Supporting information

for

Fluorometric Selective Detection of Fluoride Ions in Aqueous Media Using Ag doped CdS/ZnS Core/Shell Nanoparticles

Siddhartha Sankar Boxi, Santanu Paria*

Interfaces and Nanomaterials Laboratory, Department of Chemical Engineering, National Institute of Technology, Rourkela 769008, Orissa, India.

X-ray diffraction (XRD) pattern of pure CdS and ZnS nanoparticles

Figure S1 shows the XRD spectrum of pure CdS nanoparticles. It shows the peaks at 2θ value of 26.69, 43.02, 52.13, 54.29, and 63.63° for CdS corresponding to (111), (220), (311), (222), and (400) planes respectively, of the cubic structural phase of CdS (JCPDS card no.75-1546). Figure S2 shows the peak at 2θ value of 28.91, 33.43, 48.27, 56.53, and 59.65° for pure ZnS nanoparticles corresponding to the plane (111), (200), (220), (311) and (222), respectively, of the cubic structural phase of ZnS (JPCDS card no.80-0020).

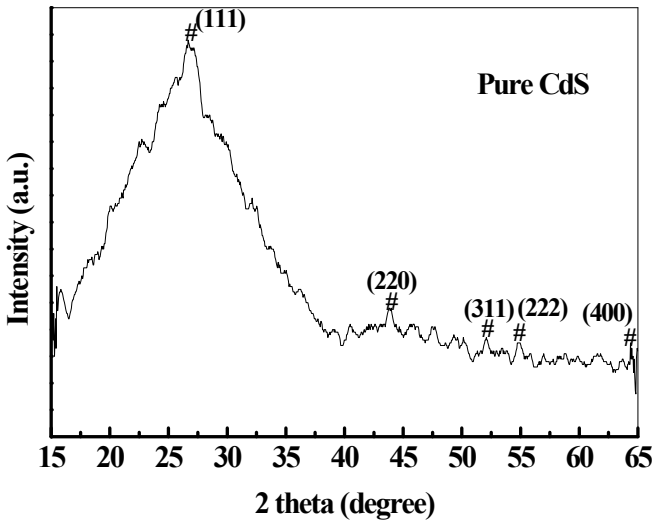

Figure S1. X-ray diffraction pattern of pure CdS nanoparticles

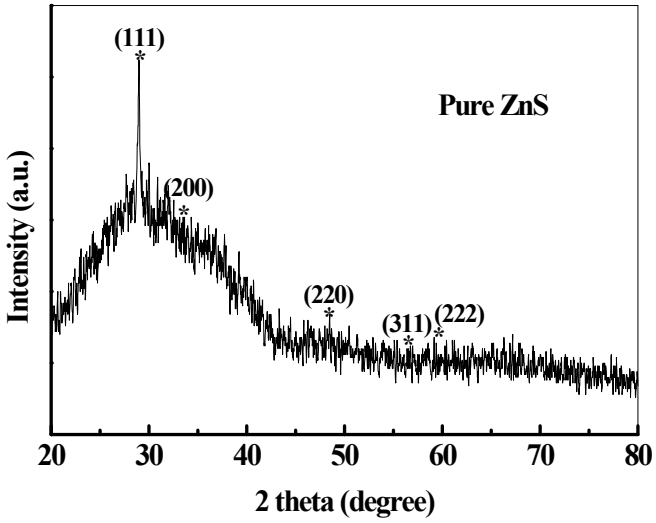

Figure S2. X-ray diffraction pattern of pure ZnS nanoparticles

Quantum yield calculation

Quantum yield was calculated using the equation (1), where phenol was taken as the reference. The refractive index and quantum yield of phenol were taken 1.5425 and 0.14 , respectively.

$$Q.Y_S = Q.Y_R\left(\frac{Grad_S}{Grad_R}\right)\times\left(\frac{\eta_S}{\eta_R}\right)^2 \quad (1)$$

Where, $Q.Y_S$ – Quantum yield of the sample

$Q.Y_R$ – Quantum yield of the reference (Phenol)

$Grad_S$ – Slope of the Integrate intensity vs. absorbance line for sample

$Grad_R$ – Slope of the Integrate intensity vs. absorbance line for reference (Phenol)

η_S – Refractive index of the sample

η_R – Refractive index of the reference (Phenol)

Table S1. The fitting equation and R^2 value of integrated intensity (from fluorescence spectra) vs. absorbance (from UV spectra) line and the QY of phenol and Ag-CdS/Ag-ZnS nanoparticles.

Material	Fitting equation	R^2 value	Quantum yield (QY)
Phenol (reference)	y=26.72x+0.3154	0.9973	0.14
Ag-CdS/Ag-ZnS	y=53.25x-4.85	0.967	0.7746

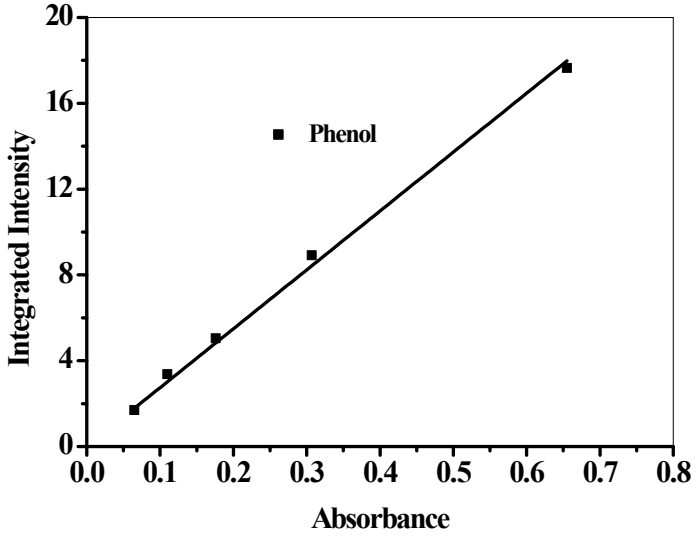

Figure S3. The plot of absorbance vs. integrated intensity of phenol as the reference solution.

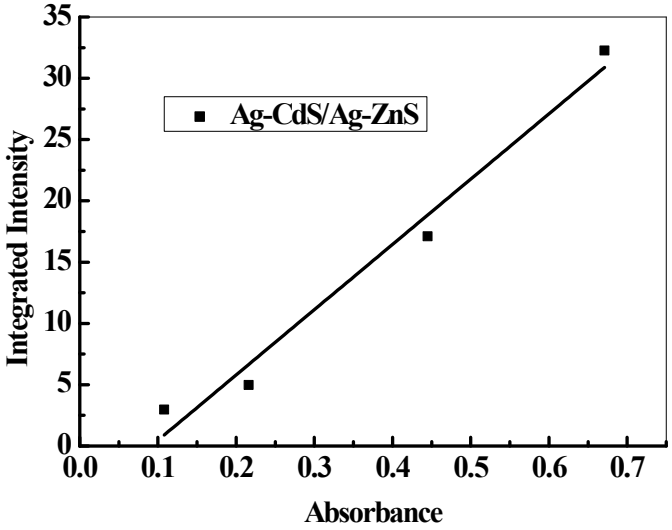

Figure S4. The plot of absorbance vs. integrated intensity of Ag-CdS/Ag-ZnS nanoparticles.

Characterization of Particles by XPS

The chemical composition and the chemical state of the Ag-CdS/Ag-ZnS nanoparticles were analyzed by XPS. The high resolution peak of Ag 3d is presented in Figure S5a. The Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks appear at binding energies of 366.375 and 372.75 eV, respectively with a slitting of 6.375 eV, confirming the presence of ionic silver instead of metallic form. Figure S5b shows the high resolution peak of Cd 3d level, where the detected major peaks at 410.625 and 404 eV are because of the Cd $3d_{3/2}$ and Cd $3d_{5/2}$ signal, and the spin-orbit separation of 6.625 eV is because of the Cd^{2+} formation. The scan for Zn 2p comprises two peaks at the binding energies of 1044 and 1020.875 eV becuse of Zn $2p_{1/2}$ and Zn $2p_{3/2}$ with a spin-orbit splitting of 23.1 eV (Figure S5c), confirming the presence of Zn^{2+}. Figure S5d confirms S 2p level at the binding energy 160.625 eV. Now there are three possible location of dopant in the bi-layer structure- (i) surface of the host material, (ii) principle reactant of the host material, and (iii) interstitial sites of the host material. From FE-SEM or TEM image it is clear that there is no surface deposition of silver on the surface. If interfacial doping is there then the silver peak should come in the XRD data, but there is no peak of individual silver. XPS data shows the presence of silver is in ionic form. So, the only possibility of silver doping is by the replacement of principle reactant in CdS/ZnS bi-layer structure. From the XRD data it is also clear that silver doping is achieved by the substitution of Cd^{2+} and Zn^{2+} by silver in the CdS and ZnS lattices.

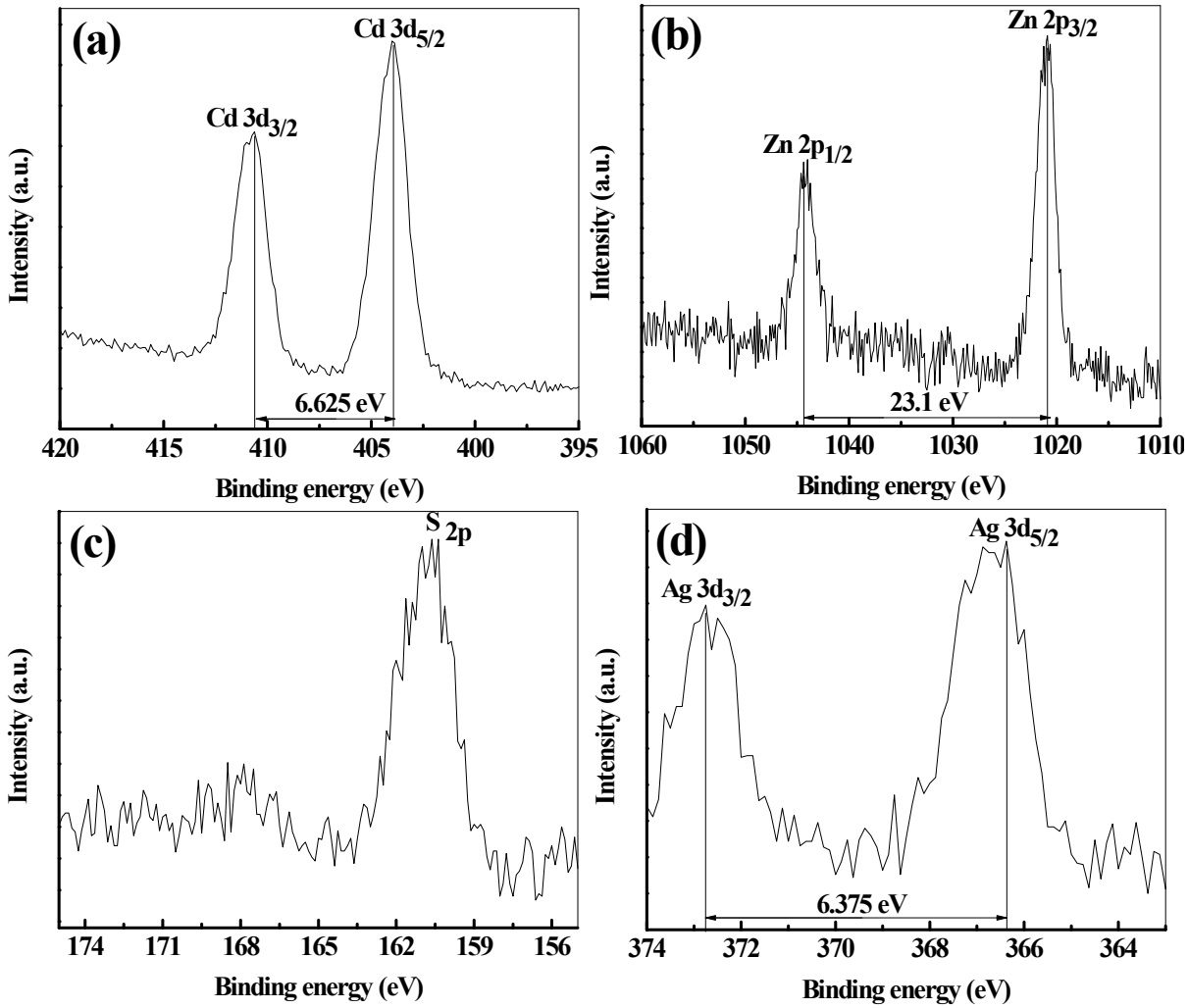

Figure S5. High resolution XPS narrow scan spectrum of (a) Ag(3d), (b) Cd(3d), (c) Zn(2p) and S(2p) for Ag-CdS/Ag-ZnS nanoparticles.

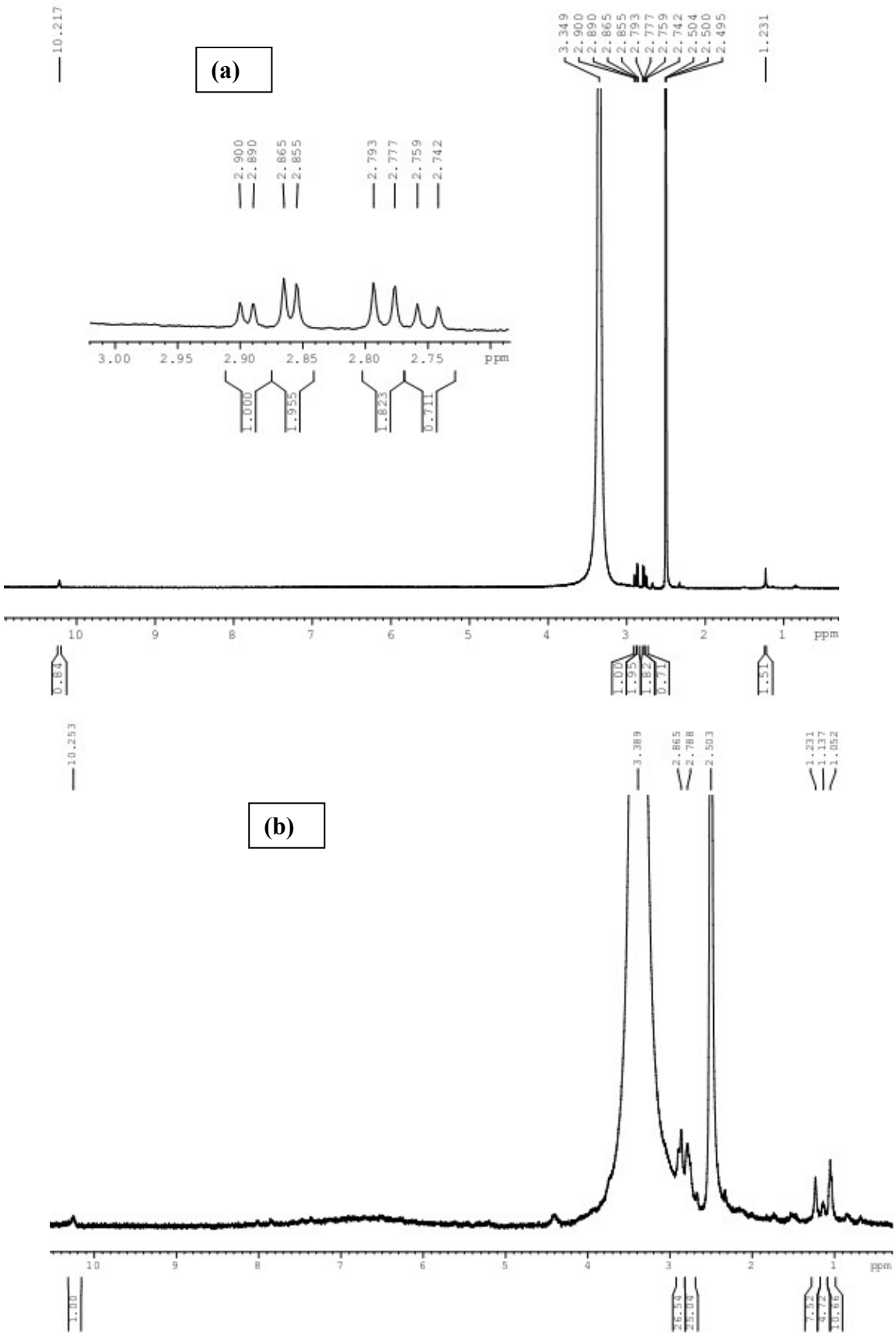

Figure S6. 1H NMR spectra of (a) L-cysteine and (b) L-cysteine with F^- in DMSO.