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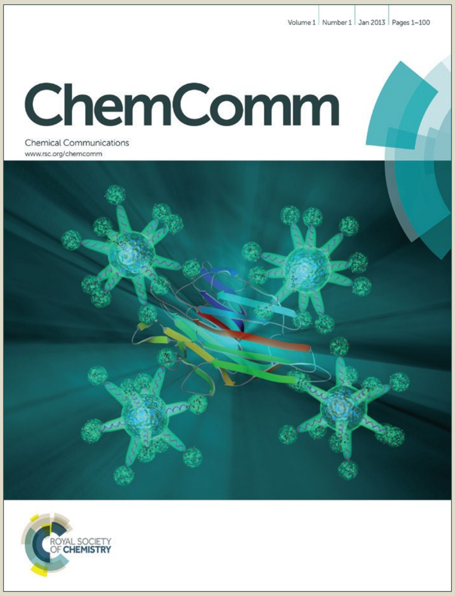

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Highly efficient and selective photocatalytic reduction of nitroarenes using Ni_2P/CdS catalyst under visible-light irradiation

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A highly efficient and selective heterogeneous photocatalytic system for nitro reduction to amino organics was established using CdS, Ni_2P and Na_2S/Na_2SO_3 as photosensitizer, cocatalyst and sacrificial electron donor in aqueous solution, respectively. Two competing pathways for photocatalytic H_2 production and nitro reduction were found. Also, the reduction of nitroarenes to aniline was confirmed to proceed through both the direct and condensation routes.

Functionalized aminobenzenes are important intermediates for the preparation of many agrochemicals,[1] pharmaceuticals,[2] dyes,[3] and pigments,[4] and can be obtained easily through the reduction of nitroarenes. Various procedures using metals or other reducing agents can achieve this purpose through the catalytic process. Traditionally technology processes use Béchamp[5] reduction employing iron and hydrochloric acid, and sulfide reduction[6] technology using H_2S or NaHS as a reducing agent, which caused large amounts of environmentally toxic waste. Moreover, Selective hydrogenation of corresponding nitro organics with other reducible groups is difficult in a catalytic process.[7] Hence, plenty of works have been focused on improving reaction activity by selective catalytic reduction.[8,9] Among these synthesis methods, photocatalytic reduction aroused by photo-generated electrons has been studied extensively to produce organics due to its non-use of dangerous reducing agents, like photocatalytic hydrogen evolution[10] and nitro-aromatics reduction.[11]

However, most of the developed photocatalysts can only utilize ultraviolet irradiation, which only accounted for 4 % of the solar energy. Recently, many researchers have focused their interest on the development of visible-light-responsive photocatalysts with the aim of efficiently utilizing the abundant visible light (λ > 420 nm), which occupies about 43 % of the solar energy spectrum.[12] Matsuoka et.al have reported an efficient photocatalyst using a Pt-deposited amino-functionalised Ti(IV) metal–organic framework (Pt/Ti-MOF-NH_2) under visible-light irradiation for nitro reduction. The initial reaction rate for Pt(1.5)/Ti-MOF-NH_2 was determined to be 132 *μmol* h^{-1}·g^{-1}. While after 70 h irradiation, a small quantity of nitrosobenzene still exists as residual.[13] As a well-known, cadmium sulphide (CdS) features a suitable band gap (2.4 eV) matching well with the spectrum of sunlight, which has prospectively high solar energy conversion efficiency and has been recognized as one of the most attractive visible–light active photocatalysts.[14] Xu and co-workers reported the assembly of one-dimensional CdS nanowires (NW) on the platform of reduced grapheneoxide (RGO) nanosheets via a simple and efficient electrostatic selfassembly method, under visible–light irradiation with the addition of ammonium formate as a holes scavenger, the CdS NW–RGO composites exhibit significantly enhanced photoactivity.[15,16] In other hand, the most frequently used catalysts are noble metals, like Pt and Au supported on active carbon, TiO_2, SiO_2, Fe_2O_3, and Ni-based systems.[17,18] Replacement of noble metals with earth-abundant metals would be desirable to clean-energy technologies. Transition-metal phosphides which possess similar characteristics of zero-valent metals are under increasing interest as catalysts for hydrotreating reaction and have exhibited high activity in electrocatalytic reactions.[19] Nickel phosphide (Ni_2P) having the hexagonal structure is a well-known hydrogen-generating catalyst.[20] Very recently, our group discovered that Ni_2P nanoparticles (NPs) can be used as an efficient cocatalyst for photocatalytic hydrogen evolution using CdS nanorods as photo-absorber from lactic acid aqueous solution, which achieved a high H_2-production rate of 34,800 *μmol*·h^{-1}·g^{-1} for the system containing 5% of Ni_2P in quality percentage.[21]

Herein, we report a highly robust and inexpensive photocatalytic system with CdS NPs as photosensitizer, Ni_2P NPs as cocatalyst, Na_2S and Na_2SO_3 as sacrificial reagents, which exhibits highly efficient and selective activity in pure water for the reduction of nitro to amino (Fig. 1). To the best of our knowledge, Ni_2P NPs was first used in the nitro reduction reaction, and inorganic sacrificial regents are favourable to the easy post-treatment.

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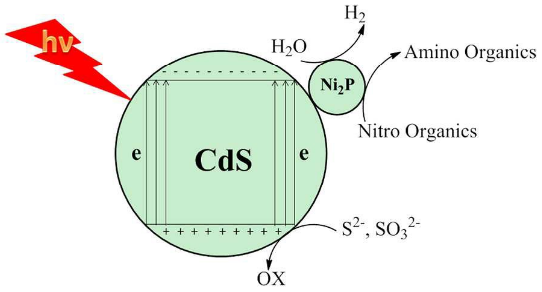

Fig. 1 Schematic representation of the Ni_2P/CdS hybrid photocatalyst for reduction of nitro organics.

CdS and Ni_2P were prepared according to literature methods.[22,23] Ni_2P/CdS hybrid material was obtained by grinding the raw CdS and Ni_2P nanoparticles with a mortar according to certain ratio to form a uniform powder. All the experimental details were shown in the Electronic Supplementary Information (ESI). Figure 2a shows the X-ray diffraction (XRD) patterns of the samples as-prepared CdS. The peaks at 2θ values of 24.9, 26.5, 28.2, 36.3, 43.6, 48.1 and 51.9 are indexed to the (100), (002), (101), (102), (110), (103) and (201) crystal planes, respectively, which are in good agreement with the expected phase of CdS (JCPDS Card No. 65-3414). The Ni_2P were obtained by a thermal synthesis route. The XRD pattern of Ni_2P can be ascribed to the stable hexagonal phase Ni_2P (JCPDS card No. 03-0953). As shown in Fig 2b, four sharp diffraction peaks with 2θ are exhibited at 40.7, 44.6, 47.4 and 54.2, which can be assigned to the (111), (201), (210) and (300) reflections, respectively.

Furthermore, the morphological and structural features of the prepared Ni_2P/CdS hybrid material were examined by transmission electron microscope (TEM) and high revolution TEM (HRTEM). From the TEM image (Fig. 2c), it can be seen that Ni_2P (the red circle) are well dispersed among the CdS nanoparticles (the yellow circle) after careful grind process. The HRTEM image further (Fig. 2d) reveals that the Ni_2P NPs are coated on CdS NPs with intimate contact, which will be helpful to realize the electron transfer between the the CdS photosensitizer and Ni_2P cocatalyst, leading to the enhanced photocatalytic efficiency. In the HRTEM image, the lattice spacing of ca. 0.33 nm belonging to the (002) plane of CdS,[19] and a different kind of lattice fringes with d spacing of ca. 0.22 nm were attributed to the high intense (111) reflection of Ni_2P.[24]

The photo-driven reduction was carried out in oxygen-free water solution at room temperature and atmospheric pressure. Typically, 5 mL of solution containing the substrate (4-nitrotoluene, 20 mg), the sacrificial reagents (Na_2S, 0.25 M and Na_2SO_3, 0.3 M) and the photocatalyst (Ni_2P/CdS, 2 mg) in a 15 mL quartz cuvette was irradiated with 30 × 3 W LED light (λ > 420 nm) under nitrogen condition with stirring. After irradiation, the products were extracted thoroughly with dichloromethane three times, dried with anhydrous $MgSO_4$ and quantified using ^1H NMR spectroscopy. ^1H NMR spectra of the substrate and product with variable-irradiation time are shown in Fig. 3. Control experiments showed that the photocatalyst, the sacrificial reagents and light were all essential for the effective reduction (see SEI†, Table S1, entries 8, 20, 21). The concentration of Ni_2P has a great influence on the efficiency of photocatalytic reduction. Comparison studies with photocatalytic efficiencies under different ratio of Ni_2P (0wt%, 1wt%, 2.5wt%, 5wt%, 7.5wt%, 10wt% and 100wt% in weight percentage) were investigated (see SEI†, Table S1, entries 1–7). These results indicate an optimized fraction of Ni_2P at 5wt% is required for the photocatalyic system. This showed that with the increasing ratio of Ni_2P, the more active catalytic sites can be provided for catalytic reduction. However, when the Ni_2P accounted for more than 5wt%, the protons absorption ability of CdS will be restrained. In addition, higher amounts of Ni_2P shields photosensitizer from incident light, resulting in the decrease of reduction efficiency.[25] The photo-generated electrons in the CdS semiconductor under visible-light irradiation can be accepted by Ni_2P, thereby decreasing the recombination probability of the photoexcited electron-hole pairs.[26] On the other hand, with the total weight of hybrid catalysts increasing, the efficiency of reduction turn better obviously (see SEI†, Table S1, entries 8-13). There is no doubt that the more Ni_2P/CdS the more active catalytic sites can be provided for reduction reaction. Meanwhile, by comparing the control experiments (see SEI†, Table S1, entries 14–18), it was found that the yield increases with the prolonging of reaction time. The reaction rates for nitro reduction were determined to be 7146 $\mu mol\ h^{-1}\cdot g^{-1}$ in the first 10 h (on the basis of the 4-nitrotoluene conversion for the system containing 5 wt% of Ni_2P).

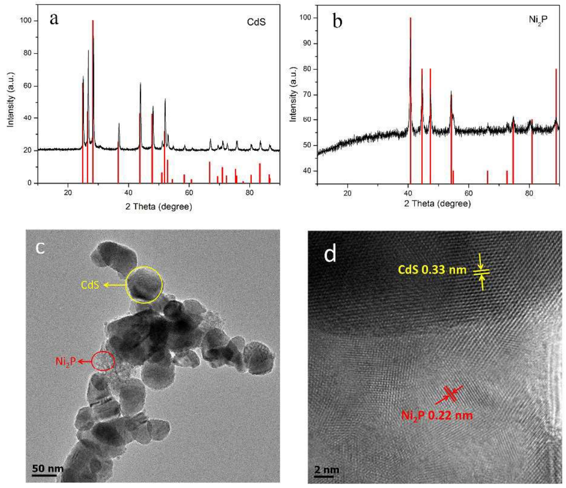

Fig. 2 XRD pattern of CdS (a) and Ni_2P (b), TEM image (c) and HRTEM image (d) of the obtained Ni_2P/CdS hybrid material.

Furthermore, we found that it is intriguing that photocatalytic hydrogen evolution was accompanied with the photoctalytic reduction of nitro in the present system (see Fig. 4). The H_2-production rate can reach up to 4624 $\mu mol\cdot h^{-1}\cdot g^{-1}$ in the system without substrate during 12 h of visible-light irradiation. However, when the substrate was added, there is almost no hydrogen detected at the beginning 10 h. After which time the amounts of hydrogen production increased quickly, accordance with most of the 4-nitrotoluene were consumed. This suggested two different

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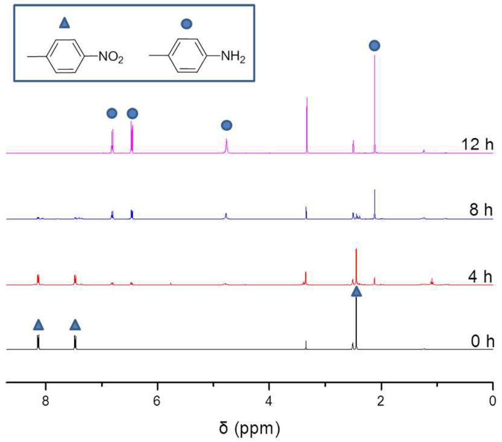

Fig. 3 ^{1}H NMR spectra of 4-nitrotoluene with variable-irradiation time in DMSO solutions.

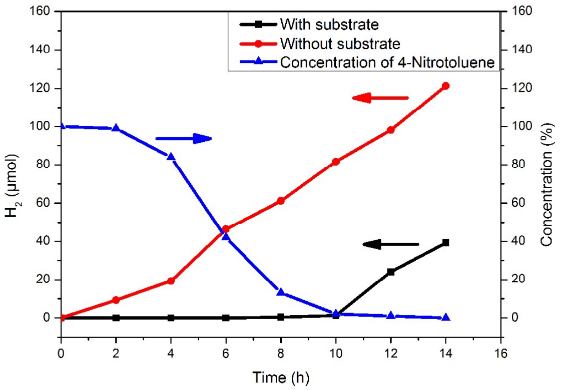

Fig. 4 Time courses of H_2-production and concentration of 4-nitrotoluene under LED.

reaction routes, viz. photogenerating hydrogen and photocatalytic reduction of 4-nitrotoluene to corresponding aniline, occur in the photocatalytic system as shown in Figure 1. To prove this competitive mechanism, control experiments were carried out (see SEI†, Table S1, entry 19). The photocatalytic reduction of 4-nitrotoluene using anhydrous acetonitrile as solvent proceeded under H_2 atmosphere with the same situation in other conditions. After irradiation, almost no reduction product was observed, which shows that H_2 didn't participate in the reduction reaction of substrate. This means that in the parallel competitive photocatalytic reduction reactions, the pathway of nitro reduction dominates the reaction process in the presented reaction system, and solvent water plays an important role of hydrogen source.

The photocatalytic stability experiment for 2 mg 5wt% hybrid photocatalyst was then performed (see SEI†, Fig. S7). The TEM image and X-ray photoelectron spectroscopy of the catalyst before and after the reaction shows no obvious difference (see SEI†, Fig. S4–S6). After the extraction of organic compounds from the reaction mixture, fresh 4-nitrotoluene (20 mg) was added into the system, reduction conversion of substrate still could be completed with prolonged reaction time (see SEI†, third cycle in Fig. S7). However, a gradual decline in the photocatalytic activity for the third catalytic cycle was observed, which is tentatively ascribed to the photocorrosion of CdS and consumption of Na_2S and Na_2SO_3.[27] When 1.0 mg CdS, 0.25 M Na_2S and 0.3 M Na_2SO_3 were added to the system, the photocatalytic activity was restored (see SEI†, fourth cycle in Fig. S7). These results indicate that Ni_2P cocatalyst in the visible-light driven system possesses high catalytic activity and stability.

Generally, the reduction of nitrobenzene to aniline are considered to procced through two processes, that either through the direct route via nitrosobenzene and N-phenylhydroxylamine intermediates, or through a condensation route via azoxybenzene, azobenzene and hydrazobenzene (Fig. 5).[28] We applied ^{1}H NMR spectroscopy and mass spectrometry to follow the photocatalytic reduction and indeed detected nitroso and hydroxylamine in the initial stage of the reaction with the generating of aniline (see SEI†, Fig. S8 and Table S2). Because hydroxylamine reduction is slow, which requires the cleavage of an O-N bond, azoxybenzene, azobenzene and hydrazobenzene were formed via a disproportionation pathway as the reaction time prolongs (see SEI†, Fig. S9 and Table S2). The formation of azoxybenzene (m/z 227.1173) and azobenzene (m/z 211.1225) were also confirmed by mass spectral analysis (see SEI†, Fig. S10 and Table S2). After the reaction completed, 4-nitrotoluene was the final product (see SEI†, Fig. S11 and Table S2). Present observations support the conclusion that two reaction pathways exist in the reaction of nitrobenzene reduction to aniline.

With the understanding of the reaction mechanism, the photocatalytic reduction was further extended to the nitrobenzene derivatives with reducible groups, and the chemoselectivity was particularly examined. Full-to-high conversions of the nitro substrates with excellent selectivity (99%) toward the respective amines were achieved in all of the tested catalytic reactions with reaction time prolongs. The substituted nitrobenzene with methyl, or methoxy groups displayed high conversions and selectivities with Ni_2P/CdS hybrid nanocatalysts. To our delight, bromo- and chloro-substituted nitroarenes, which can undergo facile dehalogenation, were selectively reduced to the respective halogenated aromatic amines without showing any sign of dehalogenation. Furthermore, in the nitrobenzene derivatives bearing other reducible functional groups, such as nitrile, ketone and aldehyde, there are only nitro groups being selectively reduced to the corresponding aromatic amines in good yields. However, when nitrobenzene was used as the substrate, hydrazobenzene was the final product (see SEI†, Figs. S12 and S13, Table S2, δ(NH-NH) = 5.601 ppm, m/z 185.1068), even the reaction time prolonged to 48 h.[29,30] Moreover, we also examined the reduction of pure diazobenzene to aniline, after prolonged reaction time of 48 h, only isolated hydrazobenzene was found. The cause of this phenomenon is not clear, further study is still progress.

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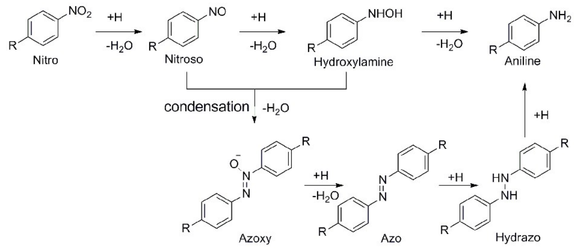
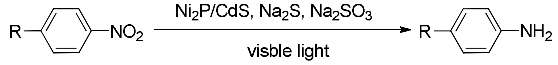


Fig. 5 Proposed mechanism for the catalytic reduction of nitro compounds to aniline derivatives.

Table 1. Catalytic reduction of nitroarenes to the corresponding anilines^{a}



Entry	R	Conversion^{b} %	Selectivity^{b} %
1	CH_3	100	99
2	OCH_3	100	100
3	Cl	98	99
4	Br	97	99
5	CH_2CN	99	99
6	$COCH_3$	91	99
7	CHO	95	98
8	H	99^{d}	99^{d}
9^{c}	azobenzene	99^{d}	99^{d}

^{a} Light source: LED (λ > 420 nm, 30 × 3 W); room temperature; substrate amount: 20 mg; Na_2S: 0.25 M and Na_2SO_3: 0.3 M; H_2O: 5 mL; irradiation time: 24 h. ^{b} Determined by ^{1}H NMR. ^{c} azobenzene as the substrate. ^{d} Determined by hydrazobenzene.

In summary, a highly efficient and selective visible-light catalytic system with Ni_2P/CdS as photocatalyst in pure water was established for nitro reduction. The reaction product was obtained in a facile way. The introduction of Ni_2P cocatalyst into CdS system displayed significantly enhanced activity in the photodriven reduction of nitro compared with the bare CdS system. These results provide a favorable approach for developing new cocatalyst in photodriven chemical conversion. Two competing reaction pathways of photogenerating hydrogen and photocatalytic reduction of nitro were suggested based on control experiments, the latter dominates the reaction process. Although investigations of product and intermediates by H^{1} NMR and ESI-MS clearly showed that reduction of nitro to aniline occurs through two routes, viz. the direct and condensation routes, when nitrobenzene was used as the substrate, the mechanistic insight into hydrazobenzene observed for final product is currently in progress.

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Entry for the Table of Contents

A highly efficient Ni_2P/CdS photocatalytic system in water for selective reduction nitro to amino and reaction mechanism was presented clearly