

Supporting information

Photocatalytic C-H activation for C-C/C=N/C-S bonds formation over CdS: effect of morphological regulation and S vacancies

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EXPERIMENTAL SECTION

Materials and Methods

Materials

Reagents were commercially available and used without further purification. Furfural, tetrahydrofuran, phenylacetylene, Cd(OAc)₂·2H₂O, thiourea, ethylenediamine and cadmium nitrate were purchased from Sigma Aldrich. Zinc chloride (ZnCl₂), thioacetamide (TAA), indium chloride (InCl₃·4H₂O), ammonium molybdate, zinc nitrate (Zn(NO₃)₂), cetyl trimethyl ammonium bromide (CTAB), nickel acetate (Ni(CH₃COO)₂), ethylene glycol, were supplied by Macklin, China.

Catalyst preparation

Preparation of CdS

CdS nanosheets were synthesized according to modified literature method.¹ 2.0 mmol Cd(OAc)₂·2H₂O and 6.0 mmol thiourea were dispersed in 60 mL ethylenediamine and then transferred to a Teflon-line stainless-steel autoclave (100 mL), heated at 100 °C for 8 h. After the reaction, the bright yellow product was separated and washed with deionized water and ethanol

several times, and then dried in vacuum oven.

CdS nanospheres were synthesized according to modified literature method.² 0.6 mmol of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and 15 mmol of thiourea were dissolved in 15 mL of deionized water to form a homogeneous solution. The mixture was then transferred into a Teflon-lined stainless-steel autoclave, heated and maintained at 140 °C for 5 h. The solid was obtained by centrifugation and washed several times with deionized water and ethanol, followed by freeze drying treatment.

CdS nanorods were prepared by a solvothermal reaction at a fixed reaction temperature of 180 °C. Cadmium nitrate (1.92 g) and thiourea (1.42 g) were dissolved in ethylenediamine and stirred for 15 min. The clear solution was transferred to a 100 mL Teflon lined stainless steel autoclave and heated at 180 °C for 18 h. After cooling down to room temperature, the yellow colored precipitates were washed with ethanol and deionized water several times and dried at 70 °C overnight.³

Sv-CdS NRs: The obtained CdS nanorods were used as precursors and were placed in a tubular furnace, heated to 800 °C at a heating rate of 10 °C/min under the protection of nitrogen and maintained for 30 min to obtain Sv-CdS NRs (Sv-CdS nanorods).

Preparation of MoS_2

MoS_2 was prepared by a hydrothermal method.⁴ Ammonium molybdate (1.236 g, 1 mmol) and thiourea (2.28 g, 30mmol) were dissolved in deionized water (40 mL) and stirred for 20 min. The solution was transferred to a hydrothermal reactor, heated to 180 °C in an oven and kept for 18 h to obtain MoS_2 precipitation. The obtained MoS_2 was filtered and washed with distilled water and alcohol, and then dried for 4 h.

Preparation of ZnS

ZnS was prepared by a hydrothermal method.⁵ Typically, $\text{Zn}(\text{NO}_3)_2$ (304.2 mg) and CTAB (260.6 mg) were dissolved in 20 mL of water in a 100 mL beaker and magnetically stirred for 30 min at room temperature. Thioacetamide (604.8 mg) was then added to the above solution. After being stirred for another 30 min, the mixture was transferred to a 50 mL stainless Teflon-lined autoclave, tightly sealed, and placed in a 160 °C oven for 16 h. The autoclave was then naturally cooled to room temperature.

Preparation of NiS

NiS was prepared by a solvothermal method.⁶ Took 2.4 mmol $\text{CH}_4\text{N}_2\text{S}$, 1.2 mmol $\text{Ni}(\text{CH}_3\text{COO})_2$ and 70 mL ethylene glycol, and added them to a 100 mL beaker. After sonicating for 20 min, place it on a magnetic stirrer for continuous stirring for 2 h. The light green solution formed was moved to a polytetrafluoroethylene (PTFE) high-pressure reactor (100 mL) and reacted in a constant temperature oven at 180 °C for 12 h. Then, the obtained precipitate was dried at 60 °C for 6 h and ground to obtain NiS powder.

Preparation of ZnIn_2S_4

ZnIn_2S_4 were synthesized according to modified literature method.⁷ During this process, 0.3 mmol

of ZnCl₂, 0.6 mmol of InCl₃·4H₂O and 2.4 mmol of CH₃CSNH₂ (TAA) were dissolved in 30 mL deionized water and the precursor solution was acquired until stirring constantly at magnetic stirrer for 30 min. Then, poured into the prepared Teflon-lined stainless steel. Following, the autoclave was heated at 160 °C for 12 h and then naturally cooled down to room temperature. The samples were rinsed with deionized water and dried in oven at 60 °C for 6 h.

Characterizations

Scanning electron microscopy (SEM) was tested with the SU1510 (Hitachi, Japan). Transmission electron microscopy (TEM) measurements were tested with the FEI corporation Tecnai G2 F20. Powder X-ray diffraction (XRD) patterns were carried out with a LynxEye array detector/Bruker D8 Advance. X-ray photoelectron spectroscopy (XPS) spectra was conducted on Thermo Scientific Escalab 250Xi. Photoluminescence (PL) spectra were tested with the Hitachi F-7000. UV-vis diffuse reflectance spectra (UV-vis DRS) were tested with a Hitachi UH4150 UV-vis DRS to investigate the optical properties of the samples. The photoelectrochemical measurements were carried out on an electrochemical workstation (CHI730E, Shanghai Chenhua Limited, China) and the electrochemical impedance spectroscopy (EIS) was achieved on Zahner electrochemical workstation (IM6ex, Zahner Scientific Instruments, German), using a standard three-electrode quartz cell with a working electrode, Ag/AgCl used as reference electrode and Pt slice as counter electrode. Fluorine-doped tin oxide (FTO, 7 Ω per square) decorated with catalyst was used as the working electrode. A 0.5 M Na₂SO₄ aqueous solution was served as the electrolyte. A commercial 300 W Xenon lamp (Beijing Newport Co., Ltd) equipped with a 420 nm cutoff filter was employed as a visible light source. Moreover, electrochemical impedance spectroscopy (EIS) was measured with an open-circuit voltage in a frequency range of 10 mHz-100 kHz with an amplitude of 5 mV. A standard three-electrode quartz cell with a working electrode was used to measure the photocurrent density of as-prepared samples. 0.3 M Na₂SO₄ solution was selected as the electrolyte. The light source was come from the xenon lamp (Perfect Light, CHF-XM500, 100 mW·cm⁻²) in the process of measure. The stability of specimens was performed in the form of photocurrent density curves at 1.0 V vs. RHE, lasting 6000 s. The reversible hydrogen electrode (RHE) potential is to shift from Ag/AgCl according to the following formula (1):⁸

$$E_{RHE} = E_{Ag/AgCl} + 0.059\text{pH} + 0.1956\text{V} \quad (1)$$

Electron paramagnetic resonance (EPR) measurement was carried out with Bruker model A300 spectrometer.

Photocatalytic reactions

General method A: Photocatalytic reaction of THF with olefins/alkynes.

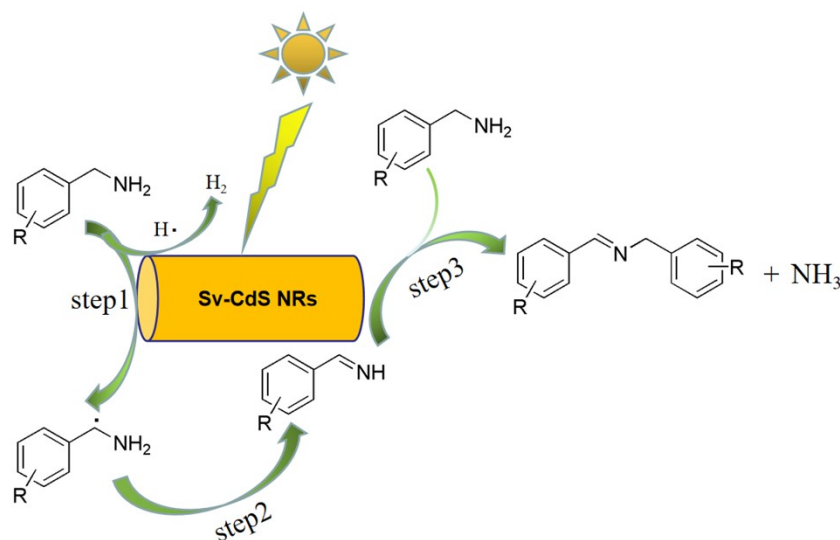
In general, the Sv-CdS NRs (10 mg) and phenylacetylene (0.2 mmol) were placed in a Schlenk tube containing tetrahydrofuran (THF) (5 ml). Prior to the reaction, the suspension was degassed and saturated with Ar to remove any dissolved O₂. The reaction was carried out under the irradiation of 0.75 W/cm² blue LED (460 nm) for 24 hours, and the reaction suspension was continuously stirred throughout the reaction process. The mixture was filtered through the porous membrane (diameter 20μm), and the filtrate was analyzed by GC and GC-MS (Shimadzu GC-2014) equipped with HP-5 capillary column and FID detector. The gas products were analyzed by GC with packed column and TCD detector.

General method B: Photocatalytic reaction of DMF with olefins.

10mg Sv-CdS NRs and 20mg base additive Cs_2CO_3 were added to a Schlenk tube, which was filled with N_2 to remove O_2 . Then, 0.2 mmol styrene/4-methylstyrene and 4 mL DMF were added to the Schlenk tube. The mixture was stirred under 0.75 W/cm^2 blue LED (460 nm) for 24 h. After the reaction, the mixture was filtered through the porous membrane (diameter $20\mu\text{m}$) and analyzed by HPLC. The gas products were analyzed by GC with packed column and TCD detector.

General method C: Photocatalytic reaction of benzylamine self-coupling.

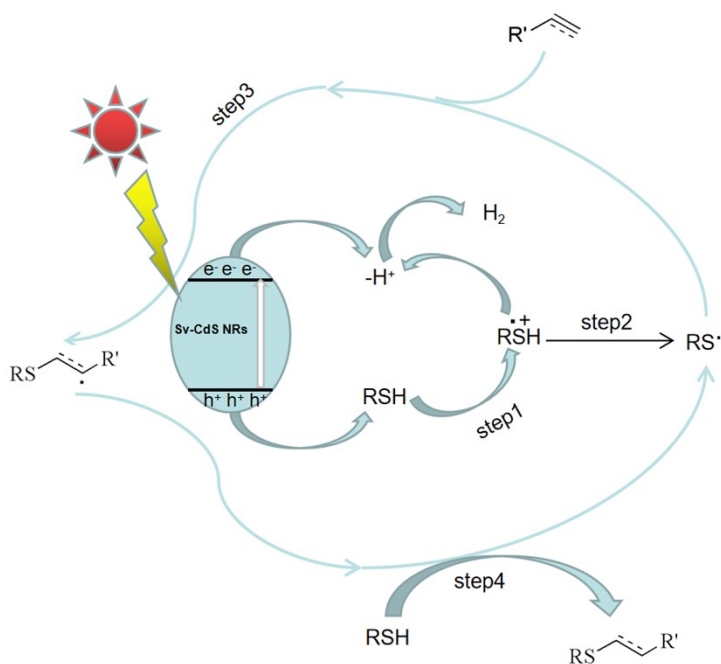
The Sv-CdS NRs (10 mg) and benzylamine (0.5mmol) were placed in a Schlenk tube containing acetonitrile (2ml). Prior to the reaction, the suspension was degassed and saturated with Ar to remove any dissolved O_2 . The reaction was carried out under the irradiation of LED lamp (0.15 W/cm^2 , 460 nm) for 12 hours, and the reaction suspension was continuously stirred throughout the reaction process. After the reaction, the mixture was filtered through the porous membrane (diameter $20\mu\text{m}$), and the filtrate was analyzed by GC and GC-MS (Shimadzu GC-2014) equipped with HP-5 capillary column and FID detector.



Scheme S1 Mechanism for C-N bonds synthesis.⁹

General method D: Photocatalytic reaction of hydrothiolation with olefins/alkynes.

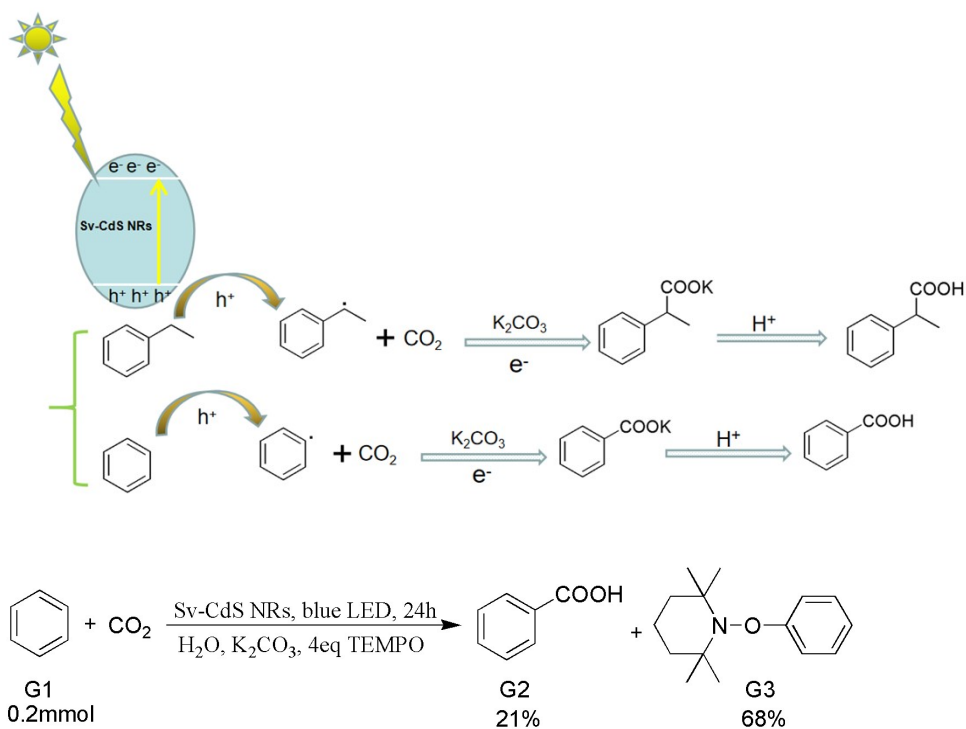
The Sv-CdS NRs (10 mg), thiols (0.1 mmol) and olefins/alkynes (0.12 mmol) were suspended in a Schlenk tube containing a solvent (4 ml). Before the reaction, the suspension was degassed and saturated with N_2 to remove any dissolved O_2 . The reaction was performed under irradiation with an LED lamp (0.75 W/cm^2 , 460 nm) at room temperature. After the reaction, the products were analyzed by GC and GC-MS (Shimadzu GC-2014) equipped with HP-5 capillary column and FID detector. The gas products were analyzed by GC with packed column and TCD detector.



Scheme S2 Mechanism for C-S bonds synthesis.¹⁰

General method E: Photocatalytic reaction of CO₂ carboxylation.

10mg Sv-CdS NRs photocatalyst and 0.3mmol base additive K₂CO₃ were added to a Schlenk tube, which was filled with CO₂. Then, 0.2 mmol ethylbenzene/benzene and 5 mL deionized water were added to the Schlenk tube. The mixture was stirred under 0.75 W/cm² blue LED (460 nm) for 24 h. The mixture was filtered through the porous membrane (diameter 20μm). The filtrate was analyzed by HPLC after acidification.



Scheme S3 Mechanism for CO₂ carboxylation,^{11, 12} and phenyl radical capture experiment.

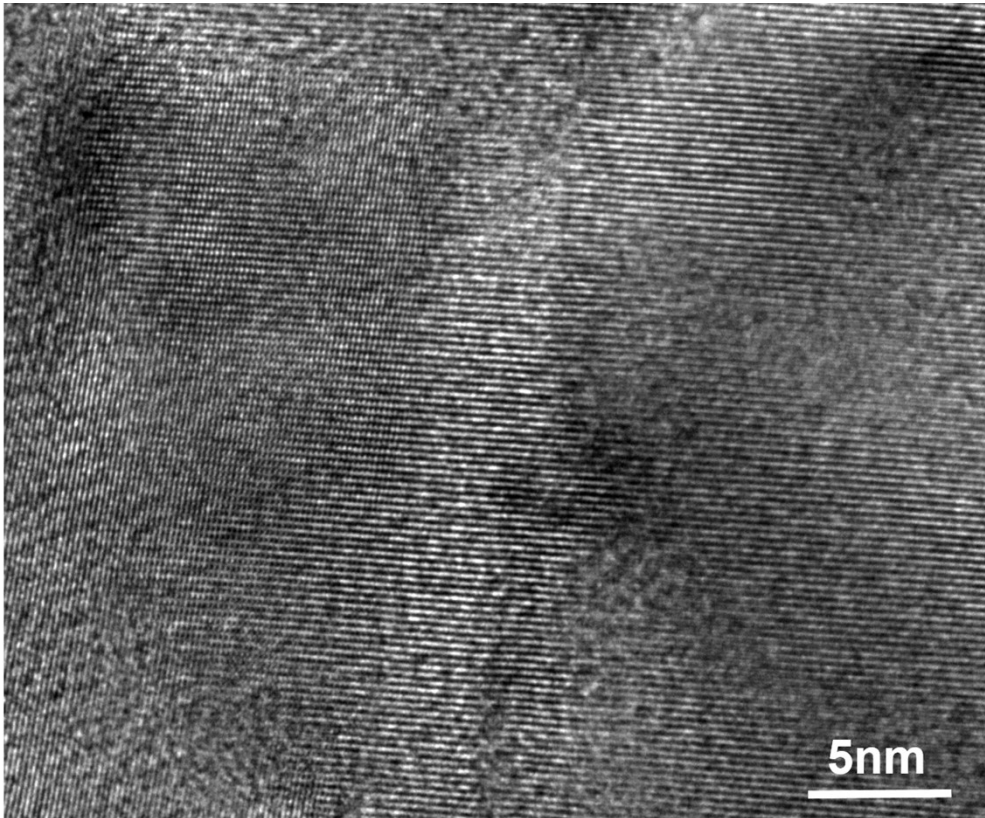


Fig. S1. HRTEM original spectrum of Sv-CdS NRs.

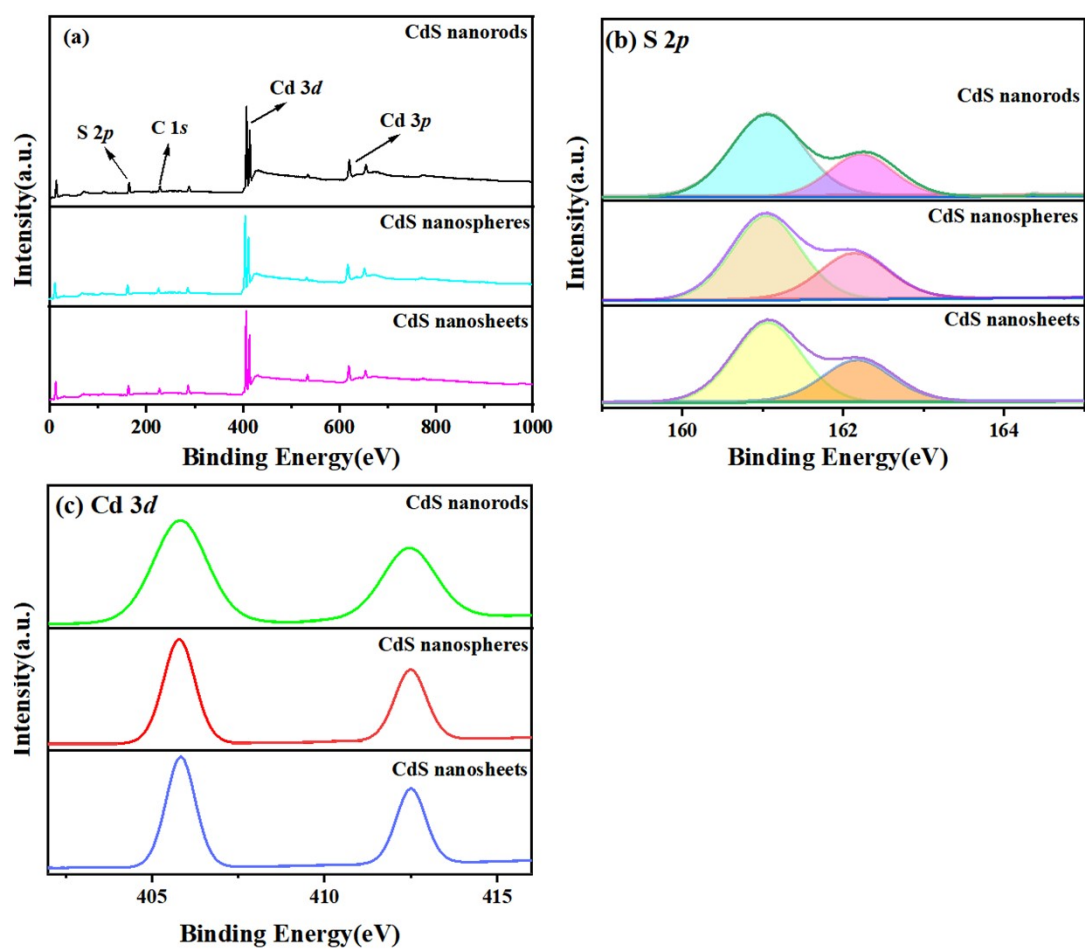


Fig. S2. (a) XPS survey, (b) S 2p, (c) Cd 3d for CdS nanorods, CdS nanospheres and CdS nanosheets.

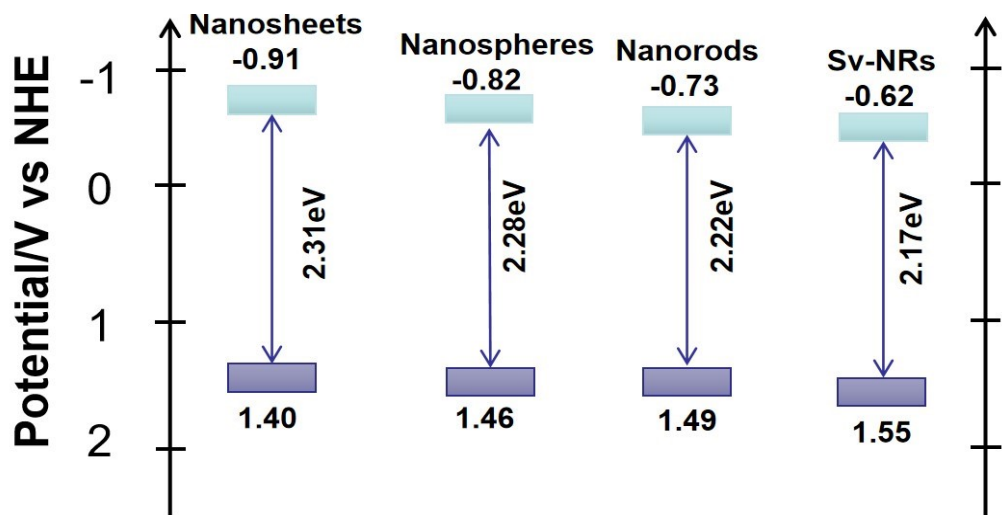


Fig. S3. Conduction band and valence band positions of selected CdS photocatalysts.

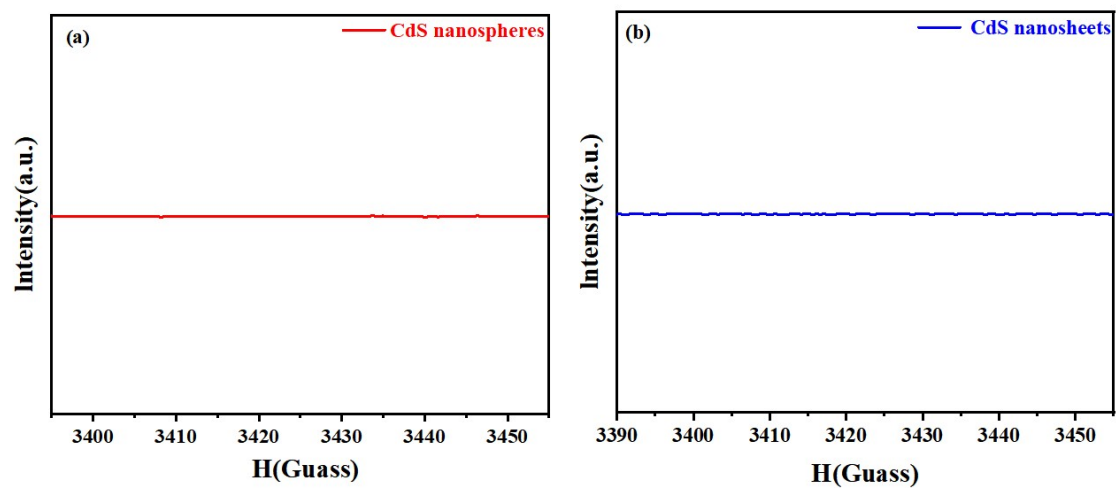


Fig. S4. EPR spectra of CdS nanospheres and CdS nanosheets.

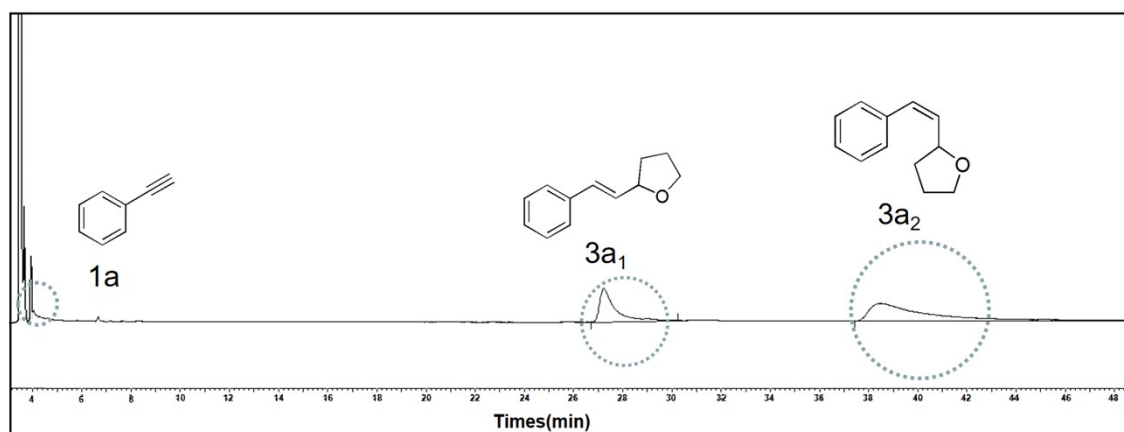


Fig. S5. GC spectrum of photocatalytic reaction between THF and alkyne.

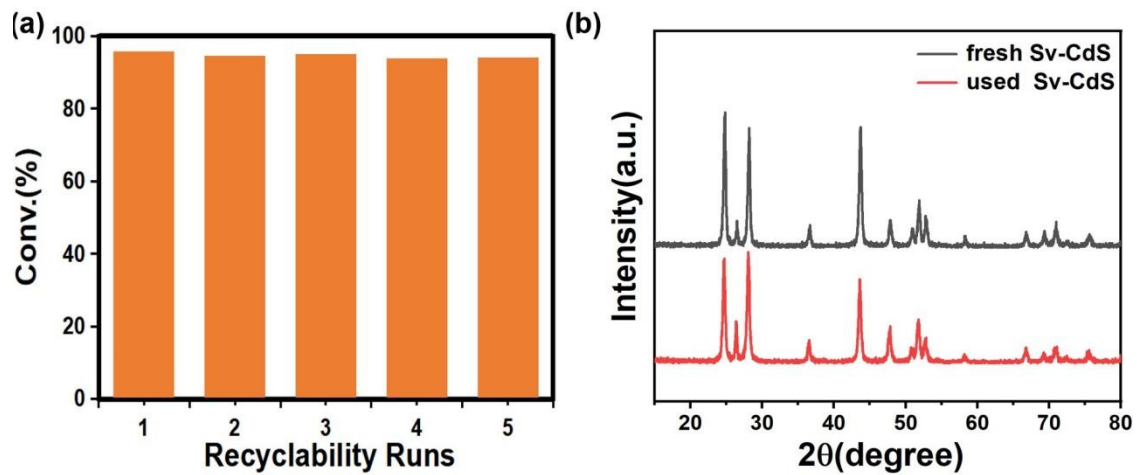


Fig. S6. (a) Cycling tests of photocatalytic coupling reaction between THF and phenylacetylene over Sv-CdS NRs; (b) XRD patterns of fresh Sv-CdS NRs and used Sv-CdS NRs after five cycling reactions.

References

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