

SUPPORTING INFORMATION

Sol-Gel Assembly of CdSe Nanoparticles to form Porous Aerogel Networks

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EXPERIMENTAL

Materials

Bis-(2-ethylhexyl)sulfosuccinate sodium salt (AOT, 96%), cadmium nitrate tetrahydrate (99%) and triethylamine (TEA, 99%) were purchased from Acros. Trioctylphosphine oxide (TOPO, 90%), cadmium oxide (99.99%), selenium powder (99.5%), trioctylphosphine (TOP, 90%), 11-mercaptoundecanoic acid (MUA, 95%), tetramethylammonium hydroxide pentahydrate (TMAH, 97%), acetone, 4-fluorobenzenethiol (FPhSH, 98%) and tetranitromethane (TNM) were purchased from Aldrich. Sodium selenide (metal basis 99.8 %) and n-tetradecylphosphonic acid (TDPA, 98%) were purchased from Alfa-Aesar. Ethyl acetate, ethyl ether, 3% aqueous hydrogen peroxide, methanol, pyridine and n-heptane were purchased from Fisher.

Room temperature synthesis of CdSe nanoparticles, gelation and aerogel formation

The synthetic procedure for CdS nanoparticle synthesis and thiolate capping (FPhS) was adapted to CdSe from Gacoin et al¹⁻³ and was conducted under air free conditions using a Schlenk line as described in the literature.^{4, 5} The resulting FPhS-capped nanoparticles were dispersed in 20 mL of acetone to form the CdSe sol. For gelation, the CdSe sol was divided into 2 mL aliquots in polyethylene vials and 0.05 mL of 3% tetranitromethane or 0.1 mL 3 % H₂O₂ was added to each aliquot. The mixture was shaken vigorously to assure homogeneous mixing and allowed to sit undisturbed for gelation. In a typical synthesis, gelation was observed 1-2 h after mixing the oxidant. Alternatively, gelation was achieved by exposing the sol to the ambient fluorescent light for 20-30 days within a closed container in an

atmosphere of air. The resulting gels were aged for 10-14 days under ambient conditions. CdSe gels were subsequently washed and exchanged with acetone 6–8 times over 2 days. For aerogel production, wet gels were transferred (under acetone) to a SPI-DRY model critical point dryer, where they were subsequently washed and immersed in liquid CO₂ at 19 °C for 16 hrs. In this step, transfer of the monolithic acetone exchanged gels from polyethylene vials into the supercritical dryer boat leads to break up of the wet gel. Alternatively, wet gels can be transferred into micro porous specimen capsules (without collapsing the gel network) and can be supercritically dried to monolithic aerogels that retain the shape of the capsules. Supercritical drying of the CdSe gel was carried out for 30 min at 40 °C and 1200 –1400 psi to obtain the CdSe aerogels.

High temperature synthesis of CdSe nanoparticles, gelation and aerogel formation

The high temperature CdSe nanoparticle synthesis was adopted from Peng et al.⁶ 0.0514 g of CdO powder, 0.1116 g of TDPA and 3.7768 g of TOPO were loaded into a 100 mL Schlenk flask and slowly heated to 300 -320 °C under argon flow for 16 h. At about 320°C, the reddish brown CdO powder dissolved in the TOPO and TDPA mixture to form a homogeneous colorless solution. The temperature of the solution was cooled to 270 °C, and a selenium stock solution containing 0.0316 g of Se powder in 2.4 mL of TOP was injected. The temperature of the resulting mixture was reduced to 150 °C immediately after the injection and slowly increased back to 250 °C (10°C per 15 min) following the injection. The resultant CdSe nanocrystals were grown at 250 °C for 4 h and precipitated with methanol.

The procedure for thiol coating of CdSe nanocrystals was adapted from Aldana et al.⁷ 0.2620 g of MUA was dissolved in 15 ml of methanol and the pH of the resulting solution was adjusted to ~10 with tetramethylammonium hydroxide pentahydrate. In the absence of light, the methanol-precipitated CdSe nanocrystals were dispersed in the above mixture and the resultant solution was stirred for 2 h under argon flow. Ethyl acetate was added to precipitate the MUA-capped nanocrystals, which were isolated using centrifugation. As-prepared MUA capped nanoparticles were washed two times with ethyl acetate to remove the excess MUA and subsequently dispersed in 16 mL of methanol to form the CdSe sol.

Gelation was achieved by adding 0.05 mL of 3 % tetranitromethane to 2 mL aliquots of CdSe sol, as described in the inverse micellar route. Alternatively, gelation was achieved by exposing the CdSe sol in closed vessels to the ambient fluorescent light for 7-10 days. The resulting gels were aged for 10-14 days under ambient conditions. Aged gels were exchanged with acetone and supercritically dried to obtain the aerogels, as previously described for the inverse micellar route. In some cases, the monolithic wet gels were exchanged with 4 mL of pyridine 8-12 times over 4 -5 days to remove the surface thiolates prior to aging, acetone exchange, and supercritical drying.

Characterization

UV-Visible Spectroscopy. Optical absorption measurements of thiol coated CdSe nanoparticles were obtained using a Hewlett-Packard (HP) 8453 spectrophotometer. Room temperature synthesized nanoparticle sols were diluted ten-fold with acetone and the diluted solutions were analyzed against an acetone blank in the region from 200 – 800 nm. High temperature synthesized nanoparticles were diluted twenty-fold with methanol and analyzed against a methanol blank in the same region.

Diffuse Reflectance UV-Visible Spectroscopy. A Shimadzu model UV-3101PC double-beam, double monochromator spectrophotometer equipped with an integrating sphere was used to measure the optical diffuse reflectance of CdSe aerogels. Powdered aerogel samples were evenly spread on a sample holder pre-loaded with a reflectance standard (powdered BaSO₄) and measured from 200 to 1760 nm. The band gaps of the samples were estimated from the onset of absorption in data converted from reflectance.^{8,9}

Photoluminescence. A Cary Eclipse (Varian, Inc.) fluorescence spectrometer with 10 nm excitation and emission slits was used for photoluminescence studies. MUA-capped CdSe nanoparticles in methanol, or FPhS-capped nanoparticles in acetone, were placed in a 10 mm quartz optical cell and analyses were done under ambient conditions. Powder aerogel samples were sealed in evacuated quartz tubes and analyses were done at liquid nitrogen temperature.

Powder X-Ray Diffraction (PXRD). A Rigaku RU 200B X-ray diffractometer with a Cu K α rotating anode source was used for X-ray powder diffraction measurements. Powdered aerogel samples were

deposited on a low background quartz (0001) holder coated with a thin layer of grease. X-ray diffraction patterns were identified by comparison to phases in the International Centre for Diffraction Data (ICDD) powder diffraction file (PDF) database (release 2000).

Energy Dispersive Spectroscopy (EDS). Elemental compositions were obtained using an *in situ* EDS unit (EDAX Inc.) attached to a Hitachi S-2400 scanning electron microscope. Powdered aerogel samples were sprinkled on carbon adhesive tabs placed on an aluminum stub, and EDS data were acquired at 25 keV in secondary electron mode.

Transmission Electron Microscopy (TEM). The TEM analyses were conducted in the bright field mode using a JOEL FasTEM 2010 HR TEM analytical electron microscope operating at an accelerating voltage of 200 kV. Nanoparticle samples were prepared by depositing a drop of sol onto the grid followed by air evaporation, whereas aerogel samples were prepared on carbon-coated copper grids by dispersing fine powders in acetone using sonication, followed by depositing a drop of solution onto the grid and evaporating the acetone. Alternatively, aerogel samples were prepared by pressing the carbon-coated side of a grid into the powder (supporting information).¹⁰ For precursor nanoparticles, average particle sizes were manually estimated by measuring the size of 80-100 individual nanoparticles in several TEM images. In the case of aerogels, primary particle sizes were manually estimated by measuring the size of 50-70 individual nanoparticles from the less aggregated areas of the aerogel network.

Surface Area Analysis. A Micromeritics model ASAP 2010 surface area analyzer was used to produce nitrogen physisorption isotherms at 77 K on powdered CdSe aerogels. The data were fit using a Brunauer-Emmett-Teller (BET) model to determine the surface areas of the aerogels. The average pore diameter and cumulative pore volumes were calculated using the Barrett-Joyner-Halenda (BJH) model. Samples were degassed under vacuum at 100 °C for 72 h prior to the analysis and employed a 30 s equilibrium interval and a 5 cc dose for a total run time of ~ 12.5 h. Three independently prepared samples were analyzed for each system.

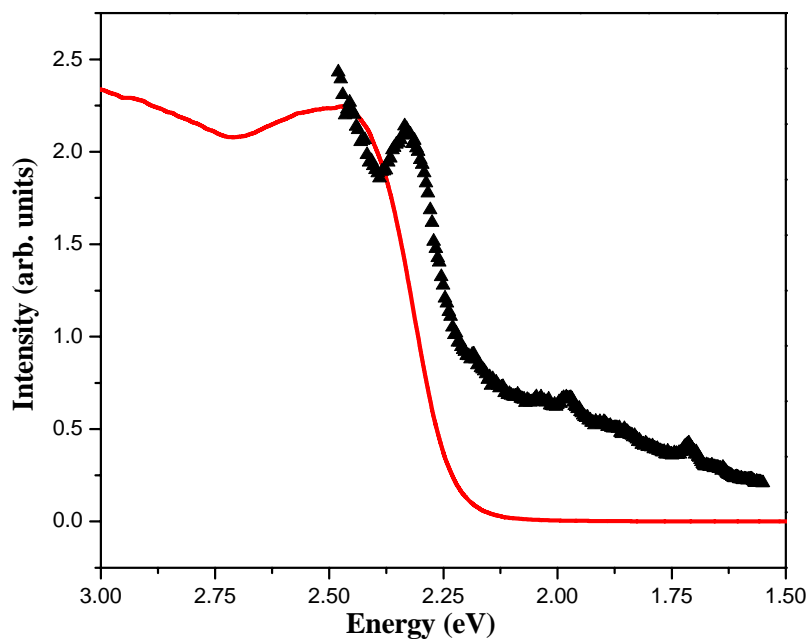


Figure S1. Diffuse reflectance UV-Visible spectra (red line) and photoluminescence spectra (filled triangles) of a CdSe aerogel prepared from nanoparticles synthesized by the inverse micellar method. The Stokes shift is approximately 0.09 eV, in the expected range.¹¹

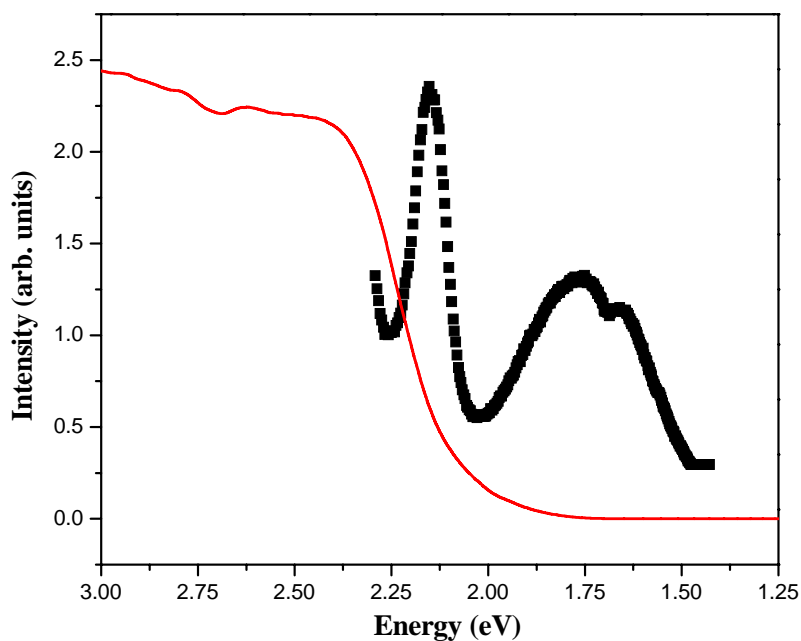


Figure S2. Diffuse reflectance UV-Visible spectra (red line) and photoluminescence spectra (filled triangles) of a CdSe aerogel prepared from nanoparticles synthesized by the high temperature method. The Stokes shift is about 0.19 eV, in the range expected.¹¹

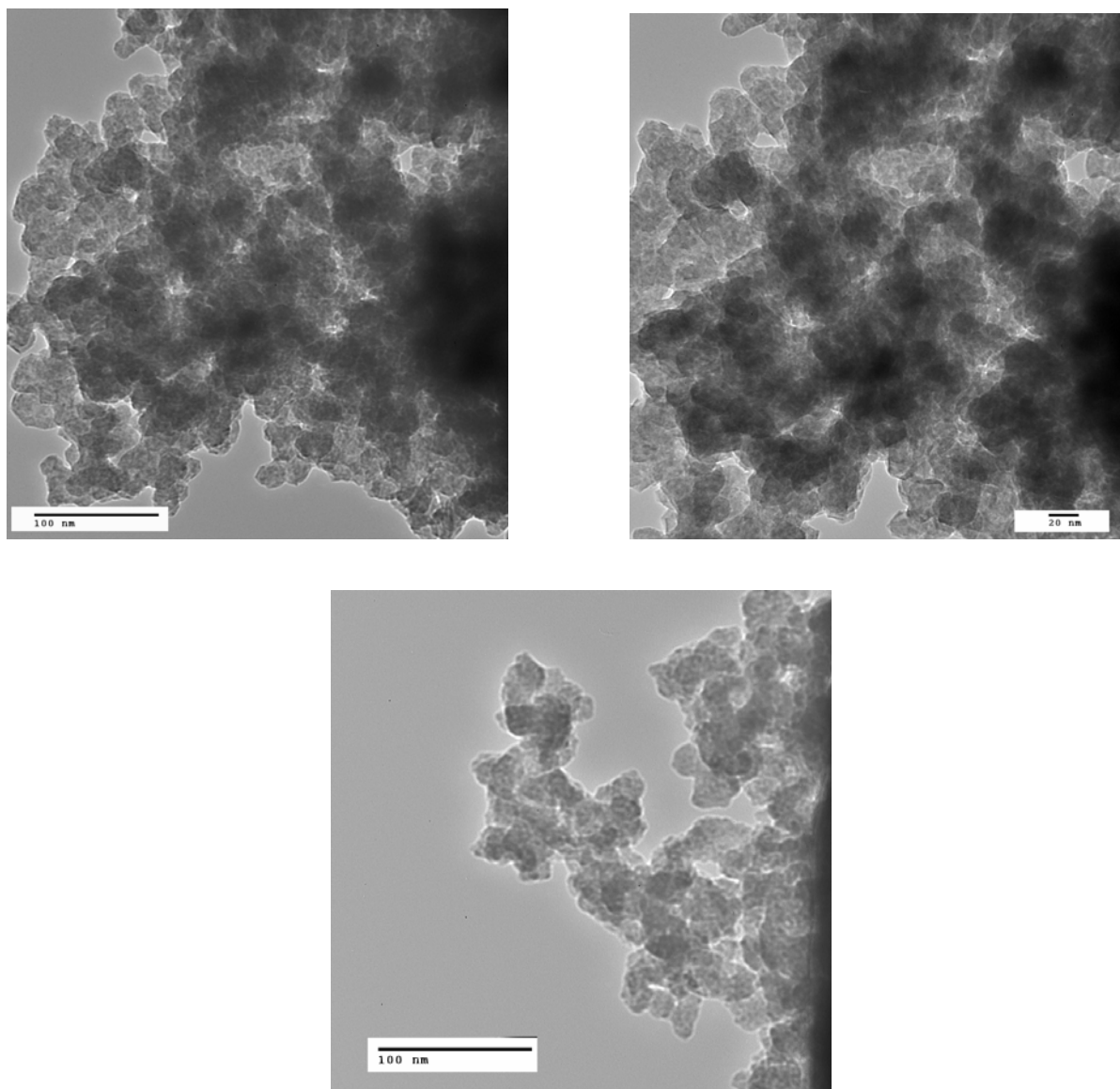


Figure S3. Transmission electron micrographs of a CdSe aerogel prepared from nanoparticles synthesized by the high temperature route and using tetranitromethane as the oxidizing agent. The TEM sample was prepared by contacting the powdered aerogel with the carbon coated Cu grid (i.e., the aerogels were not exposed to solvent in the sample preparation). The dark contrast observed within the network corresponds to areas of greater thickness (i.e., multiple layers of nanoparticles).

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