

Supporting information

EXPERIMENTAL:

Materials:

Bis-(2-ethylhexyl)sulfosuccinate sodium salt (AOT, 95%) was purchased from Tokyo Kasei Kogyo Ltd. Cadmium nitrate tetrahydrate (99.3 %), n-heptane (98.5 %), and triethylamine (TEA, 98 %) were purchased from J.T.Baker. Acetone (99.5%) and aqueous hydrogen peroxide (30 %) were purchased from Mallinckrodt. 4-fluorothiophenol (98%) was purchased from Alfa-Aesar. Silver nitrate (99.9%) was purchased from Strem chemicals and sodium sulfide was purchased from Aldrich. All chemicals were used as received.

Procedure:

The silver modified CdS (CdS/Ag) nanoparticles were synthesized by precipitation in water in oil micellar media of Bis-(2-ethylhexyl)sulfosuccinate sodium salt (AOT) in heptane. The ratio of surfactant- to- water ($W = [AOT]/[H_2O]$) was kept 6.3. For a typical reaction, 27.7 g of surfactant (AOT) was dissolved in 100 mL of n-heptane; the resulting solution was divided in half, and 2.2 mL of 0.15 M $Cd(NO_3)_2(aq)$ was added to first portion and 2.2 mL of 0.15 M $Na_2S(aq)$ was added to the second portion. The resulting microemulsions were stirred vigorously for 45 min until they became clear, and then the solution containing AOT/n-heptane/ $S^{2-}(aq)$ was added into the solution of AOT/n-heptane/ $Cd^{2+}(aq)$ to synthesize the CdS nanoparticles. The resulting CdS core nuclei were mixed with different amounts of silver stock solution to prepare nanoparticles with five different silver concentration coatings. The five molar ratios of CdS:Ag used were 22, 11, 7.3, 5.5 and 4.4.

To coat the nanoparticles, a stock solution of AOT/ n-heptane/Ag⁺(aq) was prepared, where the surfactant to water ratio was kept constant as CdS core synthesis. For typical synthesis, 9.44g of AOT was dissolved in 34.09ml of n-heptane and 1.5ml of 0.15M AgNO₃ was added. The resulting microemulsion was stirred for 45 min until it became clear.

To achieve surface complexation, 0.6 mL of 4-fluorothiophenol and 1 mL of triethylamine were added and the mixture was stirred for 1 hr, resulting in a precipitation of CdS/Ag nanoparticles. The resultant nanoparticles were isolated by centrifugation and were washed with n-heptane to remove the AOT surfactant and excess capping agent. After washing, CdS/Ag nanoparticles were dispersed in 20 mL of acetone to form the sol. For gel formation, the CdS/Ag sol was divided into 6 ml aliquots in glass vials and 0.5ml H₂O₂ (3%) was added to each vial. After addition of H₂O₂, the mixture was shaken gently to ensure homogenous mixing and was kept undisturbed for gel formation to occur. The CdS/Ag wet gels were covered and allowed to age for 7-10 days under ambient conditions. The wet gels were rinsed with acetone at least eight times over 3 to 4 days to exchange solvent in pores with acetone. The acetone exchanged gels were loaded into a supercritical dryer, where the acetone was replaced with liquid CO₂. The liquid CO₂ was brought above its critical temperature and pressure and vented. The obtained aerogels were yellowish green to greenish grey in appearance, and shrinkage during the drying process was minimal.

CHARACTERIZATION:

Ultraviolet-Visible absorption Spectroscopy: Optical absorption measurements of thiol modified CdS/Ag nanoparticles were obtained using a Shimadzu 2401-PC 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 300 – 500 nm.

Photoluminescence emission spectra: A Fluoromax -3 (Jobin Yvon, Inc.) spectrophotometer was used for photoluminescence studies. The thiol capped nanoparticles in acetone, were placed in a quartz cuvette and analyses were done under ambient conditions.

Surface Area Analysis: A Quantachrome NovaWin2 surface area analyzer was used to produce nitrogen physisorption isotherms at 77 K on CdS/Ag 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 prior to the analyses.

Scanning electron microscopy (SEM): The SEM analyses of CdS/Ag aerogels was conducted on a Hitachi S-4300 scanning electron microscope. Powdered aerogel samples were sprinkled on carbon adhesive tabs placed on an aluminum stub.

Transmission Electron Microscopy (TEM): The TEM analyses were conducted using a Hitachi H-8100 Scanning/Transmission Electron Microscope (STEM) operating at an accelerating voltage of 75 kV. The CdS/Ag aerogel samples were prepared by pressing the carbon coated side of a copper grid into the powder.

X-ray diffraction (XRD) analysis: Powder X-ray diffraction (XRD) was performed on a Rigaku Ultima III diffractometer. X-ray diffraction patterns were identified by comparison to phases in the International Centre for Diffraction Data (ICDD) powder diffraction file (PDF) database.

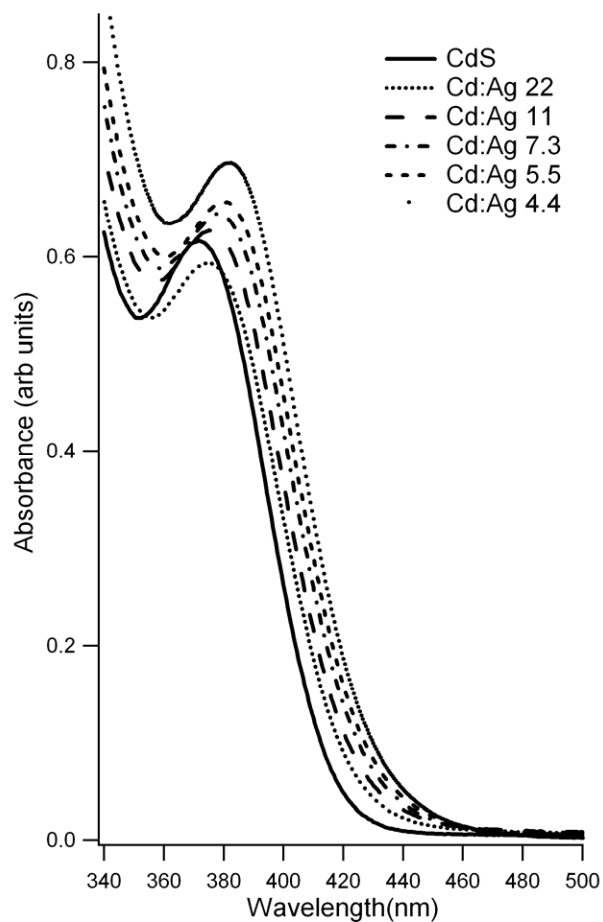


Fig. S1: UV absorption spectra for CdS and silver modified CdS nanoparticles in acetone with various Cd : Ag molar ratios.

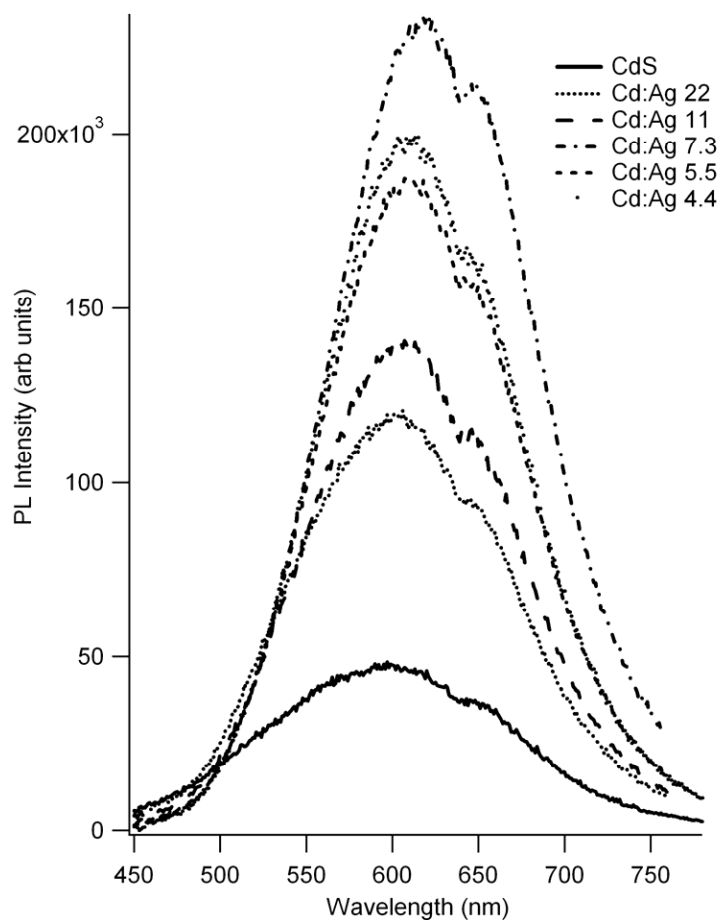


Fig. S2: PL emission spectra CdS and silver modified CdS nanoparticles in acetone with various Cd : Ag molar ratios.

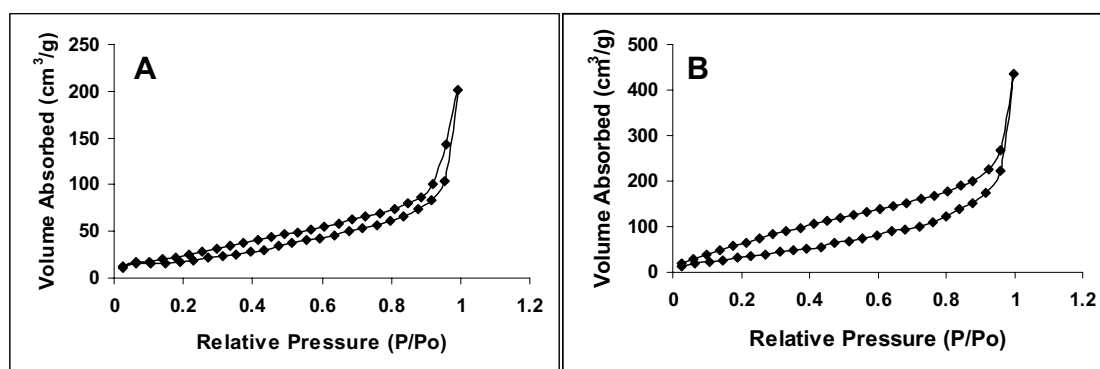


Fig. S3: Representative nitrogen adsorption–desorption isotherms CdS/Ag aerogels formed after supercritical drying where Cd: Ag molar ratio in primary particles were A) 22 B) 4.4

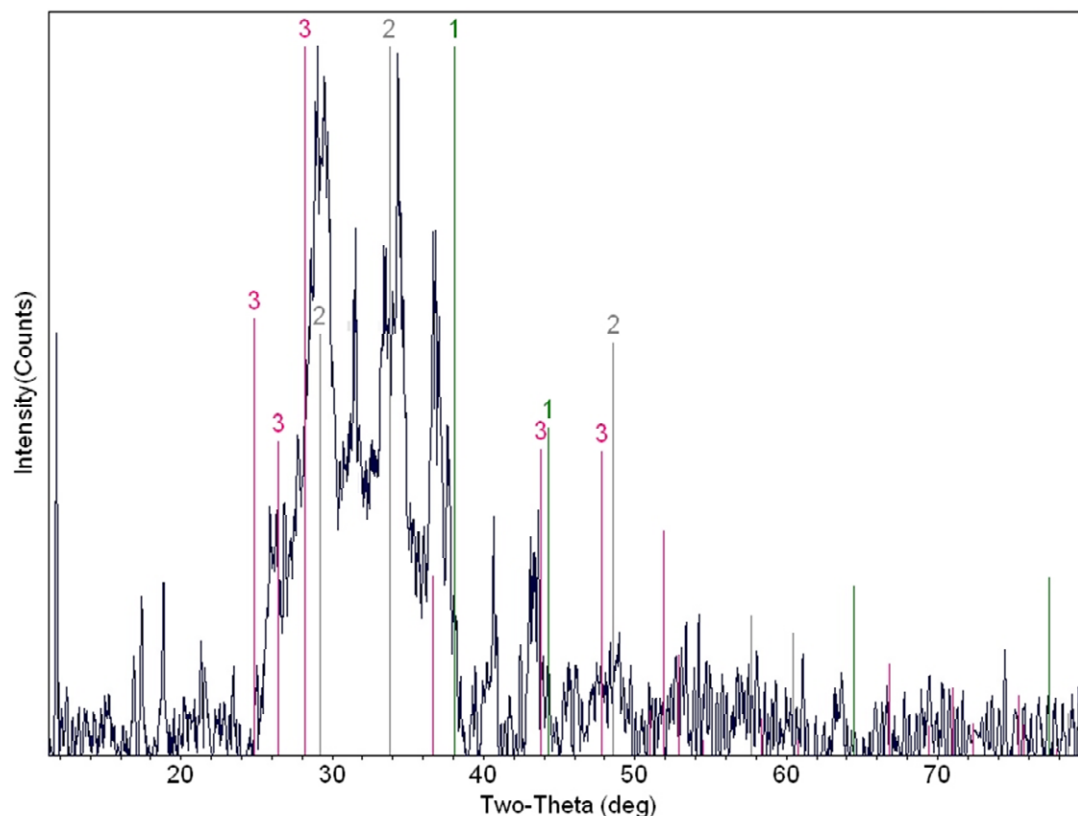


Fig. S4: XRD diffraction pattern of CdS/Ag_H annealed at 100°C. The ICDD-PDF overlay of 1) Silver (PDF File No. 03-065-287), 2) CdS (PDF File No. 01-071-4151) and 3) CdS (PDF File No. 03-065-3414), is shown as vertical lines.

The CdS/Ag aerogels were shown to be highly amorphous in nature and only weak crystalline reflections were observed. It was difficult to assign any one particular phase to the weak crystalline phase of the as-synthesized aerogel material, and it is best described as resulting from the presence of several crystalline phases. The three major species that were identified are silver (PDF File No. 03-065-287), cadmium sulfide (PDF File No. 03-065-3414) and cadmium sulfide (PDF File No. 01-071-4151).