Electronic Supplementary Information

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

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Table of Contents

Experimental Procedure

1. Chemicals and methods

All materials were of analytical grade and used without further purification. $CdCl_2 \cdot 2.5H_2O$ was purchased from Jinke chemical research institute, (Tinjin, China);

$NiCl_2 \cdot 6H_2O$] were obtained from Xilong Chemical Co. Ltd., (Guangdong, China). $Na_2S \cdot 9H_2O$ and NaOH were obtained from Aladdin Reagent Co. Ltd., (Shanghai, China). Powder X-ray diffraction (XRD) pattern was recorded on a Bruker AXS D8 X-ray diffractometer with Cu Kα (λ = 1.54056 Å). The size and lattice fringes measurements were analyzed on a transmission electron microscope (TEM) (JEM 2100F) with an accelerating voltage of 200 kV. Elemental analysis data of CdS and Ni_2P were collected by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian 710-OES, USA). X-ray photoelectron spectroscopy was determined in a PHI 5300 ESCA system. And the source was an Al Kα X-ray source with a power of 250 W. The charge effect was calibrated with the binding energy of C1s.

2. Material Synthesis

2.1 Synthesis of CdS

In a typical process, an aqueous solution of Na_2S was added slowly to $CdCl_2$ solution under vigorous stirring with the molar ratio 1.2:1. The resulting yellow mixture was stirred for 24 h and kept for an additional 24 h during the ion exchange process in the next stage. The resulting yellow slurry was filtered. The wet solid was suspended in deionized water (60 mL) and transferred to a Teflon lined stainless steel autoclave (100 mL) and heated at 200 °C for 24 h (hydrothermal treatment). After that, the yellow solid was filtered, washed with water and ethanol successively, filtered again, and then held under vacuum at 80 °C for 24 h.

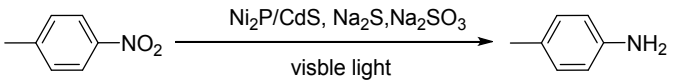
2.2 Synthesis of Ni_2P

In a typical process, the cocatalyst precursor was prepared via a mechanical mixing method. $NiCl_2$ and NaOH in aqueous solution were reacted under stirring for 30 min to obtain $Ni(OH)_2$. NaH_2PO_2 and $Ni(OH)_2$ in the ratio 5:1 was mechanically mixed in a quartz boat at room temperature. The mixture was directly heated to 270 °C and kept for 2 h in a flowing N_2. Following cooling to room temperature in continued N_2 flow, the obtained product was washed with diluted hydrochloric acid, then the raw Ni_2P was centrifugalized followed with washing by water and ethanol successively, then dried under vacuum at 80 °C for 24 h.

3. Photocatalytic activity measurement

Typically, 5 mL of solution containing the substrate (20 mg), the sacrificial reagents Na_2S (0.25 M) and Na_2SO_3 (0.3 M), 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. After irradiation, the raw products were extracted thoroughly with dichloromethane three times, dried with anhydrous $MgSO_4$ and quantified using ^1H NMR spectroscopy. The reaction rate = n(consumed nitro)/[m(cat) × h)]

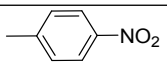
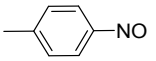
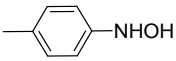
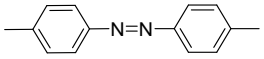
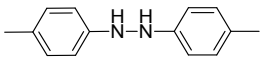
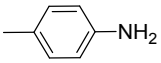
Table S1 Photocatalytic reduction of 4-nitrotoluene to corresponding amino organics.[a]



Entry	Weight % of Ni_2P [b]	Weight [mg] [c]	t [h] [d]	Conversion [%] [e]
1	0	2	12	64
2	1	2	12	76
3	2.5	2	12	94
4	5	2	12	98
5	7.5	2	12	88
6	10	2	12	78
7	100	2	12	1.7
8	5	0	12	0
9	5	1	12	69
10	5	2	12	98
11	5	4	12	99
12	5	6	12	99
13	5	8	12	100
14	5	2	0	0
15	5	2	1	0
16	5	2	4	16
17	5	2	8	87
18	5	2	12	99
19 [f]	5	2	12	2.3
20 [g]	5	2	12	0
21 [h]	5	2	12	0
22	5	10	5	76
23[i]	5	10	5	43
24[j]	5	10	5	67

[a] Reaction condition: 4-nitrotoluene: 20 mg; H_2O: 5 mL; room temperature; Na_2S (0.25 M) and Na_2SO_3 (0.3 M) as sacrificial reagent; LED (λ > 420 nm, 3W × 30). [b] Weight % of Ni_2P in hybrid catalysts. [c] Total weight of hybrid catalysts. [d] Irradiation time. [e] Determined by ^1H NMR. [f] Using acetonitrile as solvent under H_2 atmosphere. [g] No irradiation. [h] No sacrificial reagents. [i] CdS and Ni_2P were added separately. [j] CdS and Ni_2P were added separately, and the system were treated with ultrasonic for 1h before irradiation.

Table S2 ^{1}H NMR data of products and intermediates in $CDCl_3$ solutions.

Compounds	δ (ppm) [a]
	2.46 (s, 3H), 7.29 (d, 2H, *J*=8.4), 8.11 (d, 2H, *J*=8.4)
	2.44 (s, 3H), 7.27 (d, 2H, *J*=8.4), 8.17 (d, 2H, *J*=8.4)
	2.41 (s, 3H), 7.27 (d, 2H, *J*=8.4), 8.10 (d, 2H, *J*=8.4)
	2.43 (s, 6H), 7.29 (d, 4H, *J*=8.4), 7.80 (d, 4H, *J*=8.4)
	2.30 (s, 6H), 4.70 (s, 2H), 6.77 (d, 4H, *J*=8.0), 7.08 (d, 4H, *J*=8.0)
	2.24 (s, 3H), 3.52 (s, 2H) , 6.60 (d, 2H, *J*=8.0), 6.95 (d, 2H, *J*=8.0)

[a] The hydrogen number of each compound was determined by assuming that the number of methyl hydrogen is 3 or 6.

Table S3 Elemental analysis data of Ni_2P(5wt %)/CdS

	Ni	Cd	Ni_2P	CdS
Concentration (%)	3.74	73.50	4.73	94.47

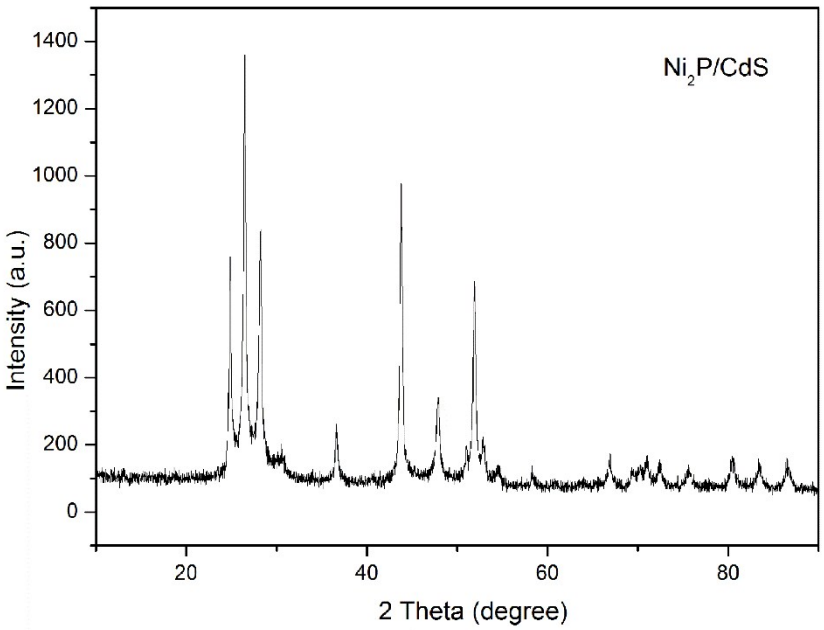


Fig. S1 XRD of the Ni_2P(5 wt%)/CdS hybrid material.

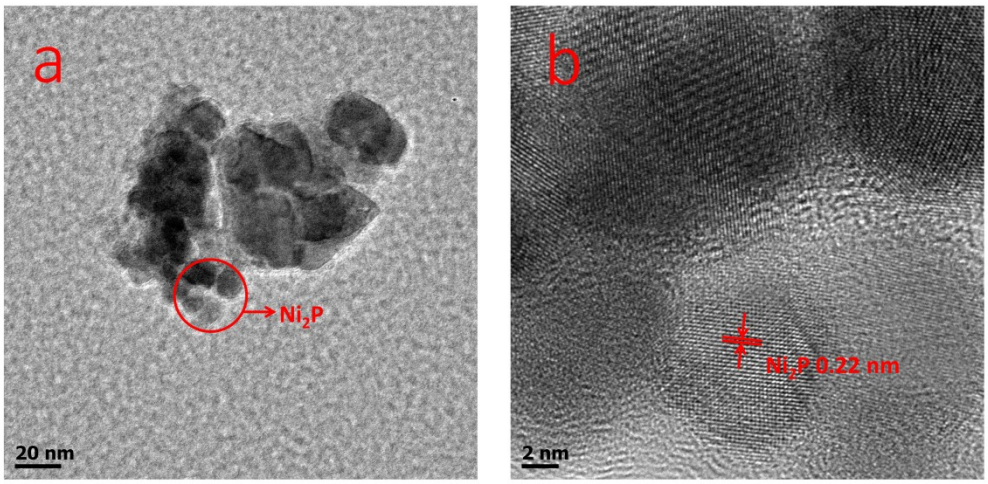


Fig. S2 (a) TEM image and (b) HRTEM image of the obtained Ni_2P.

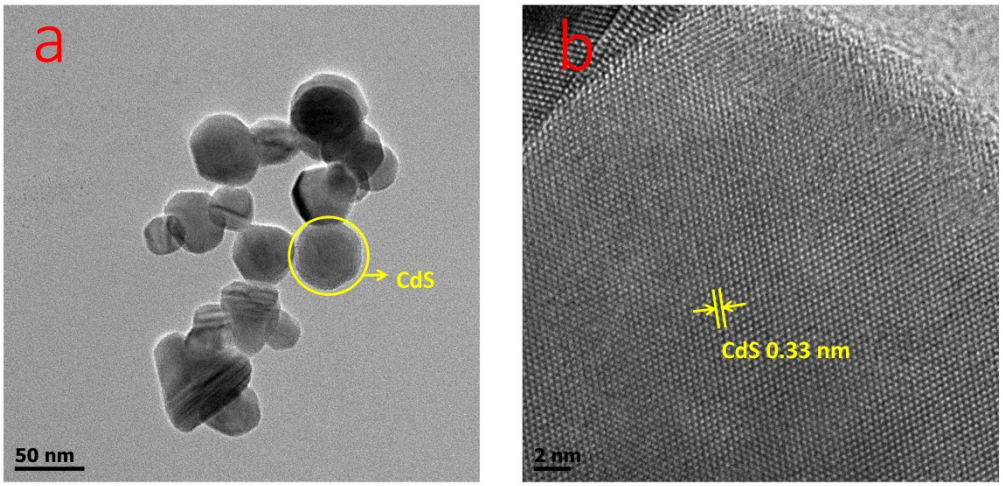


Fig. S3 (a) TEM image and (b) HRTEM image of the obtained CdS

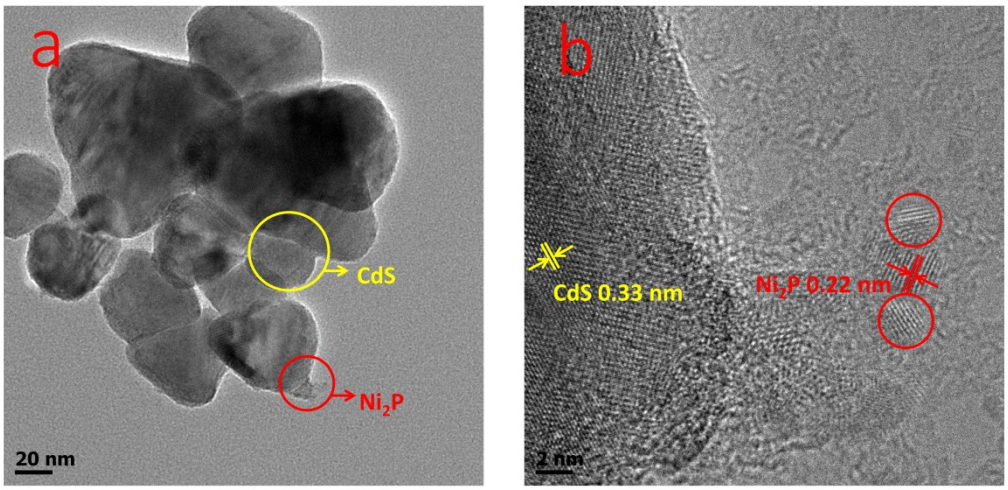


Fig. S4 (a) TEM image and (b) HRTEM image of the Ni_2P/CdS hybrid material after the photocatalytic reaction.

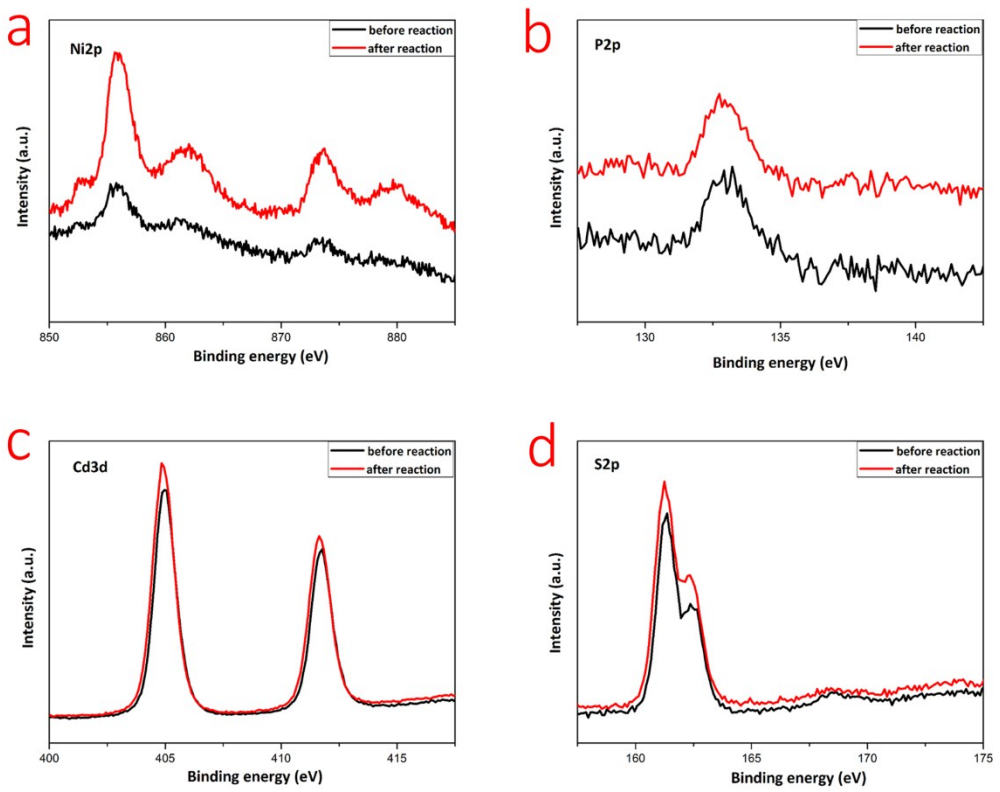


Figure S5 XPS spectra of the (a) Ni 2p, (b) P 2p, (c) Cd 3d and (d)S 2p regions in Ni_2P/CdS before and after the photocatalytic reaction.

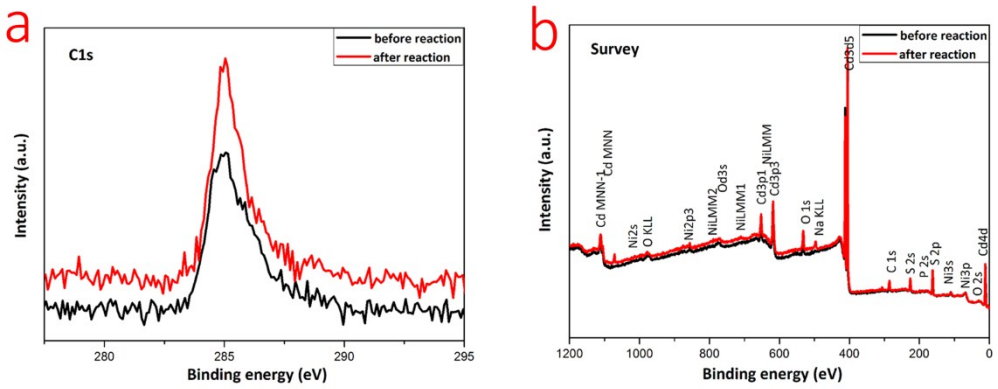


Figure S6 XPS spectrum of the (a) C 1s region and (b) survey spectrum in Ni_2P/CdS before and after the photocatalytic reaction.

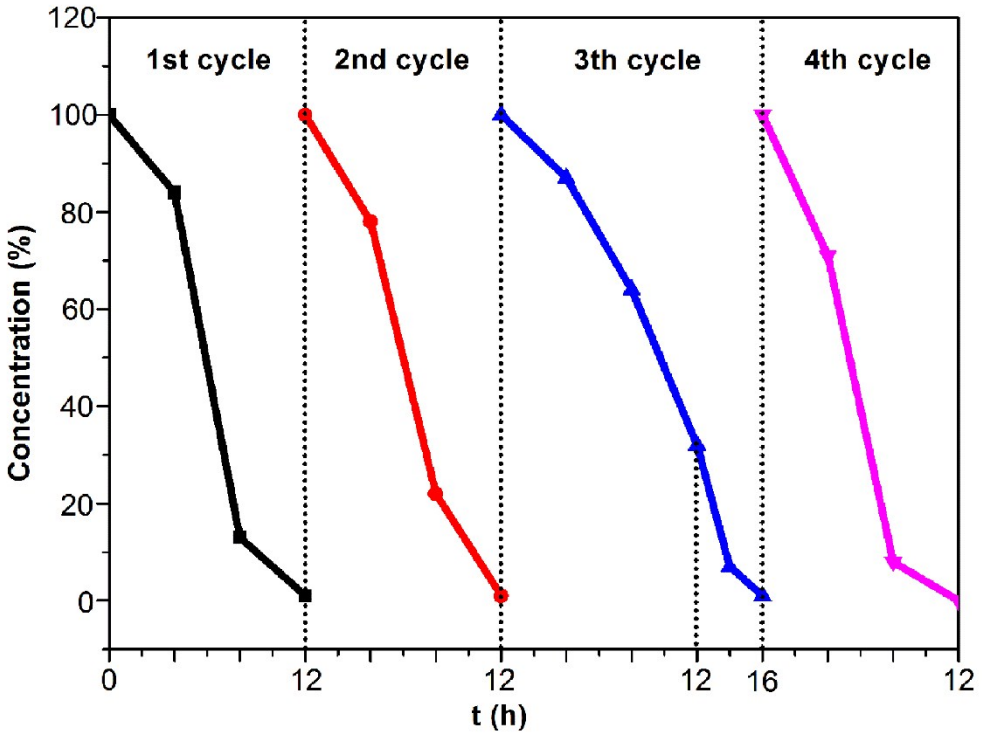


Fig. S7 Recyclability test for the photocatalytic reduction of 4-nitrotoluene.

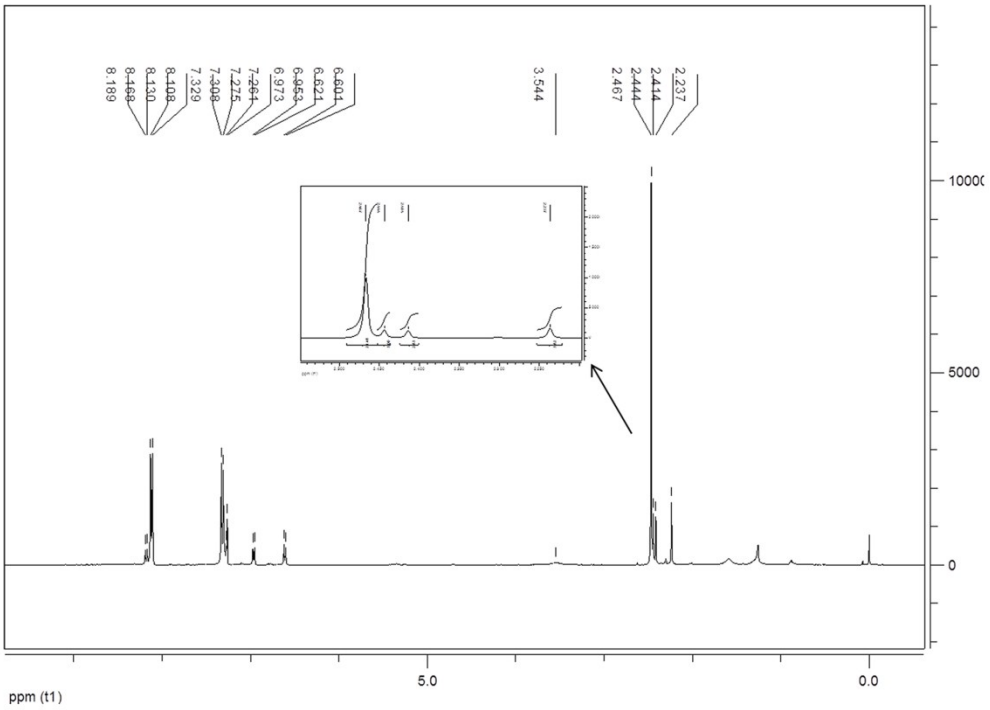


Fig. S8 ^{1}H NMR of photocatalytic reduction product of 4-nitrotoluene in $CDCl_3$ after 1 h irradiation.

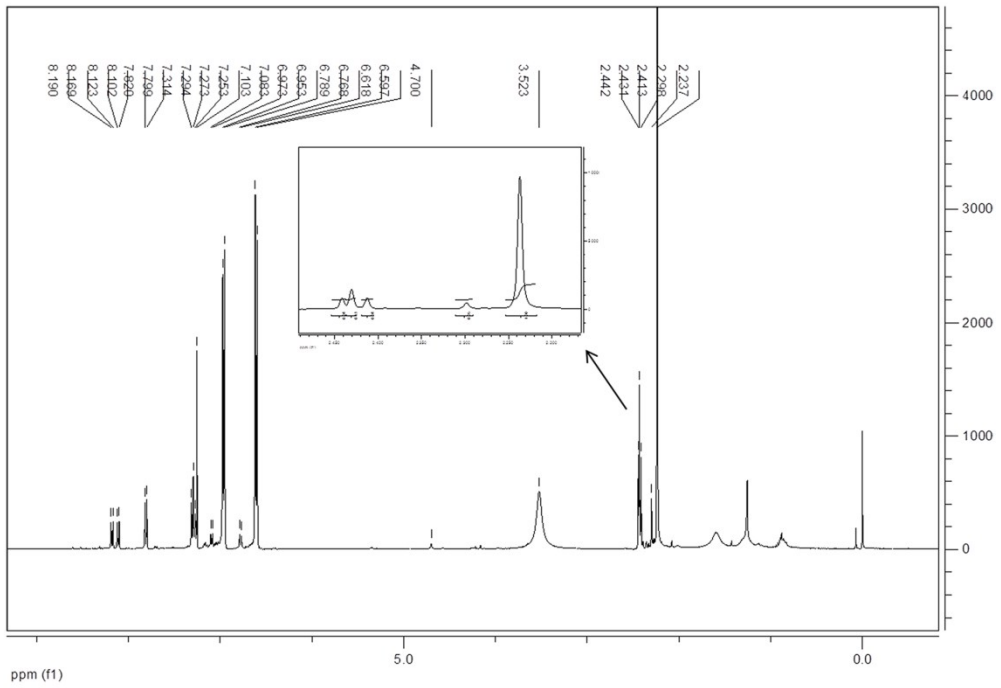


Fig. S9 ^{1}H NMR of photocatalytic reduction product of 4-nitrotoluene in $CDCl_3$ after 6 h irradiation.

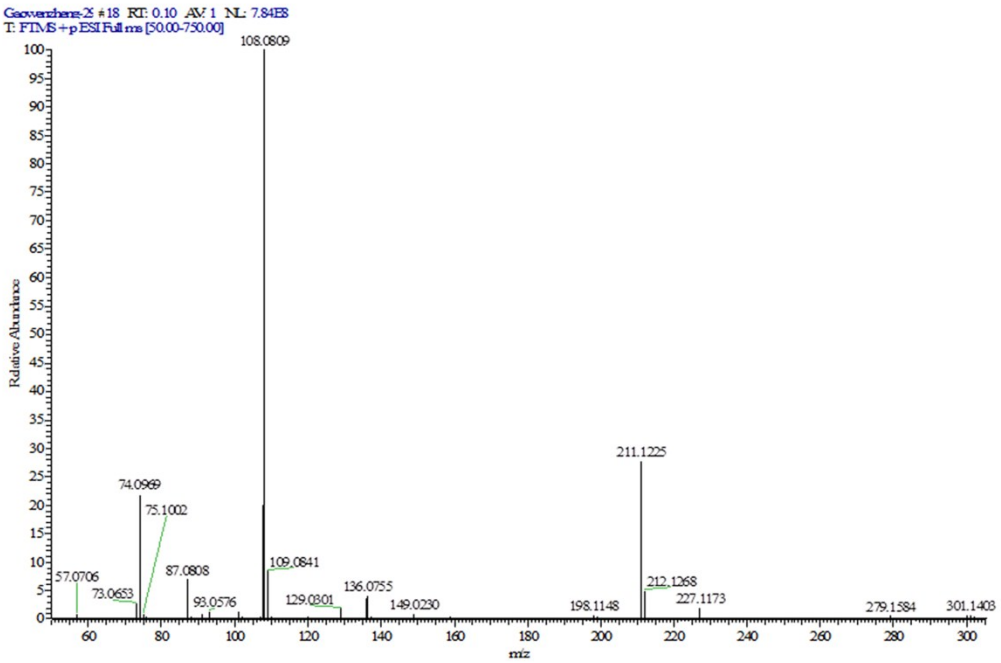


Fig. S10 ESI-MS spectrum of photocatalytic reduction product of 4-nitrotoluene after 6 h irradiation.

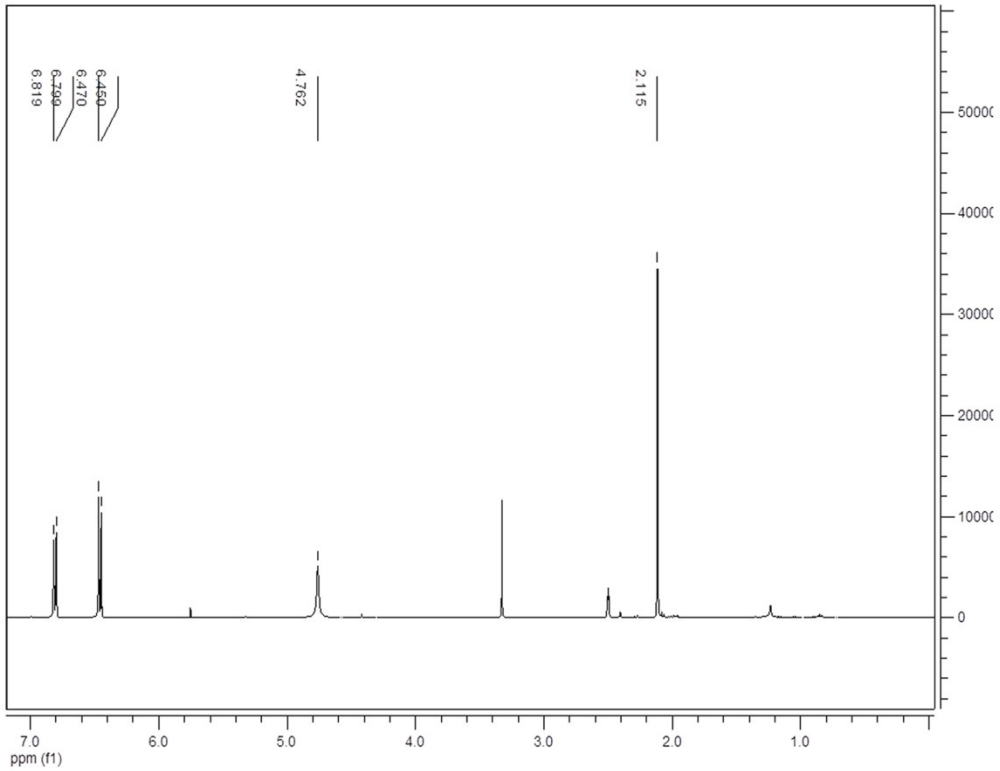


Fig. S11 ^{1}H NMR of photocatalytic reduction product of 4-nitrotoluene in DMSO after 12 h irradiation.

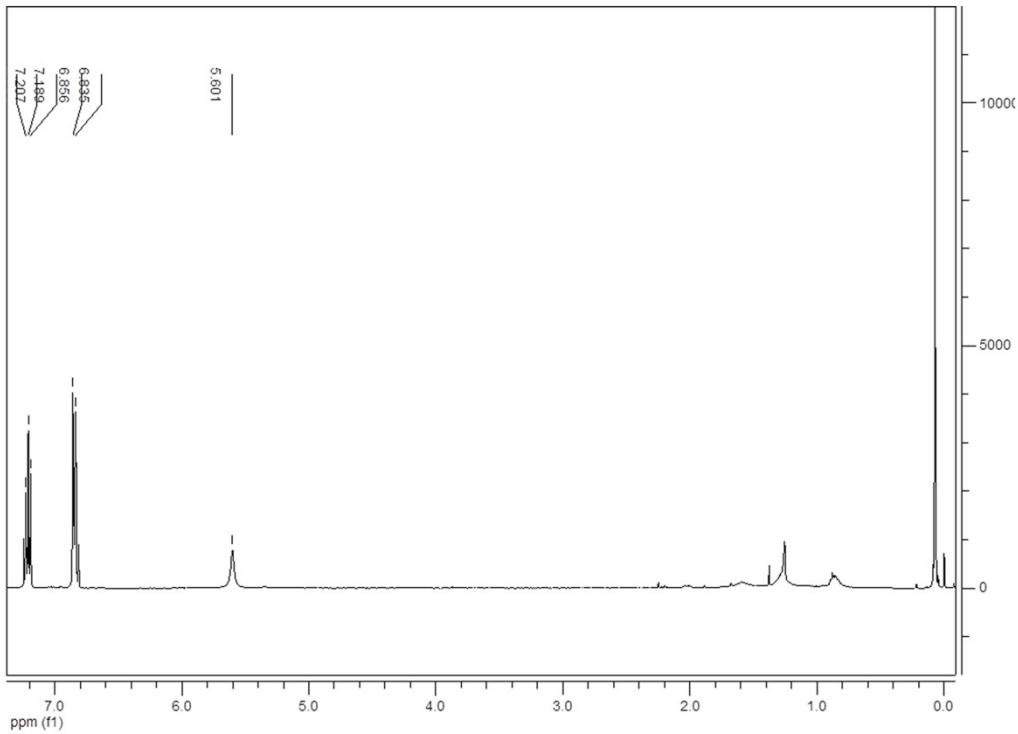


Fig. S12 ^{1}H NMR of photocatalytic reduction product of diazobenzene after 48 h irradiation.

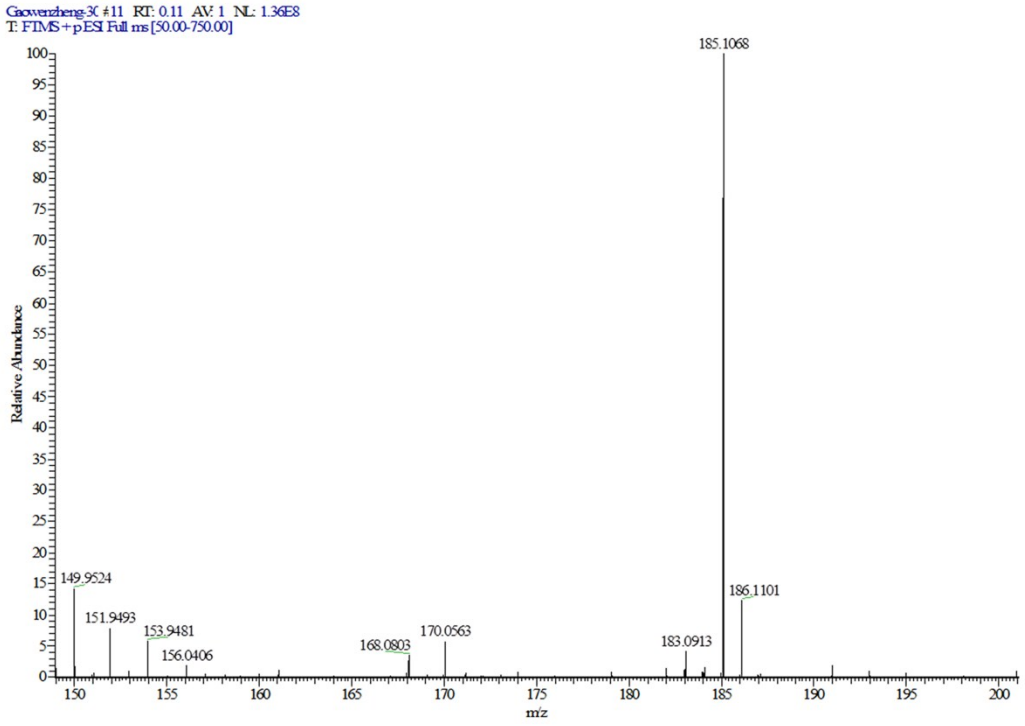


Fig. S13 MS-ESI spectrum of photocatalytic reduction product of diazobenzene after 48 h irradiation.