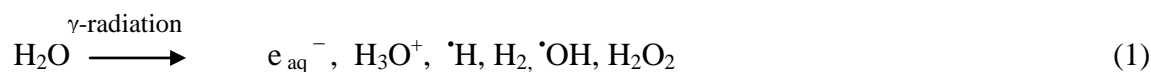


SUPPLEMENTARY INFORMATION

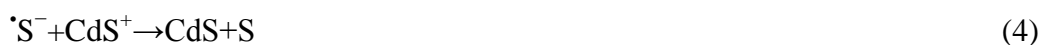
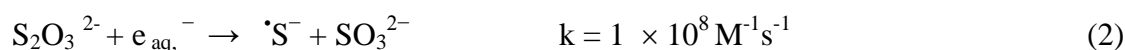
1. Formation of CdS/Dendrimer nanocomposites *via* Radiolytic Route

In gamma radiation-induced redox reaction, water-derived hydrated electrons¹ (e_{aq}^-) (eq. 1) reduce thiosulfate to sulfide ions S^{2-} , which in turn reacts with Cd^{2+} ions producing CdS *via* two electron transfer. In this method, the competition of Cd^{2+} ions for e_{sol}^- is minimized by suitable choice of the concentrations of Cd^{2+} ions and sodium thiosulfate or carbon disulfide (see the rate constants as indicated in eq 2 and 6) such that almost all solvated electrons react with thiosulfate or disulfide. Depending on functionality, a large number of $-\text{NH}_2$ or $-\text{COOH}$ groups are uniformly located on the surface of dendrimer molecules. Therefore, Cd^{2+} ions can be easily adsorbed on the surface of dendrimer molecule. The adsorbed Cd^{2+} ions further reacted with $\cdot\text{S}^-$ ions to form CdS^+ nanoparticles. A second electron transfer from $\cdot\text{S}^-$ ions produced CdS. Once CdS is formed on the surface, it can act as a nucleating site for the further adhesion of CdS formed in the bulk solution. Herein, dendrimer plays an important role in the formation of CdS nanoclusters. The possible reaction process for forming monodisperse CdS nanocluster can be described as follows:

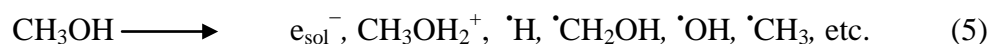
In aqueous systems, the possible reactions are as follows.



On γ -irradiation, sodium thiosulfate released S^{2-} homogeneously.



In methanolic systems, the following species are generated primarily¹



Out of these species, only the reaction of solvated electrons with carbon disulfide is of interest for the synthesis of CdS nanoparticles. The dissociative electron attachment on SCS is very probable:



The band gap (E_g) was calculated from absorption onset (λ_{onset}) in the UV-Vis absorption spectra of each nanoparticle solution using the relation, $E_g = hc/\lambda_{\text{onset}}$, where h is the Planck's constant and c the speed of light. The average size of nanoparticles (d) was obtained using the correlation of band gap shift ($\Delta E_g = E_{g(\text{nanocrystal})} - E_{g(\text{bulk})}$), and particle size deduced by tight-binding approximation (eq.9).

$$\Delta E_g = a_1 e^{-d/b_1} + a_2 e^{-d/b_2} \quad (9)$$

The values of the parameters for CdS nanocrystals are $a_1=2.83$, $b_1=8.22$, $a_2=1.96$ and $b_2=18.07$. Band Gap has been calculated from absorption onset is 3.3 eV and the calculated particle size is 2.9 nm. The particle size determined in this way was found to be in good agreement with the size obtained from TEM measurements.

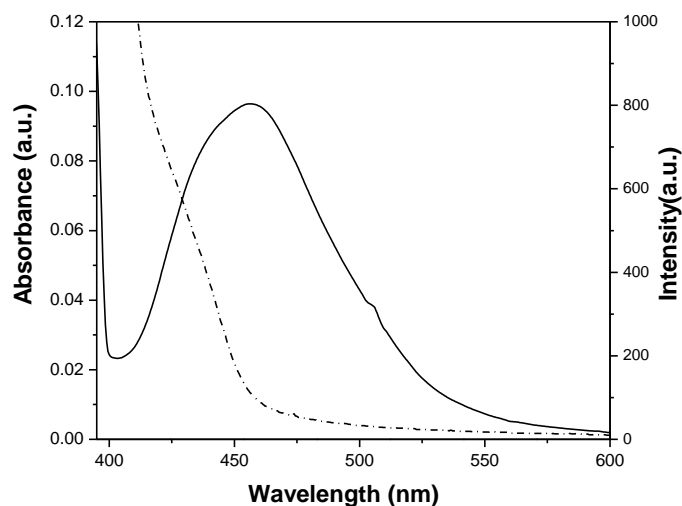


Fig. S1 Absorption (-----) and Luminescence (—) spectra of CdS nanocomposites synthesized using (G4, NH₂ terminal) carbon disulfide as sulfur source in methanol.

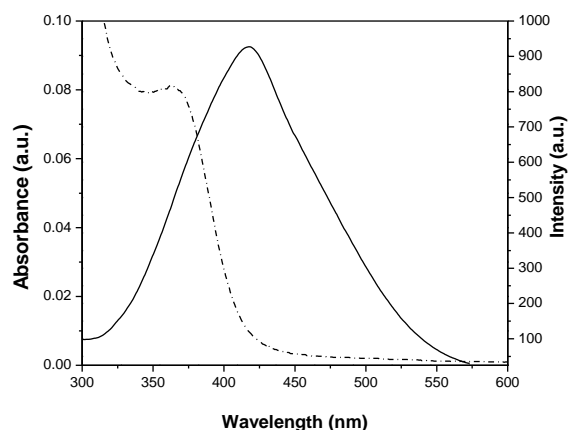
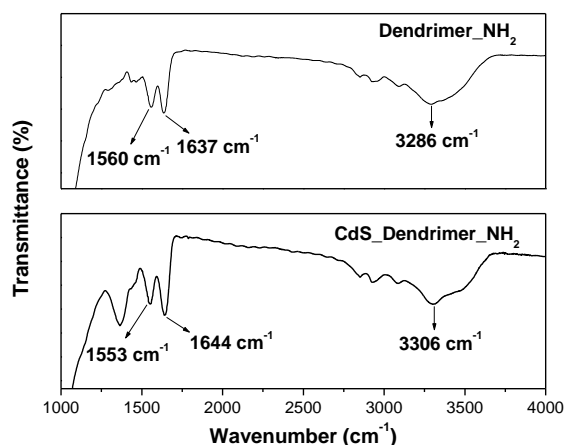
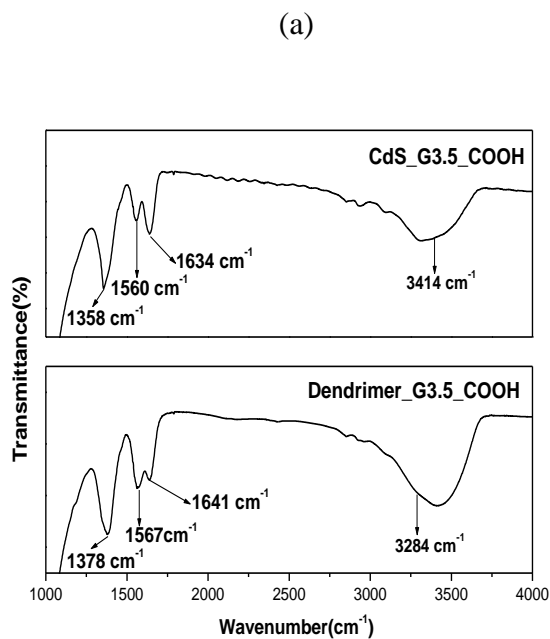


Fig. S2 Absorption (---) and Luminescence (—) spectra of CdS nanocomposites synthesized using COOH terminated dendrimer in water.

In FTIR spectra (Fig. S3a), the most significant point is that the band at 3286 cm^{-1} in NH_2 terminated dendrimer gets shifted to 3306 cm^{-1} in nanocomposites. This particular band can be assigned for stretching mode of surface amine group (NH_2) of the dendrimer and the observed shift is due to the coordination of NH_2 to the Cd atom present on the particle surface. It can also be seen that the $-\text{NHCO}-$ bands at 1637 and 1560 cm^{-1} corresponding to C = O vibration and N-H bending vibration are shifted to 1644 and 1553 cm^{-1} after formation of NPs. This observation confirms that the NPs are attached to the dendrimer through the surface amino (NH_2) group as well as internal amino group of dendrimer structure. In other case, with COOH terminated dendrimer (Fig. S3b), bands at 1378 , and 1641 cm^{-1} assigned to symmetric stretching mode of C–O and bending mode of O–H, respectively are shifted to 1358 and 1634 cm^{-1} , which suggests that NPs are attached to the dendrimer through the surface carboxyl (COOH) group.





(b)

Fig.S3. FTIR spectra of CdS/Dendrimer nanocomposites using amine terminated dendrimer (a) and carboxyl terminated (b) (Dose at 3.46 kGy, pH 6.5) (reproduced with permission from ref 30)

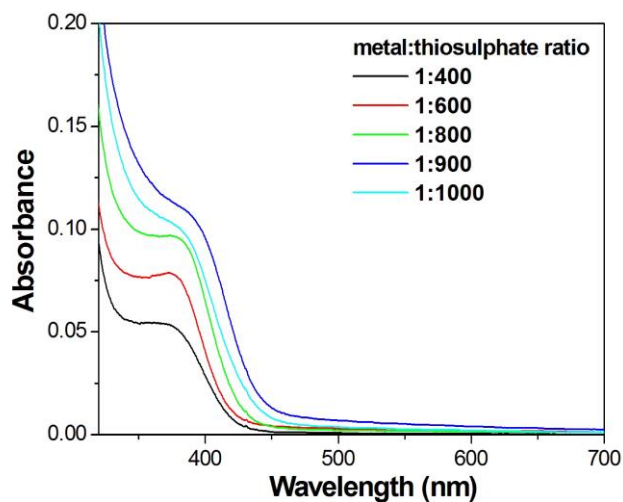


Figure S4. Absorption spectra of CdS/dendrimer nanocomposites formed with varying ratio of metal:thiosulphate. The concentration of Cd²⁺ ions was fixed at 2×10^{-3} M.

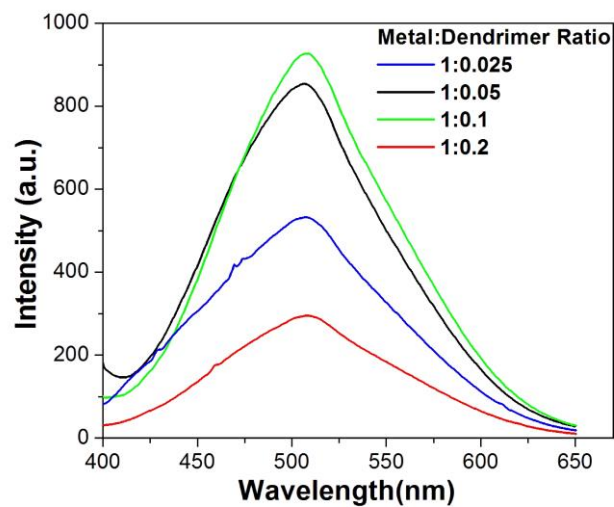


Figure S5. Photoluminescence spectra of CdS/dendrimer nanocomposites with varying concentrations of dendrimer (G4, NH₂ terminated). The concentration of Cd²⁺ ions was fixed at 2×10^{-3} M.

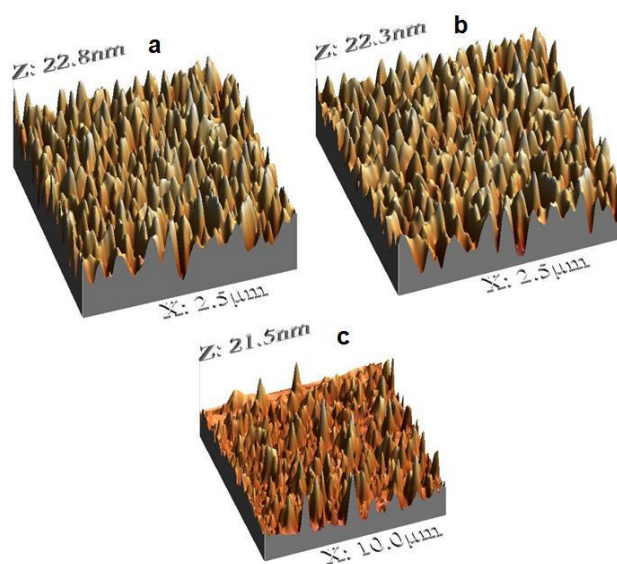


Fig.S6. Height distribution of CdS/Dendrimer nanocomposites using (a) NH₂dendrimer in methanol (b) NH₂dendrimer in water (c) COOH dendrimer in water.

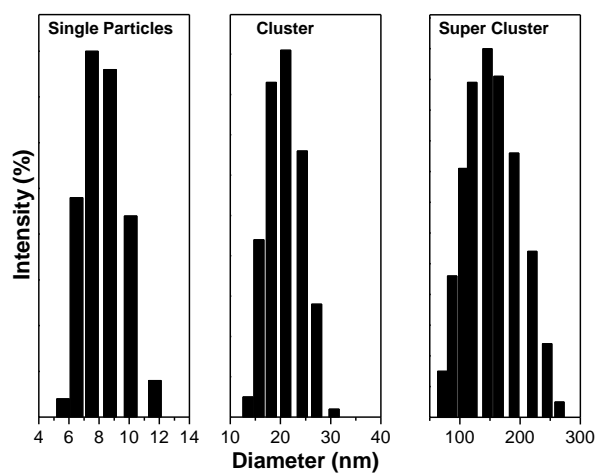


Fig.S7. Size distribution histogram of CdS/Dendrimer nanocomposites using dendrimer G4.COOH (reproduced with permission from ref 30)

References:

1. M. Mostafavi, G.R. Dey, L. Francois, J. Belloni, *J.Phys. Chem.* 2002, 106, 10184.
2. S. Sapra, D. D. Sarma, *Phys.Rev. B* 2004, 69, 125304.