)S reaction are shown in eqs 1 and 2, where x depends on the Cd(II) incorporated, \(n = \frac{y}{10}\) and y is the number of nitrate ions on the surface of the titania that is also reduced by a factor of 10 during the aging step. The value of y is around 3 to 4, which also doubles by increasing the titania content from a mol ratio of 40 to 80 if we assume that the absorption extinction coefficients of the nitrate ion coordinated to the Cd(II) and Ti(IV) sides are the same (Figure 4). The small shift from 1560 to 1540 cm\(^{-1}\) may originate from the change in the environment of the nitrate ions coordinated to the titania sides that are further condensed during the aging step. A similar mechanism is valid in the H\(_2\)Se reaction step, but the H\(_2\)Se reaction is more problematic (discussed later).

\[
\text{meso} - \text{Cd(II)-(O}_2\text{NO)}_n - \text{TiO}_2 \\
\text{H}_2\text{S} \\
\text{meso} - \text{Cd(OH)}_x - (\text{O}_2\text{NO})_n \\
\text{TiO}_2 - (\text{O}_2\text{NO})_{y/10} \\
\text{meso} - \text{CdS} \\
\text{TiO}_2 - (\text{O}_2\text{NO})_{n+y/10} \\
\]

\[(1)\]

\[(2)\]

that contains a large amount of Se. The bright spherical particles originate from the Se particles. EDS and Raman spectroscopy must be used together to resolve this issue. Relying on just EDS and Raman can lead one to a wrong conclusion. We have observed exactly the same Se/Cd intensity of bulk in some samples, but they contained Se, which can be detected by Raman spectroscopy. In other samples, the Raman spectra displayed only CdSe peaks, but EDS showed us that the reaction was only 10% complete, where the Se/Cd intensity ratio was 0.13. Therefore, the amount of H₂Se, reaction time, and reaction conditions needed to be optimized to ensure clean CdSe nanoparticles in the mesostructured titania films using both EDS and Raman spectroscopy techniques. From a series of experiments under different conditions, we found that Se chain formation is a secondary process and is slower than CdSe formation. Se formation can be eliminated by carrying out the H₂Se reactions at lower H₂Se concentrations for shorter times, such as below 50 Torr of H₂Se for 1 min. However, this treatment (a diffusion-limited process) converts only 5 to 10% of the Cd(II) ions into CdSe nanoparticles. The diffusion of H₂Se into the films can be increased by exposing the samples to an H₂Se/air (close to atmospheric pressure of 50 Torr of H₂Se in 650 Torr of air) mixture. However, this also produces Se nanoparticles at higher H₂Se concentrations (higher than 50 Torr of H₂Se) and a small number of CdSe nanoparticles (10%) at lower H₂Se concentrations. CdSe formation can be enhanced by repetitive exposure of the samples to fresh H₂Se/air mixtures, but this is a costly process and after five repetitive exposures 50% CdSe formation can be achieved. Notice that Se formation is an oxidation process in which the Se²⁻ ion is oxidized to Se(0). Therefore, the H₂Se reaction has to be carried out under a non-oxidizing environment to obtain stable meso-CdSe-TiO₂ films. We have carried out the H₂Se reaction under an N₂ atmosphere, which ensures the complete conversion of Cd(II) ions to CdSe nanoparticles in one step with no Se formation detected. The SEM images in Figure 7 clearly show that the samples under pure H₂Se produce a large number of segregated Se particles with a homogeneous small number of CdSe nanoparticles embedded into the pores, but the reaction under H₂Se/N₂ converts all of the Cd(II) into CdSe nanoparticles. The thicker samples crack upon H₂Se reaction as a result of a complete H₂Se reaction. These samples are quite light-sensitive and undergo slow decomposition to Se under a green laser. The details of these studies will be published elsewhere.

The clean, stable samples were further analyzed using EDS and Raman techniques. Figure 8 displays the EDS data of bulk CdS and CdSe and meso-13CdS-60TiO₂ and meso-10CdSe-60TiO₂. The S/Cd and Se/Cd intensity ratios of the samples and bulk crystalline samples are the same, indicating that the samples are pure CdS and CdSe, respectively, and that all of the Cd(II) ions are converted into CdS or CdSe without any other sulfur or selenium species in the film samples. The EDS data, which gives the intensity ratio of S/Ti, measured using EDS, versus the Cd/Ti mole ratio, incorporated into the film samples, of meso-xCdS-60TiO₂ (where x is 2, 5, 10, and 13).


CdSe nanocrystallites, respectively (Figure 9). The LO frequency is shifted from its bulk value, indicating that the observed peak at 207 cm$^{-1}$ is due to CdSe nanocrystallites. All other peaks in the spectra in Figure 9 are due to Si (substrate) or the surfactant.

The behavior of the nitrate ions can also be monitored using a UV absorption band at around 204 nm. The absorption band at 204 nm is due to the nitrate ions, and the broad shoulder at around 250 nm, which tails down to 330 nm is due to the titania in the UV region of the electromagnetic spectrum of the thin film samples (Figure 10). During aging, the band at 204 nm loses intensity, the temperature-dependent measurements display an isosbestic point at 230 nm, and the titania band slightly red shifts, collectively indicating the single-step decomposition of the nitrate ion from the media and the further condensation of the titania species, respectively. These observations are also consistent with the FTIR (the increase in the intensity of the peak at 580 cm$^{-1}$ and the decrease in the δ-TiOH peak at 830 cm$^{-1}$) and XRD (shift of the diffraction lines to higher angles) results.

The UV–visible absorption spectra have also been recorded after H$_2$S and H$_2$Se treatments to determine the optical behavior and the particle sizes of the CdS and CdSe nanoparticles, respectively. Figure 10 displays extra absorption over 330 nm (the absorption edge tails down to 480 nm in the meso-CdS-TiO$_2$ and down to 530 nm in the meso-CdSe-TiO$_2$ samples) due to CdS or CdSe nanoparticles, respectively. The direct gap fitting of these bands gives band gap energies of 2.60 eV for the CdS particles and 2.36 eV for the CdSe particles. The band gap values correspond to 4.3 and 3.7 nm particles of CdS and CdSe, respectively. The particle sizes were determined using Darma and Sharma’s tight binding model\(^{(3)}\) and the derived empirical formula, where the shift in the band gap energy is given as $\Delta E_g = a_1 e^{-d/b_1} + a_2 e^{-d/b_2}$ ($d$ is the diameter and the parameters $a_1$, $b_1$, $a_2$, and $b_2$ are 2.83, 8.22, 1.96, and 18.07 and 7.62, 6.63, 2.07, and 28.88 for the CdS and CdSe nanocrystallites, respectively).\(^{(31)}\) Note also that size of the particle depends on the pore size and the nature of the pore walls. The fresh samples and the samples with a lower Ti(IV)/P123 mol ratio have softer pore walls and larger unit cells (extra space between the walls) such that the CdS or CdSe produced in the freshly prepared film samples is slightly larger and the absorption edges display a red shift compared to their aged counterparts. This can be used to fine tune the band gap and the particle size of the CdS and CdSe nanocrystallites in the pore walls and pore surface. However, the nanoparticles synthesized using fresh samples are not stable. Therefore, this needs further study using pluronics such as F127 and the method developed in this work. The CdSe nanoparticles are light-sensitive and undergo CdSe to Se conversion upon exposure to the green laser of the Raman spectrometer.

### Conclusions

Well-ordered, transparent mesostructured titania films can be prepared in the presence of cadmium nitrate and nitric acid over a broad range of Cd(II) and Ti(IV) concentrations. The film samples, aged first in a 50% humidity oven at RT and then at 130 °C in a regular oven, can be exposed to an H$_2$S or H$_2$Se/N$_2$ mixture to produce stable CdS or CdSe nanoparticles in the walls and channel spaces of mesostructured titania films, respectively. To ensure the stability of the nanoparticles in the mesostructured titania, the nitrate ions (which act as the acid source upon H$_2$SO$_4$ reaction) need to be removed from the media. The coordination of the nitrate ion to the titania and Cd(II) species promotes the thermal decomposition of the nitrate ions from the media with a gentle aging step. The pure H$_2$S reaction produces CdS nanoparticles, but the H$_2$Se reaction must be carried out under an N$_2$ atmosphere to eliminate secondary reactions, such as the formation of Se species. The stabilized CdS and CdSe nanoparticles are crystalline with average particle sizes of 4.3 and 3.7 nm with optical band gaps of 2.60 and 2.36 eV, respectively. However, the particle size can be changed by changing the pore size and wall softness of the titania films. The behavior of the particle size with respect to the softness of the host media and the light sensitivity of CdSe nanoparticles needs further study. These materials are good candidates for solar energy applications.

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