Electronic Supplementary Information (ESI)

Efficient photocatalytic selective nitro-reduction and C-H bond oxidation over ultrathin sheet mediated CdS flower

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Detailed synthetic procedure:

General synthesis of CdS ultrathin sheet assembled flower:

In a typical synthetic procedure, in the 10 ml aqueous cadmium nitrate (1.88 mmol, 0.5gm) solution, aqueous ammonium hydroxide solution (4ml, 30%) was drop wise added to make a clear solution of cadmium ammonium complex solution. Then, in a hot (~60°C) biphasic mixture of water (20ml) and decanoic acid (4g), the prepared cadmium complex solution was added drop wise with constant stirring and resulted a homogeneous and transparent solution. Then, 10 ml aqueous solution of xanthate (ethyl xanthate, potassium salt, 0.32 g, was added to the above solution with constant stirring. After the addition of xanthate, the solution remains transparent but colour changes to yellowish. Immediately after the addition of xanthate, 33 ml of the resulting mixture was transferred into a Teflon-lined stainless autoclave (50 ml capacity). The autoclave was sealed and transfer to a pre heated oven and heated for 2h at 150°C. The system was then cooled to ambient temperature naturally. The final yellow product was collected and washed with methanol for several times and dried in air.

Synthesis of agglomerated CdS nanoparticles (un-stabelized). In a 20 ml water solution of 0.5 gm cadmiun nitrate, ammonium hydroxide was added drop wise to make a clear solution of solution of cadmium ammonium complex. The solution was heated to 100°C. To that hot solution, water solution of xanthate (0.26 gm in 10 ml) was added drop wise. The solution was heated for another 2 hr. Solid yellow product was isolated and washed with water and then methanol for several times. The washed product was air dried for further use

Monodispersed spherical CdS particles (5 nm) stabilized by decanoic acid: Monodispersed spherical CdS particles was synthesized using our previously reported method using supercritical ethanol.[5c] In a typical synthetic procedure required amount of oleylamine was dissolved in 3 ml ethanol and Cd- ethylxanthate. The 3 ml of resulted clear precursor solution was transferred into a 5 ml pressure-resistant vessel (SUS316). The reactor was then put into a preheated (400°C) oven for 20 min. After the reaction, the reactor was submerged into the cold water. The product was collected and washed with n-propanol for several times, centrifuged and re-dispersed in a hydrophobic solvent such as toluene or dichloromethane.

Characterizations.

Powder X-ray diffraction patterns were collected in the range of 20–80° with a Philips X'pert X-ray powder diffractometer using Cu Kα (λ = 1.54178 ˊ˚A) radiation. Transmission electronic microscope (TEM) images were collected using a JEOL JEM 2100 microscope operated at 200 kV. Samples were prepared by mounting dichloromethane dispersed samples on lacey carbon formvar coated Cu grids (300 mesh). The FT-IR spectroscopic measurements were carried out using a PerkinElmer GX spectrophotometer. The spectra were recorded in the range 400–4000cm^{-1} in KBr media. UV-Vis absorption spectra and photoluminescence spectra of toluene dispersed nanoparticles were recorded with a Shimadzu UV-2550 spectrophotometer and Fluorolog, Horiba Jobin Yvon fluorometer respectively. The electrochemical experiments were performed using a Princeton Applied Research potentiostat (PARSTATE 2273) at room temperature (24 ± 2°C). A three-electrode assembly was used in all measurements in which two platinum foils were used as working electrode and auxiliary electrode respectively and Ag/AgCl (sat KCl) as reference electrodes. The cycling was done at 100 mV/s scan rate in EtOH medium using Ammonium tetrafluoroborate as supporting electrolyte. AFM was carried out on NT-MDT (ntegra Aura) scanning probe microscope. To pursue the measurement, the nanoflowers were deposited over the HOPG (Highly Ordered Pyrolytic Graphite) by drop-cast method. The fresh surface of HOPG was exposed by cleaving the top most graphene layer before deposition of the material.

Photocatalytic activity study:

In a borosilicate test tube, 5 mg CdS nanocrystals were dispersed in 2 ml benzotrifluoride. Separately, 10 mg para nitrophenol was dissolved in 10 ml benzotrifluoride and added to the CdS dispersed solution. Then the mixed solution was left for 2 h to establish an adsorption-desorption equilibrium. To this solution 0.1 ml hydrazine hydrate was added. The mixed solution was then irradiated with a 40 watt CFL lamp at a distance of 4 cm. The progress of the reaction was monitored by UV-vis spectrometer. After the completion of reaction, the catalyst was separated by centrifuge and washed with ethanol (5 x 10 mL), dried in air and reused.

For oxidation of toluene, 10 mg toluene was dissolved in 10 ml benzotrifluoride and added to the CdS (10mg) dispersed benzotrifluoride solution. All other procedures were identical as reduction. For oxidation, reaction was carried out without addition of hydrazine hydrate and oxygen was pursed in the reaction system through balloon.

Supporting Figures:

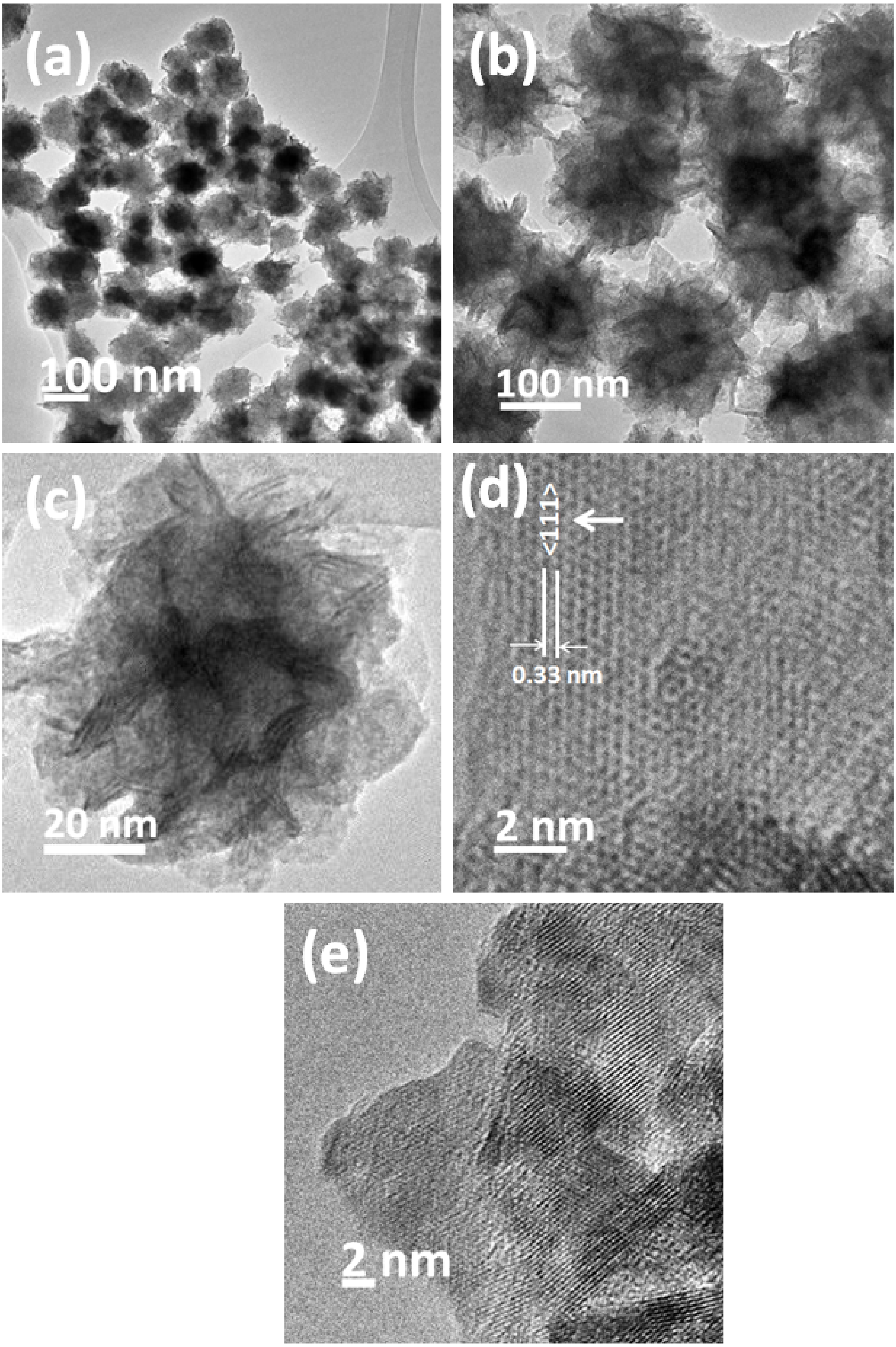

Fig. S1 TEM and HR-TEM images of synthesized ultrathin sheet mediated CdS flower.

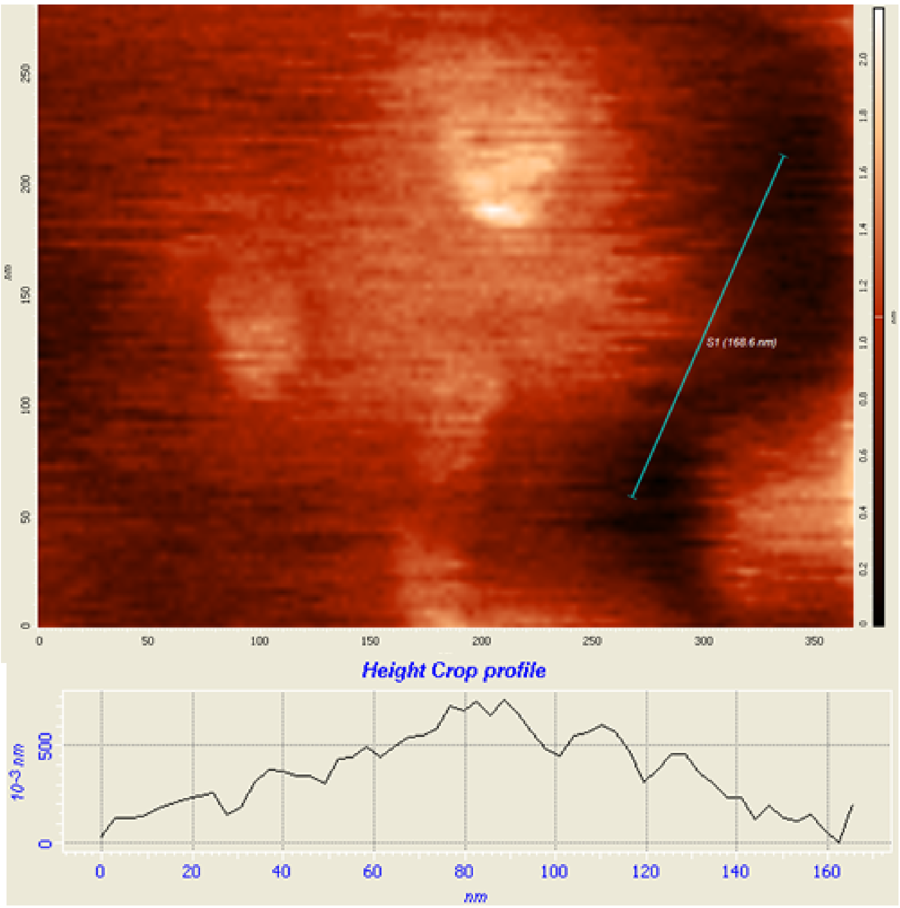

Fig. S2 AFM images of CdS flowers with corresponding height profile through the edge of the flower.

In the TEM image the individual sheets were identifiable whereas the overlapped sheets were recognized. So the height profiling in the edge were performed to get the exact thickness of individual sheets.

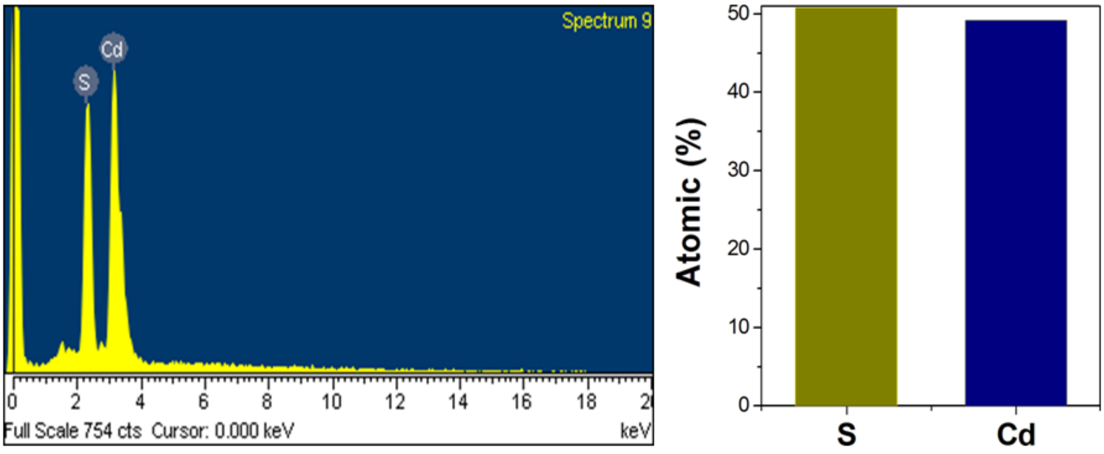

Fig. S3 EDX Spectrum and estimated atomic % of "S" and "Cd" in the synthesized CdS nanoflower.

The ratio of Cd and S in the flower shaped CdS is ~1:1, obtained from EDX spectroscopic analysis.

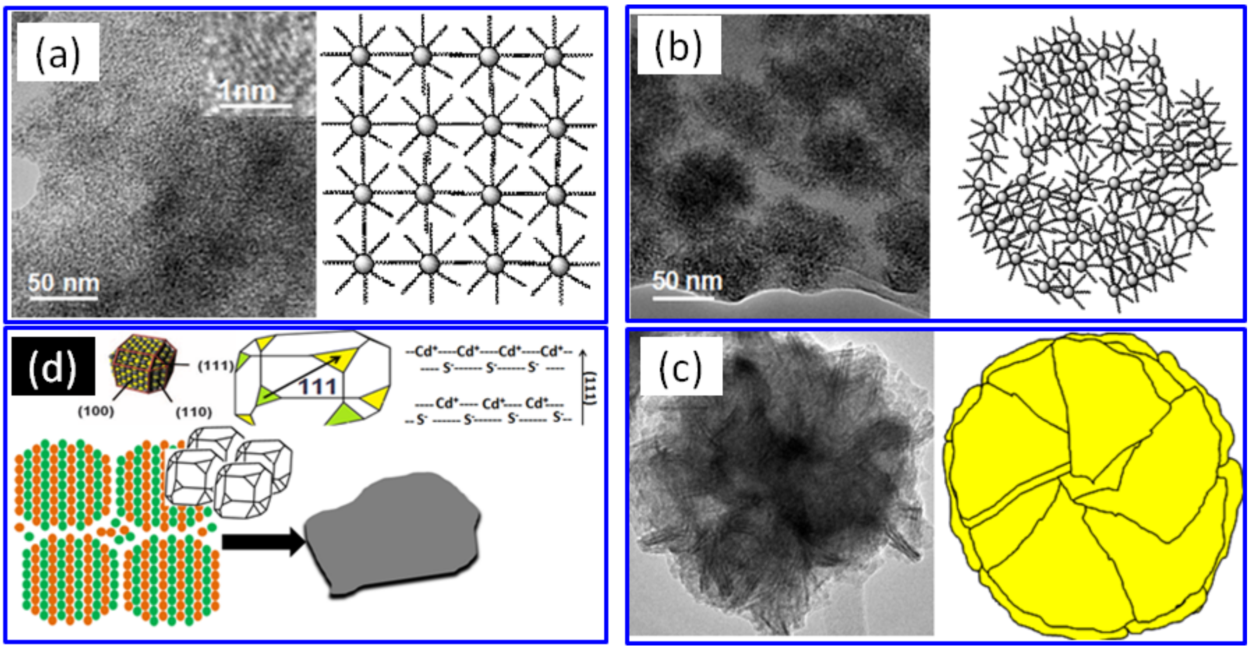

Fig. S4 TEM images and corresponding pictorial presentation of the intermediates formed, in (a) 30 min, (b) 45 min, (c) 1h and (b) proposed formation mechanism of ZB (cubic) CdS sheets through (111) direction through orientated attachment mechanism.

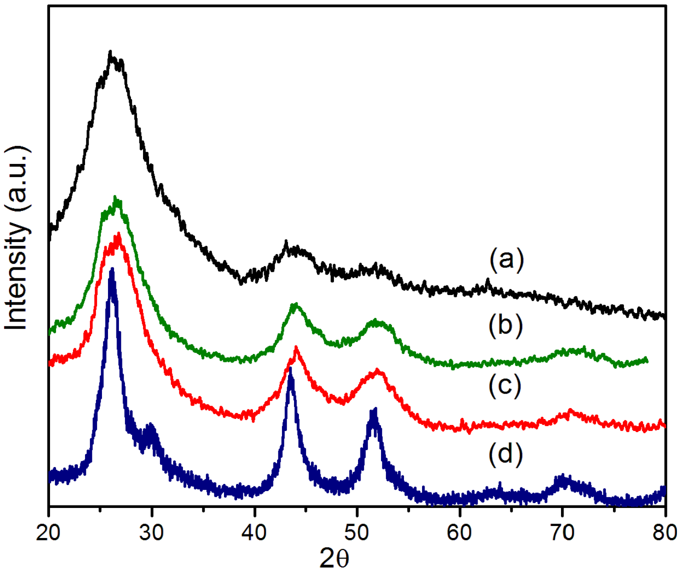

Fig. S5 XRD patterns of the CdS flowers synthesized in varying conditions; 30 min, (b) 1 hr, (c) 2hr, (d) 4hr.

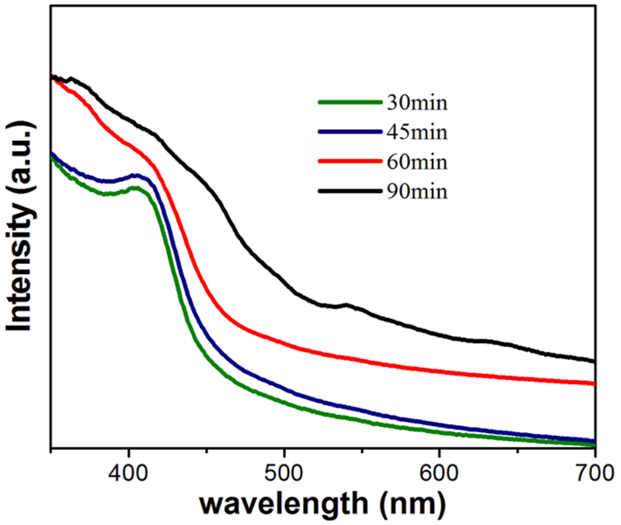

Fig. S6 UV-vis absorption spectra of CdS intermediates formed during progress of reaction.

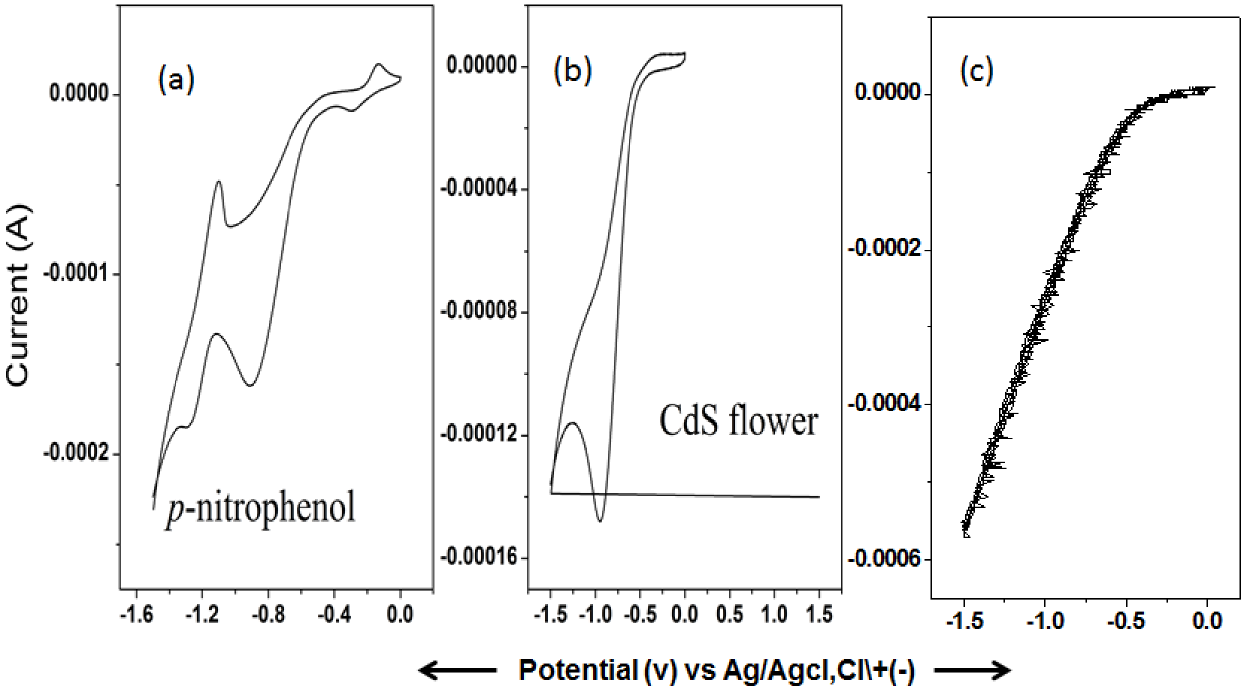

Fig. 7. Cyclic voltammogram of (a) *p*-nitrophenol (b) synthesized CdS flower in ethanol and (c) only ethanol with a scan rate of 100 mV/s.

Before going for the reaction, it is essential to check the feasibility of the photocatalytic reaction by the synthesized CdS flower. It is well known that the semiconductor catalysts generates charge carrier [hole (valance band, VB) and electron (Conduction band, CB)] on excitation by light of higher energy than its band gap and subsequent charge transfer leads to the redox reaction. The feasibility of photochemical reaction mainly depends upon the position of these VB and CB with respect to the redox potential of the reactants. For a feasible photochemical reduction the CB potential of semiconductor should be less [more negative (–ve)] than the reactant, and the subsequent charge transferred will be thermodynamically allowed. The reduction potential of CdS and para nitro phenol was measured in ethanol by cyclic voltammetry (CV). A critical comparison of the reduction potential of both the species indicates that the potential of CdS flower is sufficiently less (– ve) and thus the reduction of *p*-nitro phenol is thermodynamic feasible (Fig. S7a-b). The controlled CV (cycling in the supporting electrolyte only) does not show any faradic peak (Fig. S7c).

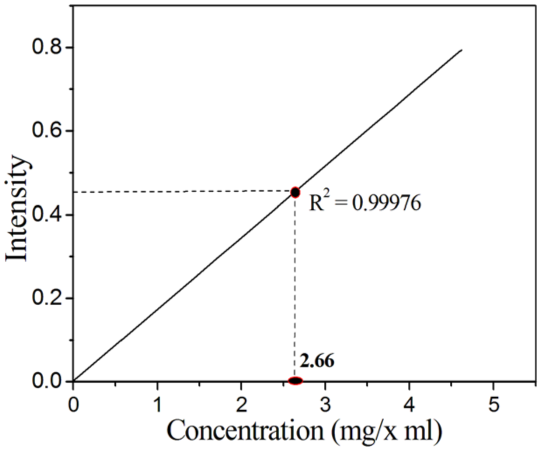

Fig. S8. The calibration curve of the para aminophenol for determination of conversion of reaction. According to the plot, >99% of conversion of para nitrophenol was observed.

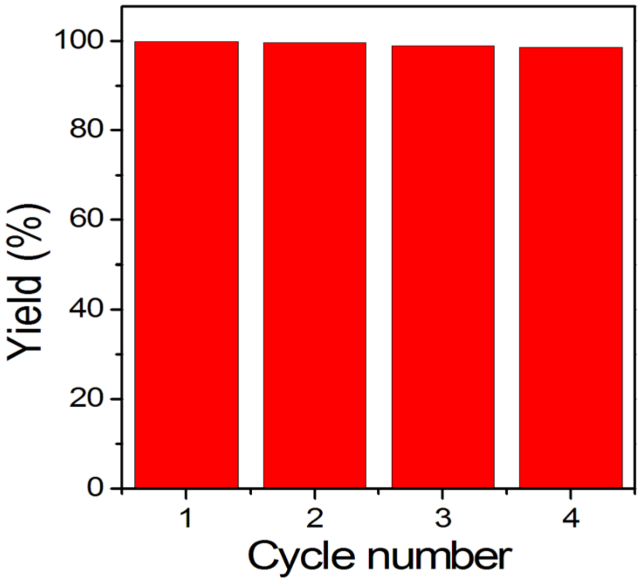

Fig. S9 Recyclability of the CdS nanofllower for nitro reduction reaction.

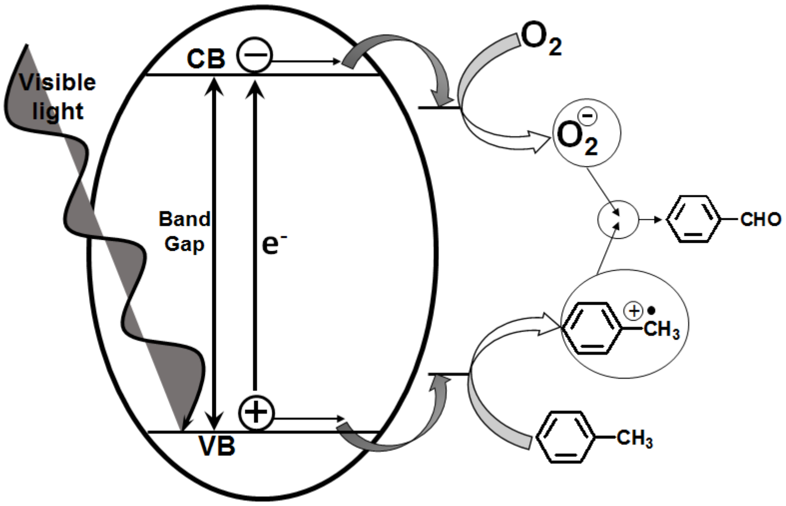

Fig S10 A Probable proposed photocatalytic pathway for oxidation of toluene to benzaldehyde in presence of molecular oxygen over synthesized CdS flower.

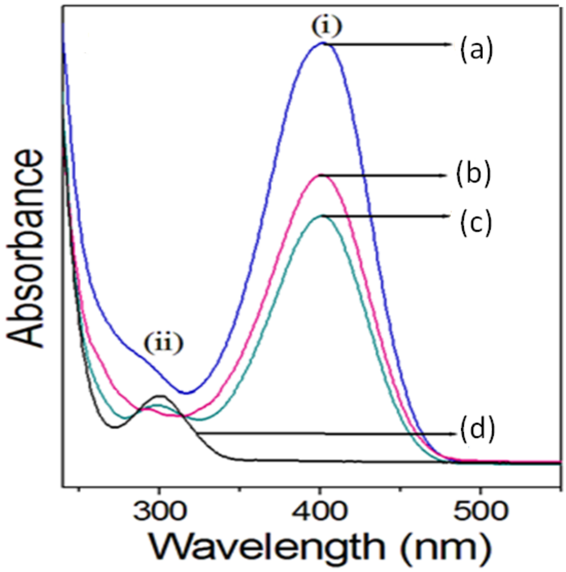

Fig. S11 UV –visible spectroscopy of reaction mixture after 90 min of reaction during p-nitrophenol reduction under 40W CFL lamp using (a) CdS bulk (b) monodispersed spherical CdS particles, (c) agglomerated CdS nanoparticles (d) synthesized CdS flowers as catalyst

To compare the photo catalytic activity of the synthesized CdS flower, the identical reaction was performed using a) CdS bulk, b) agglomerated CdS nanoparticles (un-stabilized) and c) monodispersed spherical CdS particles (5 nm). It was observed that except bulk CdS, all the studied CdS particles are active towards photocatalytic reduction of nitrobenzene uncer used CFL lamp, but the activity was much less than that of synthesized CdS flowers. The bulk CdS was almost inactive.

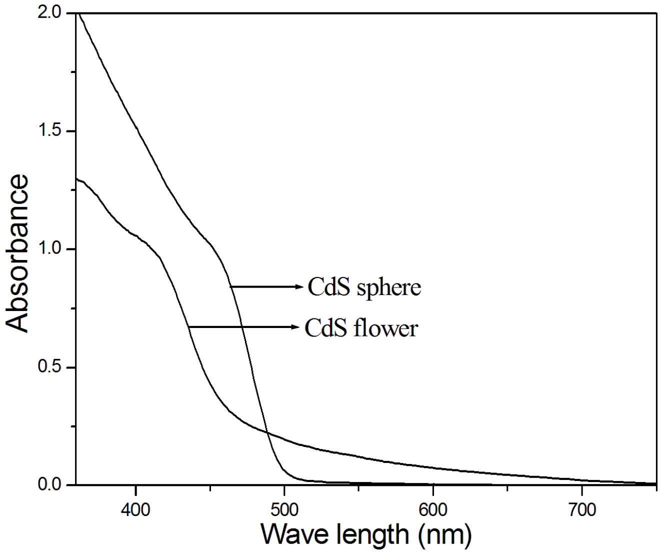

Fig. S12 UV-vis absorption spectra of the synthesized CdS flower and 5 nm CdS spherical particle (QD).

In the UV-Vis absorption spectra of toluene dispersed our synthesized CdS flower and 5 nm spheres reasonable blue shifting of absorption peak of flower confirmed the higher degree confinement for flower constructed of 0.8nm sheet and 1.2 nm wire. The quantum confinement effect of a nanowire/sheet depends on the width of the wire and thickness of the sheet. In our case, the width of the wire 1.2 nm and thickness of sheet is 0.8 nm. Whereas, the size of the quantum dot in comparison is 5 nm. Thus, the CdS flower assembled with nanowire and sheet shows better confinement with respect to other structure.

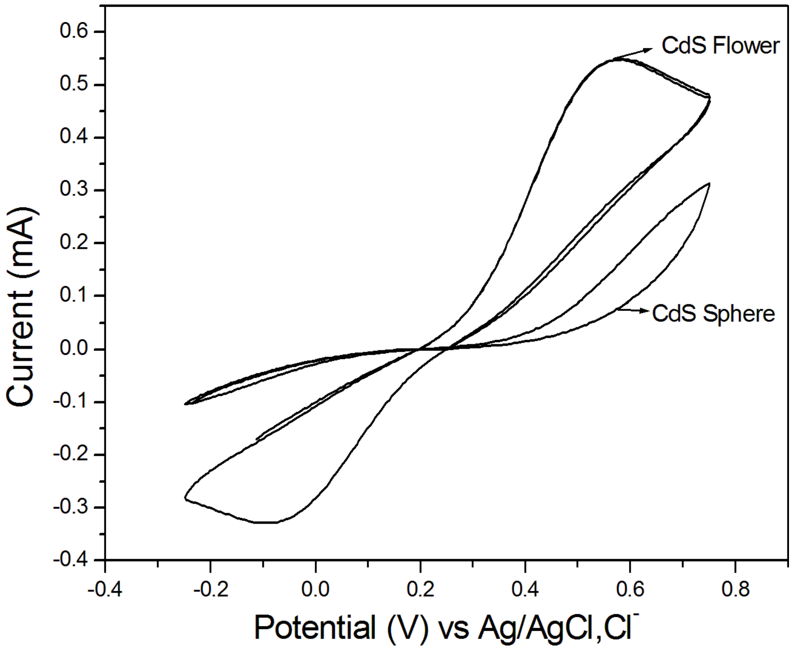

Fig. S13 Cyclic voltammogram of Fe(II)/Fe(III) redox on glassy carbon electrode after coating it with synthesized CdS flower and CdS sphere modified electrode.

It is difficult to get the surface area of the as synthesized CdS flower and CdS spheres (dot) directly by N_2 sorption, due to the presence of decanoic acid. For this, to compare the surface area of both the sample the cyclic voltammetry for Fe(II)/Fe(III) redox was recorded after modifying the glassy carbon electrode with CdS flower and CdS –spherical particle. Higher faradic current was obtained in case of CdS-flower than CdS sphere. The higher magnitudes of faradic current for two electrodes having equal geometrical area indicate that CdS nanoflower have higher surface area than CdS sphere.

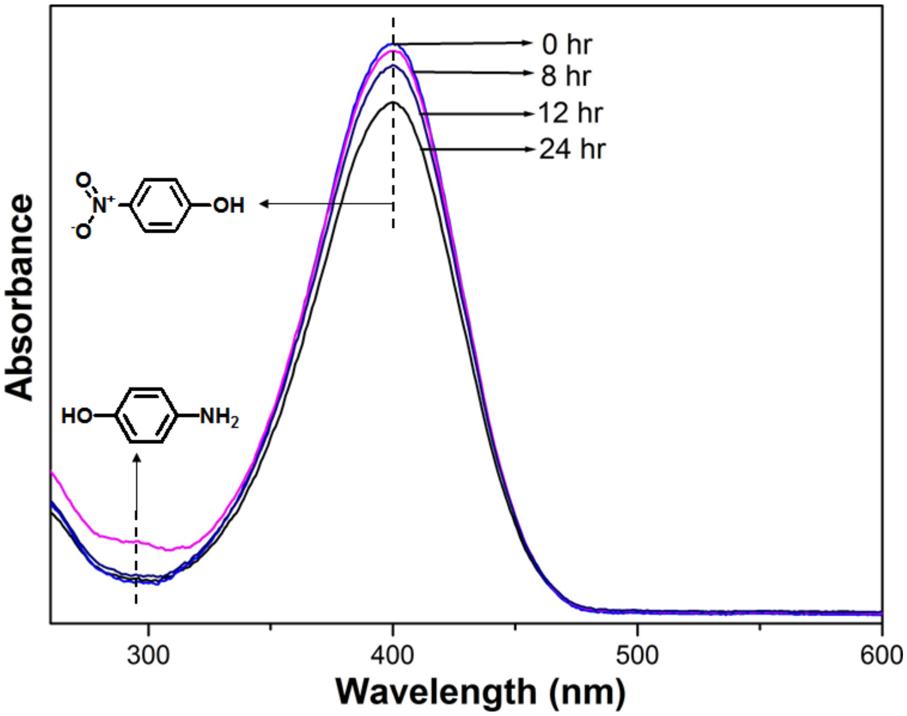

Fig. 14: UV –visible spectroscopy of reaction mixture in varying time of reaction during p-nitrophenol reduction in presence of hydrazine and absence of CdS, i.e. catalyst, under 40W CFL lamp.

The observed conversion of p-nitrophenol was very negligible and confirmed that the performed reaction is strictly photocatalytic

Table S1 Comperative chart of photocatalytic selective para nitrotoluene reduction of CdS reported in literature with the synthesized CdS flower.

	Types of CdS and modified CdS	Light source	Time taken for 100% nitro reduction
(a)	CdS-Flower (Present work)	40 W CFL lamp	90 min
(c)	CdS prepared by co-precipitation [1]	3 W LED lamp (blue light)	270 min
(d)	Hierarchically Ordered CdS Quandum Dots-TiO_2 Nanotube Arrays [2]	300 W Xe lamp	>60 min
(e)	CdS Nanospheres/Graphene Hybrid [3]	300 W Xe arc lamp	16 min (N_2

			atmosphere with sacrificial agent)
(f)	CdS Nanowires–Reduced Graphene Oxide Nanocomposites [4]	300 W Xe arc lamp	20 min (N_2 atmosphere with sacrificial agent)
(g)	Au Deposited CdS Nanostructures [5]	150 W halogen lamp	240 min

(1) A. H.Gordillo, A. G. Romero, F. Tzompantzi,S. O.Ruizb and R. Gomez, *Journal of Photochemistry and Photobiology A: Chemistry,* 2013, **257**,44-49.

(2) F.-X. Xiao, J. Miao, H.-Y. Wang and Bin Liu, *J. Mater. Chem. A*, 2013, **1**, 12229-12238.

(3) Z. Chen, S. Liu, M.-Q. Yang, and Yi-Jun Xu, *ACS Appl. Mater. Interfaces*, **2013**, *5*, 4309-4319.

(4) S. Liu, Z. Chen, N. Zhang ,Z.i-R. Tang, and Y.-J. Xu, *J. Phys. Chem. C*, **2013**,*117*, 8251-8261.

(5) N. Gupta and B. Pal, *J. Nanosci. Nanotechnol*, **2013**, *13*, 4917-4924.