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## COMMUNICATION

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

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**We report here a visible light driven selective nitro reduction and oxidation of saturated sp<sup>3</sup> C-H bonds using ultrathin (0.8 nm) sheet mediated uniform CdS flowers as catalyst under house hold 40W CFL lamp and molecular oxygen as oxidant. The CdS flower was synthesized using a simple surfactant assisted hydrothermal method.**

Reduction of organic nitro-compounds to corresponding amine without affecting the other reducible groups and oxidation of saturated sp<sup>3</sup> C-H bond using molecular oxygen as oxidant to value added products are really challenging and most important class of reactions in organic synthesis as well as in chemical industry.<sup>1-2</sup> Both the reactions required harsh reaction condition, expensive reagents, additional steps to protect other functional group and mostly generate hazardous waste.<sup>3</sup> Thus, development of simple, green and selective routes for these reactions are highly desirable. Owing to the only sustainable energy resource on earth, solar energy has great potential as clean and economical energy source. Hence, efficient conversion and/or harvesting of solar energy to electrical energy or chemical energy, i.e., visible light driven chemical conversion (photocatalysis) is promising and have been triggered worldwide during last two decade.

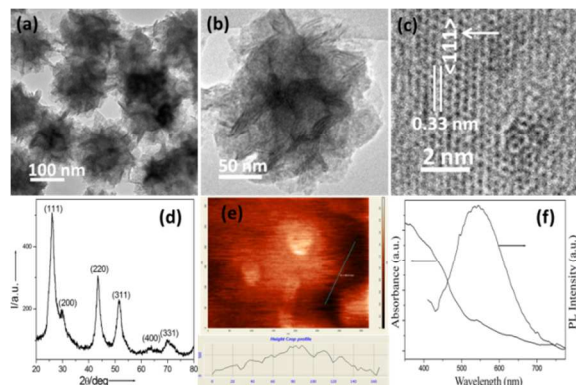
Semiconductor based heterogeneous photocatalysts are advantageous over transition metal complex based homogeneous photocatalyst with respect to waste generation and reuse. Recent studies revealed that CdS is one of the important visible light driven semiconductor photocatalysts.<sup>4-7</sup> Efficiency of pure CdS, bulk-/nanoparticle, is not satisfactory due to the recombination of the photo-generated electron-hole.<sup>8</sup> Thus prolonging the recombination through enhancement of lifetime the electron in conduction band and efficient transfer of the electron to the reacting substrate are the effective path to improve photocatalytic efficiency. To improve the lifetime of the photo-generated electron different attempts have been made through the formation of one dimensional (1D) rod and wire, composites of CdS-graphene, CdS-TiO<sub>2</sub>-graphene, CdS- noble metal nanocomposites.<sup>5-7</sup> After the discovery of graphene, 2D semiconductor nanosheets are getting interest for their high surface area, quantum confinement and most importantly improved lifetime

of photogenerated electron due to the transportation of electron, originating from its long range lattice periodicity which provides better channel for electron transport.<sup>7,9</sup> However, there are very few reports on CdS sheets, with the thickness in a quantum confinement region. Xu *et al.*<sup>7a</sup> reported exfoliated CdS flower with ~ 4nm thick. Zhang *et al.*<sup>7b</sup> reported bulk CdS sheets without any confinement. Best of our knowledge there are no reports on the synthesis of CdS sheet as well as their assembly with thickness beyond its Bohr radius, i.e., ≤ Bohr radius (2.8nm).

Here, we report for first time the synthesis of ultrathin (0.8 nm) CdS sheet and their assembly towards uniform flowers with cubic phase (ZB) in the presence of decanoic acid (DA) as a ligand, potassium orthoethyl xanthate (XA) as sulphur source and water as solvent in hydrothermal condition. Furthermore, the synthesized ultrathin CdS flower showed excellent visible light, from 40W simple house hold CFL lamp, driven photocatalytic activity towards selective nitro reduction and oxidation of saturated sp<sup>3</sup> C-H bonds using molecular oxygen as oxidant in ambient condition. Generally, the photocatalytic reactions, specifically the oxidation of saturated sp<sup>3</sup> C-H bonds, were performed under Xe lamp for good activity and special precautions are needed. Here, for the first time we have used 40W simple house hold CFL lamp to make the procedure simple and synthesized CdS flowers is too active to give excellent results under the used CFL lamp.

In the developed synthetic strategy, use of aqueous ammonium cadmium [ $\{Cd(NH_3)_4\}^{2+}$ ] complex solution enables the procedure suitable for assembled CdS sheet in basic medium through the desolation of decanoic acid in water by *in-situ* ammonium salt formation. The whole synthesis comprise by the following steps; formation of ZB CdS nucleated nanoparticles through decomposition of *in-situ* generated cadmium xanthate formed by the reaction of ammonium complex of cadmium [ $\{Cd(NH_3)_4\}^{2+}$ ], simultaneous desolation of DA in aqueous reaction media by ammonium decanoate formation and stabilization of newly formed CdS particles, formation of CdS sheets by oriented attachment (Experimental section, see ESI<sup>†</sup>).

The synthesized flowers are uniform in size and self-assembled (Fig. 1a & S1, see ESI<sup>†</sup>) with a 100-125 nm. The flowers are constituted of assembled thin sheets. The sheets are overlapped on



**Fig. 1** TEM and HR-TEM images (a-c), XRD pattern (d), AFM image with height profile (e) and UV-vis absorption and corresponding normalized PL spectra (f) of synthesized CdS sheet assembled flower.

each other and dark positions are probably the edge-curved nano-sheets (Fig. 1b). In the high-resolution TEM images, the interplanar distance of  $0.33 \pm 0.05$  nm of sheets with the  $d$ -value of (111) plane of CdS ZB structure (JCPDS File No. 01-75-1546) depict the sheets were grown through  $\langle 111 \rangle$  direction (Fig. 1c). The well resolved X-ray diffraction peaks of the synthesized CdS flower can be indexed to cubic structure (Zinc blend) of CdS (Fig. 1d) and support the TEM observation. The thickness of the individual sheets, obtained through AFM height profiling in the edge of the flower, are  $\sim 0.8$  nm. (Fig. 1e & S2, see ESI†). The observed compositional ratio of Cd and S ( $\sim 1:1$ ) from energy-dispersive X-ray spectroscopy (EDX) (see ESI†, Fig. S3) confirmed the composition of synthesized assembled sheet as CdS.

During progress of reaction, time resolved TEM analysis of intermediates revealed that the long range self-assembled very small nano-dots ( $\sim 1$  nm) was formed in 30 min (see ESI†, Fig. S4a). Then, the dots were re-assembled in a localized manner in a spherical shape with a diameter of  $\sim 100$  nm in 30-45 min (see ESI†, Fig. S4b). After 45 min, the dots within the spherical assembly aligned themselves, merged through 2D oriented attachment and resulted sheets. Finally, after 1.5 h, it gave a complete flower shape, where sheets are petal of flower (Fig. 1b, S4d see ESI†). All the above described intermediates were of zinc blend structure (see ESI†, Fig. S5). The absorption spectra of assembled dots, formed in initial stage (in 30 and 45 min), clearly shows structured spectra with an absorption maxima at 407 nm. Whereas the flower gave the fully unstructured spectra keeping the spectral position unchanged which further confirmed the sheets were formed from dots through 2D oriented attachment (see ESI†, Fig. S6). Similar observation was reported by Weller and his group.<sup>9d</sup> for PbS sheets. Reasonable blue shifted absorption maxima compared to the bulk CdS (490 nm, 2.5 eV) established the presence of strong quantum confinement effect from its ultrathin feature.

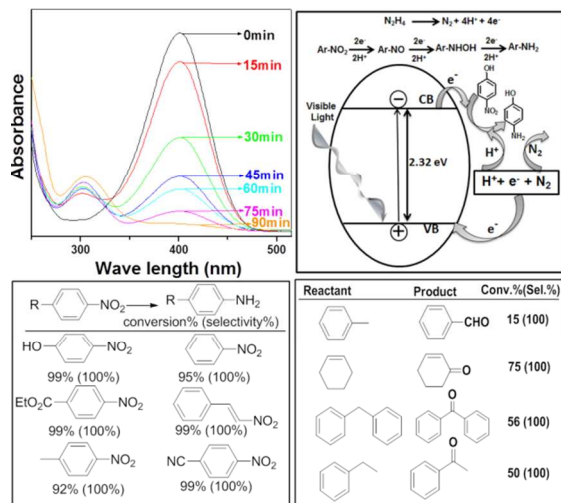
Based on the above mentioned experimental results a probable formation mechanism is proposed (see ESI†, Fig. S4). In the developed procedure water has a crucial role in the formation of spherical assembly and in-turn sheet assembled flower shape. After the formation of self-assembled decanoic acid stabilized very small ( $\sim 1$  nm) CdS dots (Fig. S4a see ESI†), reassembled in a spherical assembly due to the hydrophobic interaction (repulsion) of the aliphatic tail of DA attached to the CdS dot surface and polar solvent water, and attraction force between hydrophobic tail (Fig. S4b, see ESI†).<sup>10</sup> In the favourable synthetic condition the dots are aligned themselves locally within the spherical assembly through a common crystallographic facet  $\{111\}$  and attached together to give the sheet structure in (111) direction through orientated attachment. The

probable driving force for anisotropic growth through orientated attachment of symmetric cubic (zinc blend) CdS dot is dipole moments in the cubic crystal originating from the distribution of the chemically inhomogeneous planes.<sup>9d</sup>  $\{111\}$  facets of cubic CdS are terminated by either Cd or S atoms with varying electronegativity and contain dipole moments.<sup>11</sup> In the present case, due to the high surface energy of the  $\{111\}$  planes, originating from higher packing density and the number of unsaturated atoms on the  $\{111\}$  facets, the high index  $\{111\}$  facets grown faster. Thus, to reduce the surface energy, the CdS dots aligned themselves through chemically inhomogeneous  $\{111\}$  facet and merged through orientated attachment to give sheet structure (Fig. S4c, see ESI†). In the intermediate stage of sheet formation some void space was also observed and void space was filled by Ostwald ripening and finally resulted uniform sheet. For the Ostwald ripening the width of the sheets was less than that of parental spherical particles.

In the 1<sup>st</sup> set of reaction, reduction of *p*-nitrophenol to *p*-aminophenol was chosen as a model reaction to check the catalytic efficiency of synthesized sheet mediated CdS flower using hydrazine as a reducing agent and ethanol as solvent. A critical comparison of the reduction potential of both CdS flower and *p*-nitrophenol indicates that the reduction of *p*-nitrophenol is thermodynamically feasible, as the potential of CdS flower is sufficiently less ( $-ve$ ) (Fig. S7, see ESI†). The reaction was performed systematically and the progress of the reaction was monitored using UV-Vis absorption spectroscopy. The characteristic peak of *p*-nitrophenol at 400 nm decreased gradually and a new peak of *p*-aminophenol at 304 nm appeared and the peak intensity increased gradually during the progress of the reaction (Fig. 2, upper left panel). It takes 1.5 h for the complete reduction of *p*-nitrophenol to *p*-aminophenol. We have replaced the reducing agent hydrazine by  $\text{NaBH}_4$  but unfortunately did not show any significant improvement. The conversion was calculated by UV-Vis spectroscopy (Fig. S8, see ESI†) and it was further supported by NMR spectroscopy indicates  $>99\%$  conversion of the reaction. Full conversion of *p*-nitrophenol in various solvents other than ethanol, like 1,4-dioxane, toluene, confirm that hydrazine is working as source of electron and proton, and reduces the probable photo corrosion of CdS as photo catalyst. Based on the above mentioned observation, we have proposed a mechanism for the effective conversion of the nitro compounds (Fig. 2b, upper right panel). According to proposed mechanism, the valence band electron of CdS transfer to its conduction band, leaving a hole in the valence band on the visible light irradiation. The high energy conduction band electron goes to the nitro group and subsequent amination took place by taking  $\text{H}^+$  from hydrazine. The photo-generated hole in the VB of CdS was subsequently filled by the electron which was formed from the decomposition of hydrazine.

As this methodology was found highly effective for photocatalytic reduction of *p*-nitrophenol, we extended the substrate scope to different aromatic nitro compounds, e.g. *p*-nitro toluene and *p*-nitro benzonitrile (Fig. 2, lower left panel). To our delights it selectively reduced the nitro groups in presence of other reducing functional group like nitrile, alkene and ester group with excellent conversion and selectivity. We reused the catalyst for 4 cycles for the reduction of nitrophenol, no significant change in catalytic efficiency was observed compared to fresh catalyst (Fig. S9, see ESI†).

As our catalyst works effectively for aromatic nitro reductions we realize that it would work on selective oxidation of primary C-H bonds. The synthesized ultrathin CdS flower showed excellent photocatalytic activity towards oxidation of saturated  $\text{sp}^3$  C-H bonds using molecular oxygen as oxidant and benzotrifluoride as solvent in ambient condition under visible light, from 40W simple house hold CFL lamp. Results depict that the synthesized CdS ultra-thin sheet assembled flowers is too active to activate the  $\text{sp}^3$  C-H bonds with



**Fig. 2** Upper left panel: Successive UV-vis spectra during reduction of para nitrophenol; upper right panel: A Probable proposed photocatalytic pathway for reduction of nitroarenes over synthesized CdS flower; lower left panel: photocatalytic reduction of aromatic nitro compounds; lower right panel: photocatalytic oxidation of saturated sp<sup>3</sup> C-H bonds.

moderate to good conversion to corresponding oxidized product aldehyde or ketone with 100 % selectivity (Fig. 2, right lower panel). It is active towards primary C-H bond of toluene as well as secondary C-H bond of cyclohexene, ethylbenzene and diphenylmethane (Probable oxidation mechanism, Fig.S10, see ESI†).

The controlled experiments, for visible light induced photocatalytic reduction of p-nitrophenol using CdS bulk, agglomerated CdS nanoparticles (un-stabilized), and monodispersed spherical CdS particles (5 nm) under identical condition, confirmed that the activity of the synthesized CdS flower is much superior (Fig. S11, see ESI†). Further, the obtained results for the reduction of p-nitrophenol using synthesized CdS flower under simple house hold 40W CFL lamp is comparable or sometime better with respect to the literature reported pure CdS and CdS modified with costly graphene under undesirable 300 W Xe lamp (Table S1). The superior photocatalytic activity of the synthesized CdS flower is most probably due to the highest quantum confinement (Fig. S12, see ESI†) which exhibit higher rate of interfacial charge transfer, large surface area (Fig. S13, see ESI†) and long range of lattice periodicity in sheets that provides a better channel for electron transportation. Whereas, under identical condition in absence of CdS, i.e., catalyst, and presence of hydrazene the conversion of p-nitrophenol was negligible and confirmed that the reaction is strictly photocatalytic (Fig. S14, see ESI†).

In summary, we have developed a simple synthetic protocol for ultrathin (0.8 nm) sheet mediated uniform CdS flowers and use water as solvent make the procedure advantageous and greener. During synthesis, water took a crucial role in short range spherical assembly 1nm CdS dots and the dots were transformed to sheets in the spherical assembly through oriented attachment. The synthesized CdS flowers showed excellent visible light driven photocatalytic activity for selective reduction of nitroarines to corresponding amino compounds under simple house hold 40W CFL lamp. The CdS flower also active for oxidation of saturated sp<sup>3</sup> C-H bonds in molecular oxygen as oxidant. The photocatalytic activity is comparable or sometime better with respect to the literature reported pure CdS and CdS modified with costly graphene under hazardous 300 W Xe lamp. Finally, the catalyst can be utilize for other photocatalytic reactions and may be the potential material for the fabrication of photovoltaic devices.

## Notes and references

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Electronic Supplementary Information (ESI) available: [detailed experimental procedure, additional TEM, catalytic results, electrochemical data]. See DOI: 10.1039/c000000x/

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