Electronic Supplementary Material

Porous Single-crystalline CdS Nanosheets as Efficient Visible Light Catalysts for Aerobic Oxidative Coupling of Amines to Imines

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1. Experimental Details

1.1 Materials

All chemicals were of analytical grade and were used as received without further purification.

1.2 Preparation of ZnS-DETA nanosheets

ZnS-DETA nanosheets was prepared according to the literature:[1] In our typical synthesis, $Zn(NO_3)_2$ (1.5 mmol) and thiourea (CH_4N_2S) (1.5 mmol) were added to a mixed solvent of diethylenetriamine (DETA) and distilled water (18 mL, $V_{DETA} : V_{H2O} = 4:1$) to form a homogenous solution under constant strong stirring. The mixed solution was then transferred into a Teflon-lined autoclave (with a filling ratio of 80%). The sealed vessel was then maintained at 180 °C for 10 h. The samples were collected and washed three times with ethanol and water, respectively. In our manuscript, the hybrid sheets are named as ZnS-DETA.

1.3 Transformation of inorganic-organic ZnS-DETA nanosheets into porous CdS nanosheets

The synthetic procedure was carried out according to our recently reported literature:[2] The as-prepared ZnS-DETA nanosheets (0.3 mmol) were dispersed into distilled water. $CdCl_2 \cdot 5/2H_2O$ (0.6 mmol) was added into the dispersion under constant stirring. The mixed solution was then transferred into a Teflon-lined autoclave. The sealed vessel was then maintained at 160 °C for 6 h. The samples were collected and washed three times with ethanol and water, respectively.

1.4 Photocatalytic coupling of amines to imines

Visible-light catalysis for aerobic oxidative coupling of amines was performed as the following. In a typical process, a mixture of catalyst (8 mg) and organic compounds (0.1 mmol) was dissolved in the solvent (1.5 mL) of *N*,*N*-Dimethylformamide (DMF), which was saturated with pure molecular oxygen (purity > 99.99%) from a gas cylinder. The above mixture was transferred into a 10 mL Pyrex glass bottle and stirred for 10 min to make the catalyst blend evently in the solution. The suspensions were irradiated by a 300 W Xe arclamp (CEL-HXF300 / CEL-HXUV300, Beijing Aulight Co. Ltd.) with a UV cutoff filter ($\lambda > 420$ nm). After the reaction, the mixture was centrifuged at 12000 rpm for 10 min to completely remove the catalyst. The remaining solution was diluted by diethylether (Et_2O) before being analyzed with Gas Chromatograph. Bromobenzene was used as an internal standard for the determination of conversion level. Control photoactivity experiments using different radical scavengers (ammonium oxalate as scavenger for holes, benzoquinone as scavenger for superoxide radical species) were performed similar to the above photocatalytic oxidation of amines except that the radical scavengers (0.1 mmol) were added to the reaction system.

1.5 Characterization

The morphology was characterized by scanning electron microscopy (SEM) using Hitachi S-4800 scanning electron microscope (SEM, 5 kV). Transmission electron microscopy (TEM) and higher magnification transmission electron microscopy (HRTEM) images were obtained with JEOL-2100F system equipped with EDAX Genesis XM2. Specimens for TEM and HRTEM measurements were prepared via dropcasting a droplet of ethanol suspension onto a copper grid, coated with a thin layer of amorphous carbon film, and allowed to dry in air. The X-ray diffraction patterns (XRD) of the products were recorded with BDX 3300 using a Cu Kα source ($\lambda = 0.154178$ nm). The optical properties of the samples were analyzed by a Shimadzu UV-2550 ultraviolet/visible diffuse reflectance spectroscopy (DRS), during which $BaSO_4$ was employed as the internal reflectance standard. The surface area and pore size distributions of the synthesized materials were determined by nitrogen physisorption using Quadrasorb SII Quantachrome Instrument. The surface area was calculated using the Brunauer-Emmett-Teller method. Pore size distributions were calculated using the Barrett-Joyner-Halenda method from the desorption branch. The conversion was analyzed by gas chromatograph Aglient (GC-7890A). The injector temperature was set at 280 ℃. Nitrogen was used as the carrier gas at 1.5 mL / min. Split ratio was 30 : 1. The average error for this determination was < 0.5 %. All reported data are averages of experiments performed at least in duplicate (errors < 2%). GC-MS was carried out with TRACE DSQ. The chemical structures of products were confirmed by comparison with standard chemicals of GC-MS (TRACE DSQ). Identification of the reactants and products was done by mass spectrum authentication.

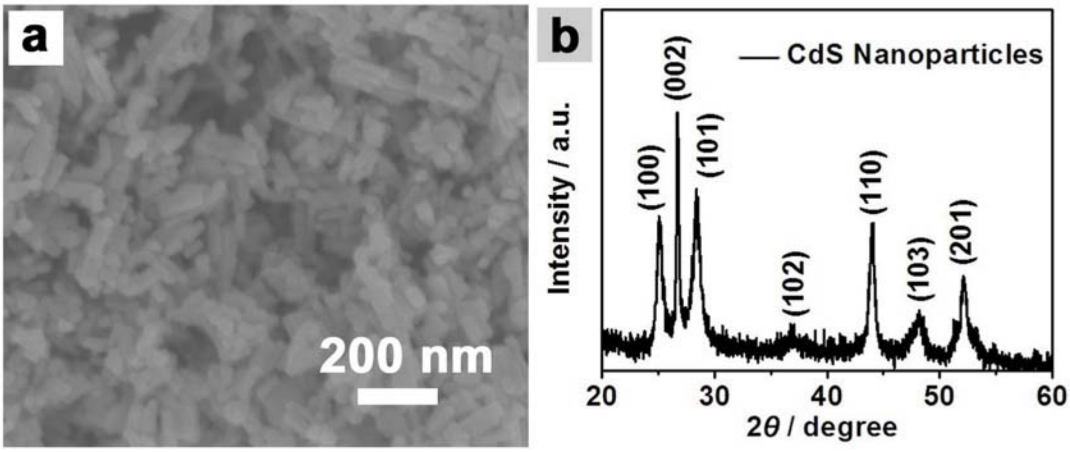


Figure S1 (a) SEM image, (b) XRD pattern of the CdS nanoparticles prepared according to the reference.[2]

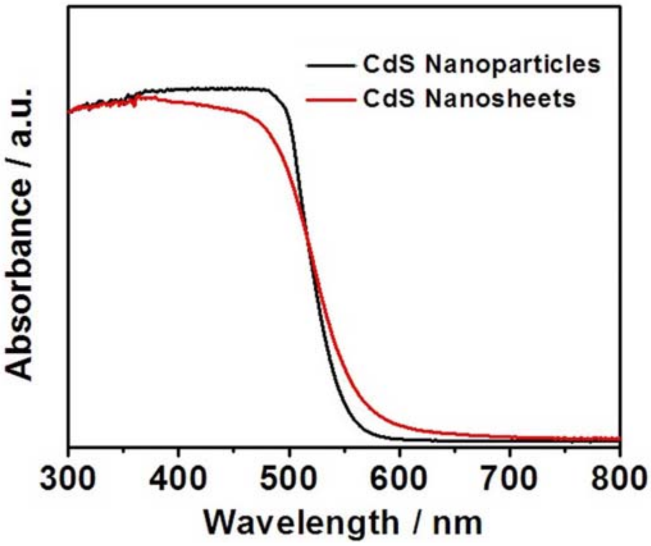


Figure S2 UV-Vis diffuse reflectance spectroscopy of CdS nanoparticles and single-crystalline CdS porous nanosheets.

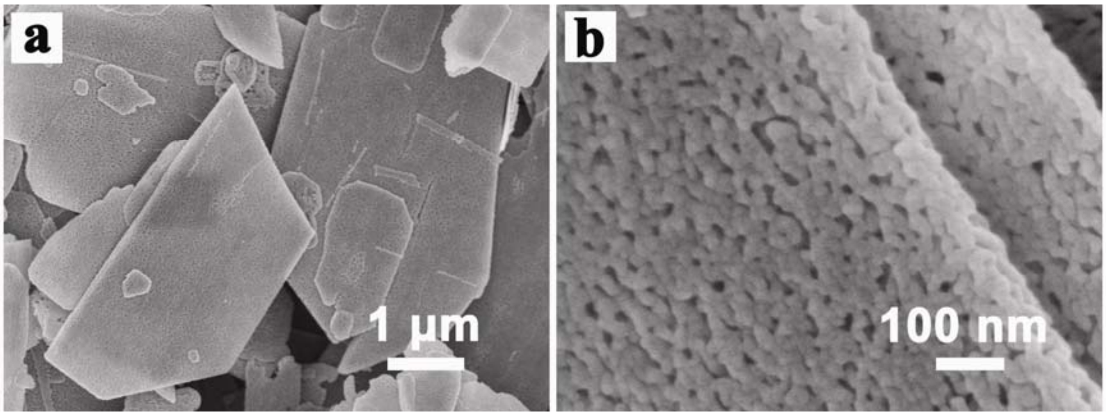


Figure S3 SEM image of porous CdS nanosheet catalysts after the catalysts were recycled. It suggested the high stability of CdS nanosheets used as photocatalyts for the aerobic coupling amines to imines.

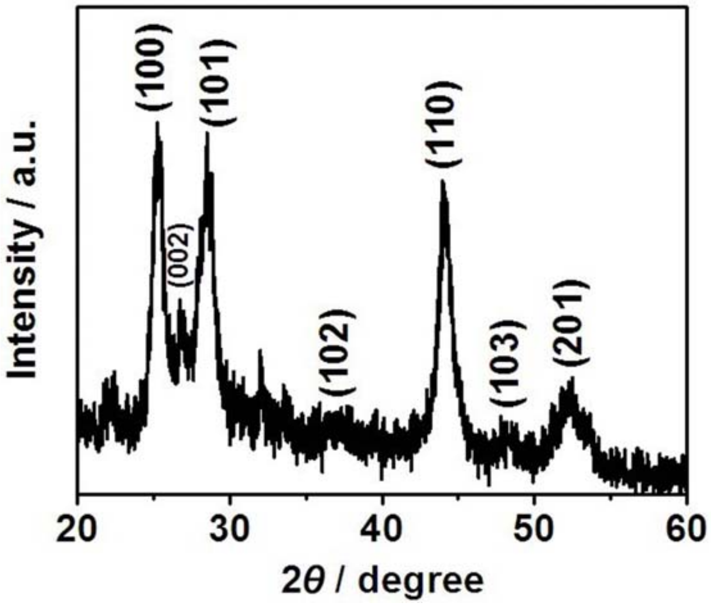


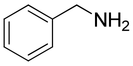
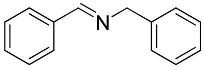
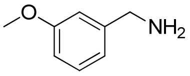
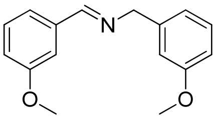
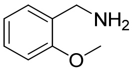
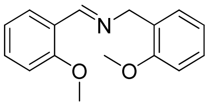
Figure S4 XRD of the porous CdS nanosheets after the catalysts were recycled. It further confirmed the high stability of CdS nanosheets used as photocatalyts for the aerobic coupling amines to imines.

Table S1 The light intensity measured at different wavelength of the incident light.[a]

Wavelength / nm	425	535	635	785
Light Intensity / W cm^{-2}	0.618	0.195	0.095	0.007
Light Intensity after attenuation / W cm^{-2}	0.25	0.07	0.037	0.0003

[a] The distance between the light source and Pyrex glass bottle was about 15 cm. The light intensity was measured by a lulllinometer (PM100D by Thorlabs). Light intensity was attenuated by an additional attenuation slices purchased from Beijing Aulight Co. Ltd..

Table S2 Photocatalytic aerobic oxidative coupling reaction of a series of benzylamines to the corresponding imines at air atmosphere under visible light (λ > 420 nm) irradiation for 4.5 h.[a]

Entry	Substrate	Product	Conv.[b] [%]	Sel.[c][%]
1			99	99
2			74	99
3			47	99

[a] The reaction conditions: 0.1 mmol of substrates, 8 mg of porous CdS nanosheets were dispersed in 1.5 mL of DMF with the irradiation of visible-light for 4.5 h at room temperature under air atmosphere. [b] GC Yield. [c] GC Selectivity.

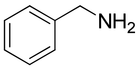
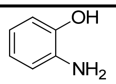
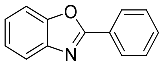
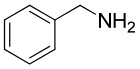
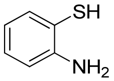
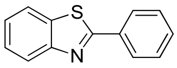
Table S3 Control experiments using different radical scavengers for the photocatalytic aerobic oxidative coupling of amines.[a]

Entry	Radical Scavenger	Con. (%)[b]	Sel. (%)[b]
1	–	99	>99
2	ammonium oxalate	91	>99
3	benzoquinone	95	>99

[a] Reaction conditions: substrate (0.1 mmol), radical scavenger (0.1 mmol), nanopourous CdS nanosheets catalyst (8 mg), oxygen-saturated *N*,*N*-Dimethylformamide (DMF, 1.5 mL), 25 °C, O_2 (0.1 MPa). [b] GC yield (%).

Table S4 Photocatalytic aerobic oxidative coupling of two substrates into corresponding compounds over porous single-crystalline CdS nanosheets under visible light (λ > 420 nm) irradiation for 6 h.[a]

$$\text{Substrate 1 + Substrate 2} \longrightarrow \text{Product 3}$$

Entry	Substrate 1	Substrate 2	Product 3	Con.(%) [b]	Sel.(%) [b]
1				98	10
2				97	46

[a] Reaction conditions: substrate 1 (0.1 mmol), substrate 2 (0.3 mmol), catalyst (8 mg), O_2 (0.1 MPa), DMF (1.5 mL), λ > 420 nm, 25 °C, photoirradiation time (6 h). The conversion is calculated from the amount of 1. [b] GC-MS yield (%).

Figure S5 GC-MS measurements of coupling benzylamine to N-benzylidene benzylamine. The column temperature was held at 80 ℃ for 1.5 min, then raised to 250 ℃ at 30 ℃ / min and kept for 2.0 min.

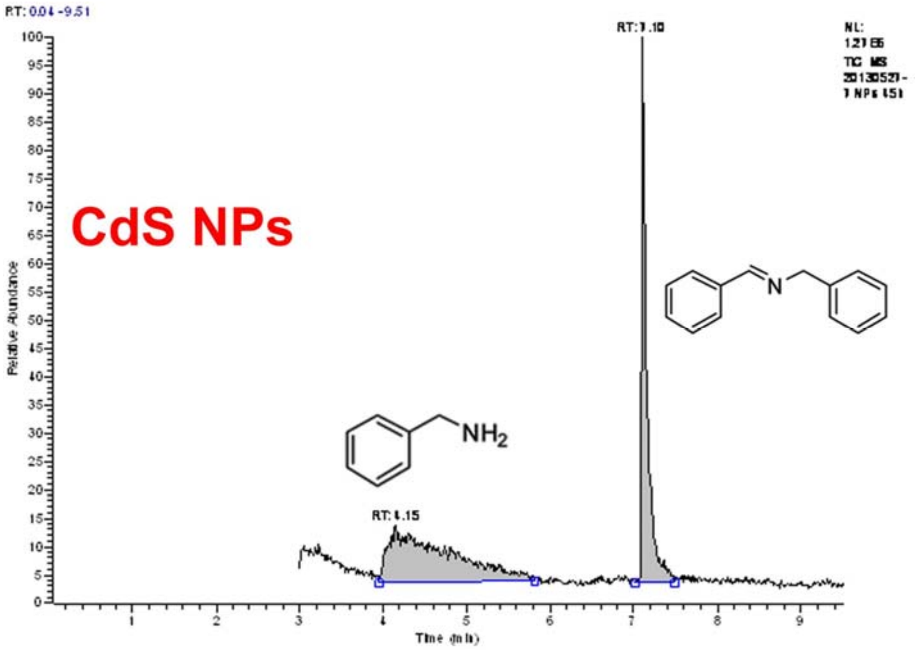


Figure S5-1 shows GC traces of benzylamine, N-benzylidene benzylamine catalyzed by CdS nanoparticles for 4.5 h, demonstrating the co-existence of reactants and products.

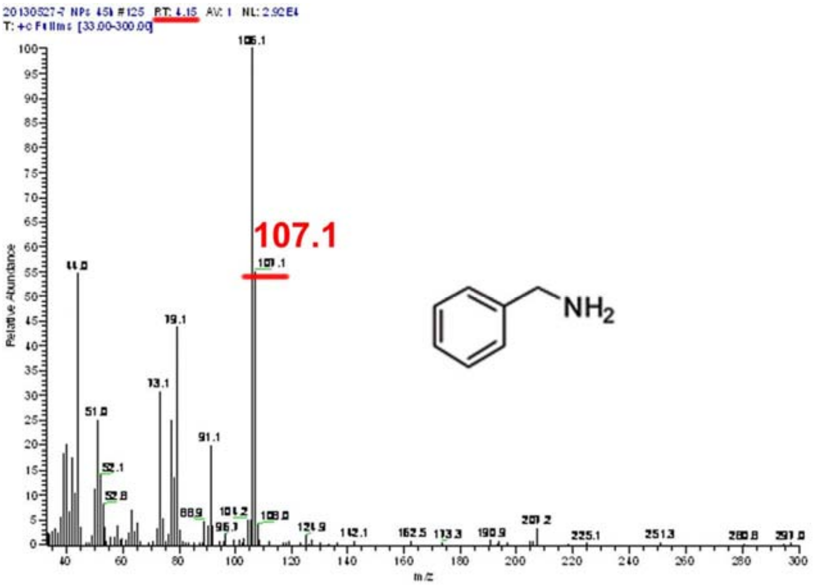


Figure S5-2 displays the mass spectrogram of the retention time at 4.15 min. The chemical structures were confirmed by mass spectrum authentication for benzylamine.

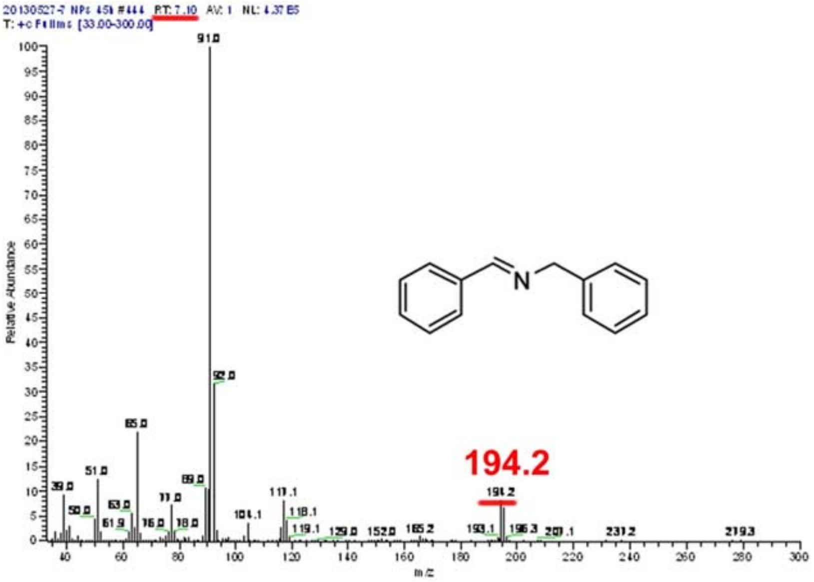


Figure S5-3 shows the mass spectrogram of the retention time at 7.10 min. The chemical structures were identified by mass spectrum authentication for N-benzylidene benzylamine.

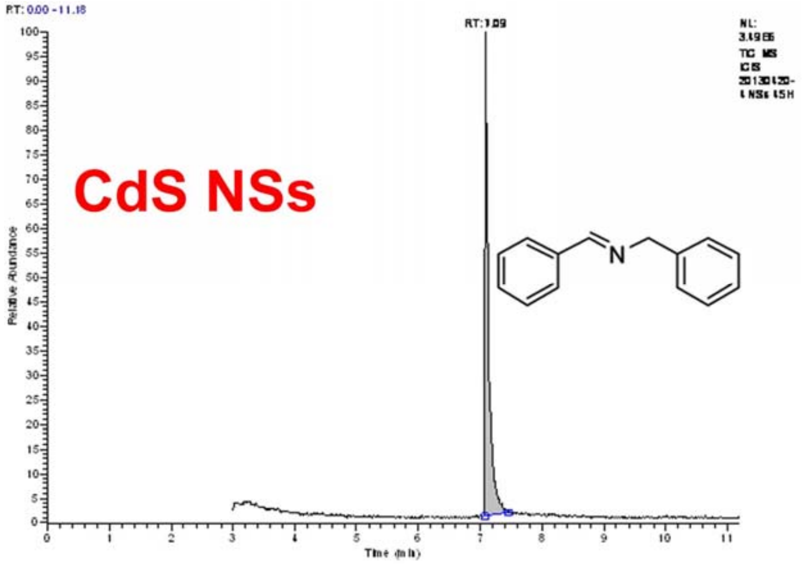


Figure S5-4 shows GC traces of benzylamine, N-benzylidene benzylamine catalyzed by CdS porous nanosheets for 4.5 h.

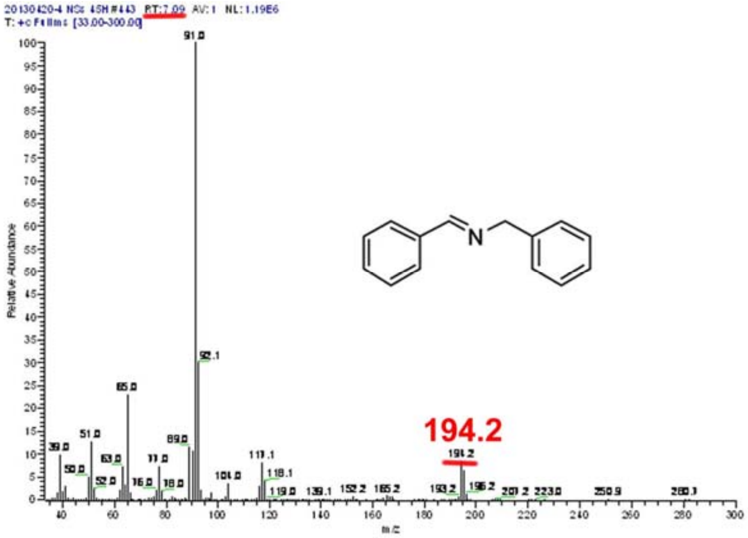


Figure S5-5 shows the mass spectrogram of the retention time at 7.09 min. The chemical structures were identified by mass spectrum authentication for *N*-benzylidene benzylamine.

Reference:

1. W. T. Yao, S. H. Yu, L. Pan, J. Li, Q. S. Wu, L. Zhang, J. Jiang, *Small*, 2005, **1**, 320.

2. S. Biswas, S. Kar, S. Santra, Y. Jompol, M. Arif, S. I. Khondaker, *J. Phys. Chem. C* 2009, **113**, 3617.