# *Electronic Supplementary Information for the manuscript*

## A nanotree-like CdS/ZnO nanocomposite with spatially branched hierarchical structure for photocatalytic fine-chemical synthesis

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## *Experimental section*

### 1 Preparation

### 1.1*Materials*

Sodium diethyldithiocarbamate trihydrate ($C_5H_{10}NNaS_2\cdot 3H_2O$), cadmium chloride ($CdCl_2\cdot 2.5H_2O$), ethylenediamine ($C_2H_8N_2$), potassium hydroxide (KOH), zinc acetate dihydrate ($C_4H_6O_4Zn\cdot 2H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot 6H_2O$), hexamethylenetetramine ($C_6H_{12}N_4$, HMT) and methanol ($CH_3OH$) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All materials were analytical grade and used as received without further purification. Deionized water used in the synthesis was from local sources.

### 1.2 *Synthesis of CdS nanowires*

Uniform CdS NWs were grown through a modified method.[S1] In a typical process, 1.124 g of cadmium diethyldithiocarbamate ($Cd(S_2CNEt_2)_2$), prepared by precipitation from a stoichiometric mixture of sodium diethyldithiocarbamate trihydrate and cadmium chloride in deionized water, was added to a Teflon-lined stainless steel autoclave with a capacity of 50 mL. Then, the autoclave was filled with 40 mL of ethylenediamine to about 80% of the total volume. The autoclave was maintained at 180 °C for 24 h and then allowed to cool to room temperature. A yellowish precipitate was collected and washed with absolute ethanol and deionized water to remove residue of organic solvents. The final products were dried in oven at 60 °C for 12 h.

### 1.3 *Synthesis of ZnO seed*

ZnO sol-gel solution was prepared as reported previously.[S2] 125 mL zinc acetate dehydrate solution in methanol (0.01 M) was prepared under vigorous stirring at 60 °C. Then, 65 mL KOH solution in methanol (0.03 M) was injected dropwise into the above solution. The sol-gel solution of ZnO seeds was obtained after continuous stirring at 60 °C for 2 h.

### 1.4 *Synthesis of branched hierarchical CdS/ZnO (CZ) nanocomposites*

Then, the obtained CdS NWs (80 mg) were dispersed in the prepared ZnO seed solution. After 30 min stirring, the suspension was centrifuged at 4500 rpm. Then, the yellowish precipitate was dispersed in a 100 mL aqueous solution composed of equimolar zinc nitrate (0.015 M) and hexamethylenetetramine (HMT) (0.015 M). After incubation at 95 °C for 6 h, the yellowish precipitate was collected by centrifugation, rinsed thoroughly with deionized water, and dried in the air. Blank ZnO is synthesized by the similar processes without adding CdS NWs.

## 2 Characterization

Field-emission scanning electron microscopy (FE-SEM) was used to determine the morphology of the samples on a FEI Nova NANOSEM 230 spectrophotometer. Zeta potentials ($\xi$) measurements of the samples were determined by dynamic light scattering analysis (Zeta sizer 3000HSA) at room temperature of 25 °C. The crystal phase properties of the samples were analyzed with a Bruker D8 Advance X-ray diffractometer (XRD) using Ni-filtered Cu K$\alpha$ radiation at 40 kV and 40 mA in the 2$\theta$ ranging from 20° to 70° with a scan rate of 0.02° per second. The optical properties of the samples were analyzed using a UV−vis spectrophotometer (Cary-500, Varian Co.) in which $BaSO_4$ was used as the background. The photoluminescence (PL) spectra for solid samples were investigated on an Edinburgh FL/FS900 spectrophotometer with the excitation wavelengths of 360 nm and 420 nm, respectively. The Brunauer−Emmett−Teller (BET) specific surface area ($S_{BET}$) of the samples was analyzed by nitrogen ($N_2$) adsorption−desorption in a Micromeritics ASAP 2020 apparatus.

The photoelectrochemical analysis was carried out in a conventional three-electrode cell using a Pt plate and an Ag/AgCl electrode as the counter electrode and reference electrode, respectively. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass that was cleaned by sonication in ethanol for 30 min and dried at 80 °C. The boundary of FTO glass was protected using Scotch tape. The 5 mg sample was dispersed in 0.5 mL of N, N -dimethylformamide (DMF) by sonication to get slurry. The slurry was spread onto the pretreated FTO glass. After air drying, the working electrode was further dried at 120 °C for 2 h to improve adhesion. Then, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin. The exposed area of the working electrode was 0.25 $cm^2$.The photovoltaic performance of the samples was measured using a source meter (Keithley 2400). A PEC-L11 AM 1.5 solar simulator (Peccell, with a 1000 W Xe lamp and an AM 1.5 filter) was used to give an irradiance of 100 mW $cm^{-2}$ (the equivalent of one sun at air mass (AM) 1.5) at the surface of the samples. The current–voltage characteristics of the samples under these conditions were obtained without applying external potential bias. Action spectra of the monochromatic incident photon-to-collected electron conversion efficiency (IPCE) were collected using a PEC-S20 (Peccell). The incident light intensity was calibrated according to a standard for amorphous silicon solar cells that was produced by the Japan Quality Assurance Organization. Photovoltaic performance was measured by using a metal mask with an aperture area of 0.25 $cm^2$. The photocurrent measurements were performed in homemade three electrode quartz cells with a PAR VMP3 Multi Potentiostat apparatus. The electrolyte was 0.2 M aqueous $Na_2SO_4$ solution (pH = 6.8) without additive. The electrochemical impedance spectroscopy (EIS) measurements were performed in the presence of 0.2 M aqueous $Na_2SO_4$ solution (pH = 6.8) without additive by applying an AC voltage with 5 mV amplitude in a frequency range from 1 Hz to 100 kHz under open circuit potential conditions.

## 3 Photocatalytic activity

### 3.1 Selective reduction of nitroaromatic compound

The photocatalytic selective reduction of nitro compound 4-nitroaniline (4-NA) to amino compound 4-phenylenediamine (4-PDA) was performed in a self-designed photochemical reactor equipped with an electromagnetic stirrer.[S3] In a 100 mL glass flask equipped with a magnetic stir bar and a three-hole plug, 10 mg of catalyst was dispersed in 30 mL of a 20 mg·L$^{-1}$ aqueous solution of 4-NA with 40 mg of ammonium formate as hole scavenger.[S4] The mixture was stirred in the dark for 1 h to ensure the establishment of adsorption–desorption equilibrium between the sample and reactant. Then, the above suspension was irradiated with a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd.) without filter in the wavelength ranging from 320 nm to 780 nm. During the process of the reaction, 4 mL of sample solution was taken from the reaction system at a certain time interval. Then, the solid photocatalyst was immediately separated from the mixed phase by centrifugation, and the remaining supernatant was analyzed on a Varian UV–vis spectrophotometer (Cary 50, Varian Co.). The whole experimental process was conducted under $N_2$ bubbling at the flow rate of 80 mL·min$^{-1}$. Conversion of 4-NA, yield and selectivity for the target product 4-PDA was defined as follows:

$$\textbf{conversion (\%)} = [(C_0\text{-}C_n)/C_0]\times 100$$

$$\textbf{yield (\%)} = C_p/C_0\times 100$$

$$\textbf{selectivity (\%)} = [C_p/(C_0\text{-}C_n)]\times 100$$

where $C_0$ is the initial concentration of 4-NA, and $C_n$ and $C_p$ are the concentrations of 4-NA and product 4-PDA, respectively, at a certain time after the photocatalytic reaction. The photograph of the experimental setup was displayed in the follows (**Fig. S1**†).

### 3.2 Selective oxidation of thioanisole

The photocatalytic selective oxidation of thioanisole was performed as done in previous research. A mixture of thioanisole (0.1 mmol) and 10 mg of photocatalyst was dispersed in the solvent of oxygen-saturated HCl/ethanol (0.02 M, 1.5 mL). The above mixture was transferred into a 10 mL Pyrex glass bottle filled with molecular oxygen at a pressure of 0.1 MPa and stirred for 30 min to make the catalyst blend evenly in the solution. The suspensions were irradiated by a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd.) without filter in the wavelength ranging from 320 nm to 780 nm. After the reaction, the mixture was centrifuged at 12000 rpm for 10 min to completely remove the catalyst particles. The remaining solution was analyzed with an Agilent gas chromatograph (GC-7820). Controlled photo-activity experiments using different radical scavengers (ammonium oxalate as scavenger for photo-generated holes,[S4-S6] $K_2S_2O_8$ as scavenger for photo-generated electrons,[S7] *tert*-butyl alcohol as scavenger for hydroxyl radicals[S8] and benzoquinone as scavenger for superoxide radical species[S4]) were performed similar to the above photocatalytic oxidation of thioanisole except that the radical scavengers (0.1 mmol) were added to the reaction system. Conversion of thioanisole, yield of methylsulfinylbenzene, and selectivity for methylsulfinylbenzene were defined as the follows:

$$\textbf{conversion (\%)} = [(C_0\text{-}C_t)/C_0]\times 100$$

$$\textbf{yield (\%)} = C_m/C_0\times 100$$

$$\textbf{selectivity (\%)} = [C_m/(C_0\text{-}C_t)]\times 100$$

where $C_0$ is the initial concentration of thioanisole and $C_t$ and $C_m$ are the concentration of the substrate thioanisole and the corresponding methylsulfinylbenzene, respectively, at a certain time after the photocatalytic reaction. The photograph of the experimental setup was displayed in the follows (**Fig. S2**†). The photocatalyst was collected by centrifugation and washed with deionized water for 3 times. Then, it was dispersed in the solvent of oxygen-saturated HCl/ethanol (0.02 M, 1.5 mL) together with 0.1 mmol thioanisole for recycling testing. The above mixture was transferred into a 10 mL Pyrex glass bottle filled with molecular oxygen at a pressure of 0.1 MPa and stirred for 30 min to make the catalyst blend evenly in the solution. The suspensions were irradiated by a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd.) without filter in the wavelength ranging from 320 nm to 780 nm. After the reaction, the mixture was centrifuged at 12000 rpm for 10 min to completely remove the catalyst particles. The remaining solution was analyzed with an Agilent gas chromatograph (GC-7820).

**Fig. S1** Photograph of the experimental setup for photocatalytic reduction of nitro compound.

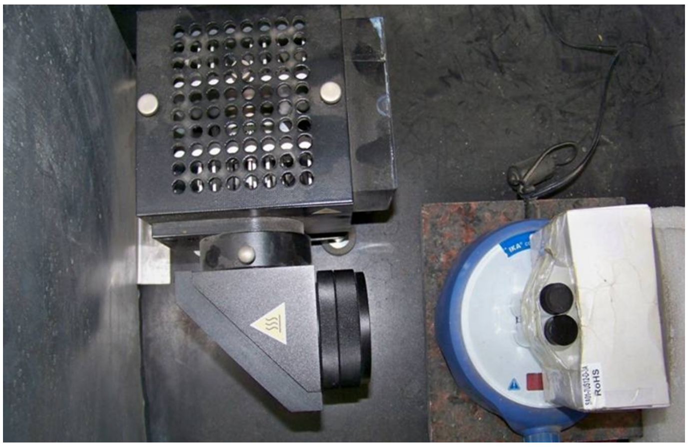

**Fig. S2** Photograph of the experimental setup for photocatalytic oxidation of thioanisole into corresponding methylsulfinylbenzene.

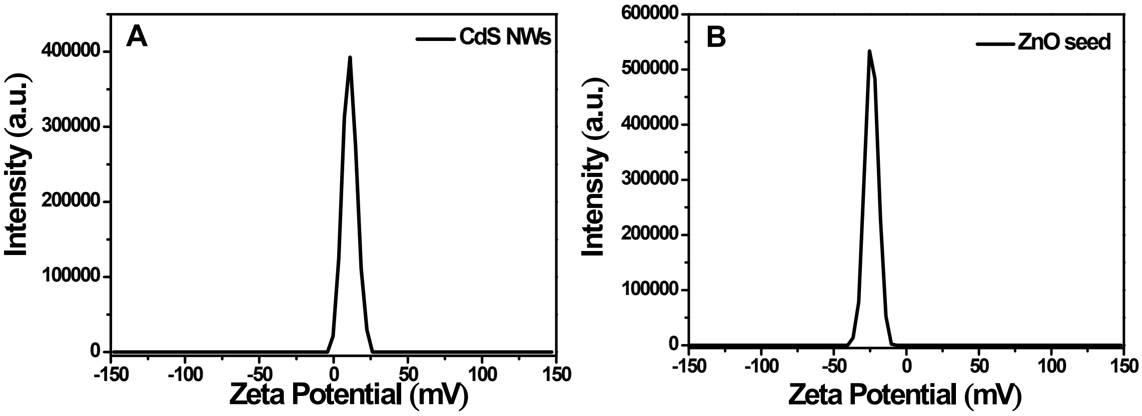

**Fig. S3** The zeta potentials (ξ) of CdS NWs (A) and ZnO (B) in deionized water with adjusting pH values at 10.

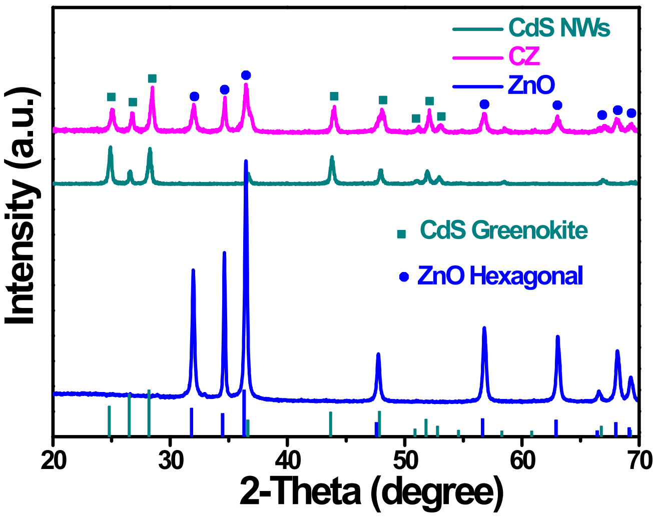

**Fig. S4** XRD patterns of CdS NWs, blank ZnO and branched hierarchical CZ nanocomposites.

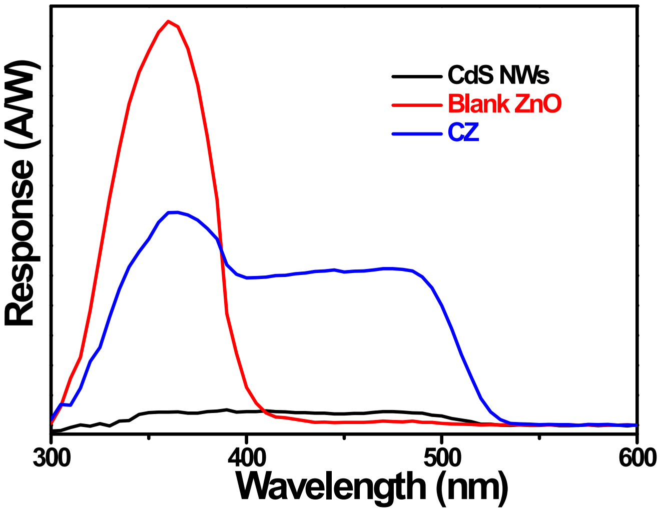

**Fig. S5** IPCE spectra of CdS NWs, blank ZnO and branched hierarchical CZ nanocomposites.

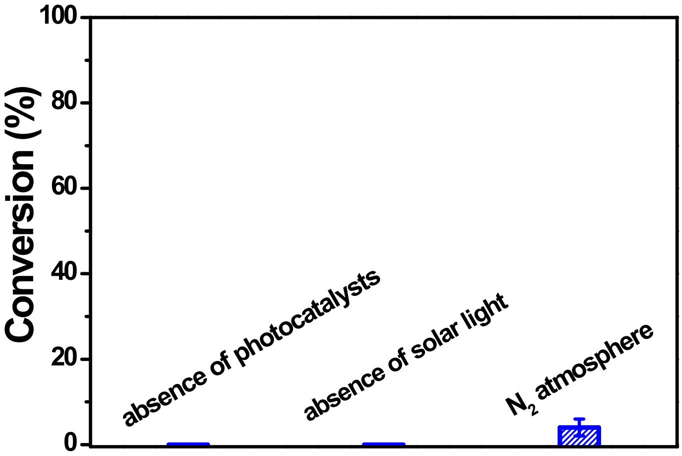

**Fig. S6** Blank experiments for selective oxidation of thioanisole in the absence of photocatalysts or solar light as well as in nitrogen ($N_2$) atmosphere.

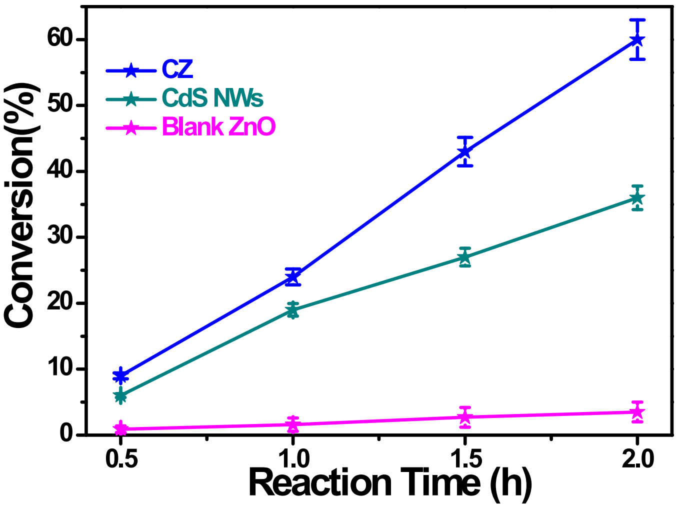

**Fig. S7** Time-online profiles of conversion of thioanisole over CdS NWs, blank ZnO and branched hierarchical CZ nanocomposites under artificial solar light irradiation.

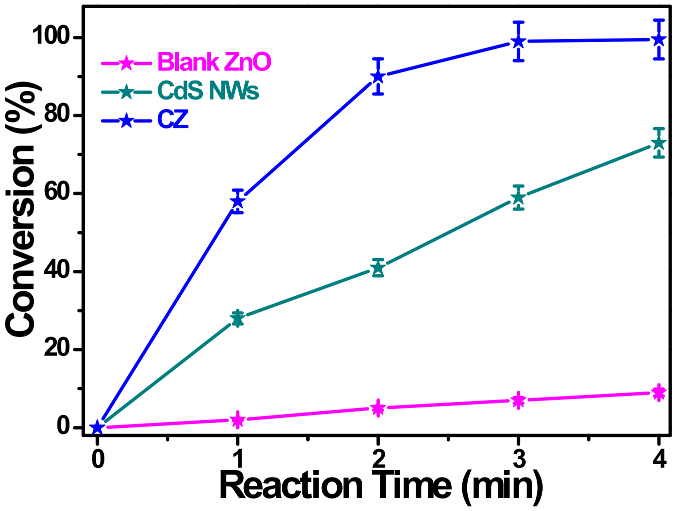

**Fig. S8** Time-online profiles of conversion of 4-nitroaniline over CdS NWs, blank ZnO and branched hierarchical CZ nanocomposites under artificial solar light irradiation.

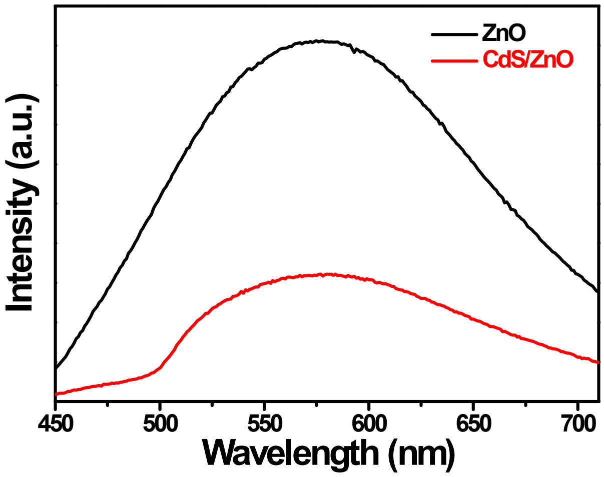

**Fig. S9** Photoluminescence (PL) spectra of the samples with an excitation wavelength of 360 nm.

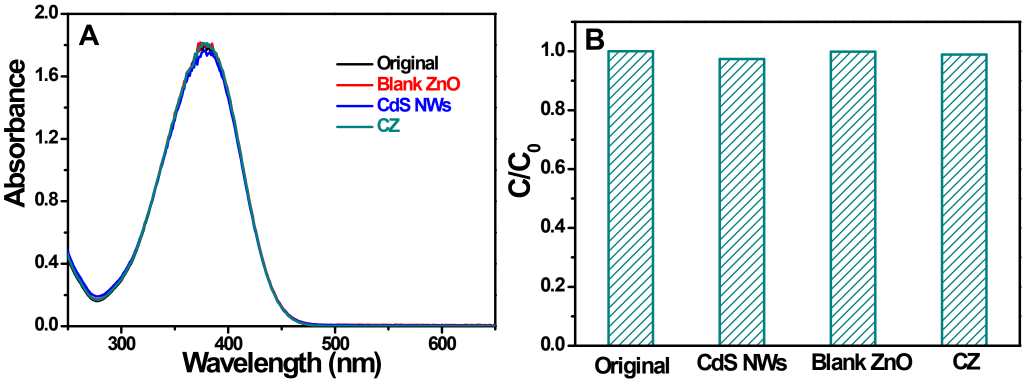

**Fig. S10** UV–vis absorption spectra of 4-nitroaniline over CdS NWs, blank ZnO and branched hierarchical CZ nanocomposites under adsorption equilibrium and column plot showing the remaining 4-nitroaniline in solution after being kept in the dark for 2 h until adsorption equilibrium of the 4-nitroaniline solution.

**Note:** 10 mg of the samples were added into 20 mL of 4-NA (20 mg·L$^{-1}$) in a quartz vial. The adsorption equilibrium of the 4-NA was achieved after being kept in the dark for 2 h.

**Table S1** Summary of surface area, pore volume and pore size of the as-prepared CdS NWs, blank ZnO and branched hierarchical CZ nanocomposites for comparison.

| **Samples** | **$S_{BET}$ ($m^2/g$)[a]** | **Total pore volume ($cm^3/g$)[b]** | **Average pore size (nm)[c]** |
|---|---|---|---|
| CdS NWs | 20 | 0.10 | 20 |
| ZnO | 8 | 0.03 | 16 |
| CZ | 19 | 0.11 | 21 |

[a] BET surface area is calculated from the linear part of the BET plot.

[b] Single point total pore volume of the pores at $P/P_0 = 0.99$.

[c] Adsorption average pore width (4*V*/*A* by BET).

## References

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