Electronic Supplementary Information for

Core-Shell Carbon Colloid Sphere@ Phosphotungstic Acid/CdS as Z-scheme Heterojunction with Synergistic Adsorption, Photothermal and Photocatalytic Performance

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Experimental section

Materials

All the chemicals used in the experiments are purchased and received without further purification. Glucose was purchased from Tianjin Kermel Chemical Reagent Co. Ltd, China. Phosphotungstic acid ($H_3PW_{12}O_{40}\cdot nH_2O$), acetic acid, deionized water and ethanol were purchased from Aladdin reagent company, China. Cadmium acetate dihydrate ($Cd(AC)_2\cdot 2H_2O$) was purchased from Tianjin Guangfu chemical Reagent company. Sodium sulfide nonahydrate ($Na_2S\cdot 9H_2O$) was purchased from Tianjin Hengxing chemical reagent company. Water through the whole experiments was deionized water, purchased from Aladdin Reagent Company.

Characterization

X-ray diffraction (XRD) was used to analyze the structure and phase purity of the crystal, measured by D8 Advance X-ray diffractometer with Cu Ka radiation (λ = 1.5406 A). Scanning electron micros-copy (SEM) images were obtained with a Philips XL-30-ESEM-FEG instrument operating at 20 kV. Transmisson electron microscope (TEM) JEOL JEM-2010 at an accelerating voltage of 200 kV was also used to record the electron micrographs of the samples. PHI-5700 ESCA instrument with Al-Ka X-ray source was used to measure X-ray photoelectron spectroscopy (XPS). $BaSO_4$ was used as the reference material in the measurement of UV-vis diffuse reflection spectra (DRS) and the DRS were recorded on a UV-vis spectrophotometer (UV-4100, Shimadzu) with an integrating sphere attachment. Surface area was estimated by BET method. The •OH radicals were detected by the fluorescence probe technique with coumarin on a RF-5301PC fluorescence spectrophotometer and a 300 W xenon lamp with UVIRCUT filter (420-780 nm) was used as visible-light source. The photoluminescence (PL) spectra were measured with a PELS 55 spectrofluorophotometer at excitation wavelength of 325 nm. The work function of samples was tested by scanning Kelvin probe (SKP) (SKP5050 system, Scotland). The temperature of the sample was measured using the Testo 865 infrared thermograph.

Synthesis

Synthesis of carbon colloid spheres

Carbon colloid spheres were prepared via one-step hydrothermal and calcination method. Typically, glucose (5 g) was dissolved in deionized water (50 mL). After stirring for 1 h, the clear solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 150 °C for 12 h. Waiting the autoclave cooling down to the room temperature, the deep brown product was isolated from the solution by centrifugation and washed with deionized water and ethanol several times. The product was dried in oven overnight at 90 °C and then annealed at 800 °C at a heating rate of 2 °C/min for 2 h under the flowing of N_2.

Synthesis of C@HPWcolloid spheres

In this procedure, 100 mg carbon colloid spheres were added into 20 mL acetic acid solution, stirring for 12 h continuously. The solution was dried overnight at 60 °C after centrifuging and washing by deionized water. The formed product was added into the phosphotungstic acid water solution (20 mL, 0.05 M), ultrasound until the solute dissolved completely. The formed solution was stirred for 5 h. Finally, the brown powders were dried overnight at 60 ℃ after centrifuging and washing by ethanol, and deionized water 3 times, respectively.

Synthesis of C/CdS colloid spheres

C/CdS colloid spheres were prepared via calcination method. Typically, carbon powders (100 mg) were dissolved in 100 mL deionized water under stirring for 30 min. Then, 0.01 mol $Cd(AC)_2$•$2H_2O$ aqueous solution was added in the mixture and stirred for 24 h. Then, 0.01 mol Na_2S•$9H_2O$ were dissolved into 20 ML DI water and dropwised in the formed solution under stirring for 24 h. The mixture solution was aged for 24 h. Then, the product was collected after centrifuging and washing by ethanol and deionized water. Finally, the product was transferred to muffle furnace calcination at 300 ℃ for 1 h to obtain the C/CdS composite catalysts.

Synthesis of C@HPW/CdS colloidal spheres

Via a simple calcination method, we made C@HPW/CdS colloidal spheres where CdS nanoparticles were distributed on the surface C@HPW colloid spheres. Typically, C@HPW powders (100 mg) were dissolved in 100 mL deionized water under stirring for 30 min. Then, 0.01 mol $Cd(AC)_2$•$2H_2O$ aqueous solution was added in the mixture and stirred for 24 h. Then, 0.01 mol Na_2S•$9H_2O$ was dissolved into 20 ML DI water and dropwised in the formed solution under stirring for 24 h. The mixture solution was aged for 24 h. Then, the product was collected after centrifuging and washing by ethanol and deionized water. Finally, the product was transferred to a muffle furnace calcination at 300 ℃ for 1 h to obtain the C@HPW/CdS composite catalysts.

Photocatalytic hydrogen evolution

Photocatalytic H_2 evolution experiment was conducted in a photocatalytic hydrogen production system (AuLight, Beijing, CEL-SPH2N). In the photocatalytic hydrogen evolution reaction, the sample (100 mg) was dispersed in 100 mL of methanol/H_2O solution (volume ratio 1/4). Before visible light irradiation, the reactor and the entire gas circulation system are completely degassed by vacuum pump to remove air for 30 min. The 300 W Xenon is then fitted with optical filter ($\lambda \geq 420$ nm) as a visible light source. The evolution of photocatalytic H_2 was analyzed by gas chromatograph (SP7800, TCD, molecular sieve 5a, N_2 carrier, Beijing Keruida Limited).

Photocatalytic degradation

2,4-DCP, a kind of highly toxic and harmful organic contaminants, which was widely used in the production of pesticides and pharmaceutical intermediates. Furthermore, methyl orange (MO), methylene blue (MB) and rhodamine B (RhB) were both common organic dye and were often used in photocatalytic degradation tests. Therefore, 2,4-DCP, MO, MB and RhB were selected to test the photocatalytic degradation performance. The experiment was carried out in the winter in Harbin (44° 04′ N and 125° 42′ E), and the room temperature was kept at 12 ± 2°C. In a typical experiment, the photocatalysts (30 mg) was added to MO solution (30 mL, 10 mg L^{-1}), MB solution (30 mL, 10 mg L^{-1}), RhB solution (30 mL, 10 mg L^{-1}) or 2,4-DCP solution (30 mL, 10 mg L^{-1}), respectively. Then, the suspension was placed in the dark to ensure adsorption desorption equilibrium. The suspension was irradiated with a 300 W Xenon lamp equipped with UVIRCUT filter (420-780 nm). The residual MO, MB, RhB or 2,4-DCP concentrations was analyzed by T6 UV-vis spectrophotometer. The species trapping experiments was to add additional trapping agents (1 mM) such as EDTA-Na, BQ and IBA. The photocatalytic efficiency was calculated from the following equation (1):

$$\eta = \left[\frac{(C_0 - C)}{C_0}\right] * 100\% \tag{1}$$

where η is the photocatalytic efficiency, C_0 is the initial concentration of the contaminants and C is the concentration of the contaminants at the reaction time t. Furthermore, the photocatalytic degradation tests were carried out under infrared light irradiation. The room temperature was kept at 20 ± 2 °C and the suspension was irradiated with a 300 W Xenon lamp equipped with UVCUT filter ($\lambda \geq 420$ nm). Other experimental conditions are consistent with visible light.

Apparent quantum efficiency (AQE)

The reaction system was placed under a 300W Xenon lamp (PLS-SXE300) with a 420 nm cutoff filter as light source (43.68 mW/cm^2), the other experimental conditions are similar to the photocatalytic hydrogen evolution measurement as described before. The light intensity was obtained with an optical power meter (CEL-NP2000, CEAULIGHT, Beijing), and the light receiving area is S (cm^2), and N_A is Avogadro constant (6.02×10^{23}). The irradiation area was 28.3 cm^2 (3 cm radius). The apparent quantum efficiency is calculated to the following equation:

The AQE calculation method is as follows: The AQE calculation method is as follows:

$$\text{AQE [\%]} = \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \times 100$$

$$= \frac{number\ of\ \ evolved\ hydrogen\ molecules\ \times\ 2}{number\ of\ incident\ photons} \times 100$$

$$\text{number of incident photons} = \frac{E\lambda}{hc}$$

$$E = PSt$$

P: represent the energy density of incident light (W/m^2);

S: the light receiving area (cm^2);

t: represent illumination time;

Plank's constant h: 6.626068E-34

c: 3.00E+08 represents the speed of light.

Photoelectrochemical measurement

The electrochemical impedance spectroscopy and photocurrent curves were examined by the three-electrode Princeton workstation, which employed the three-electrode configuration. Na_2SO_4 (0.1 M) aqueous solution was used as the electrolyte solution. Pt foil was the counter electrode and Ag/AgCl electrode was used as the reference electrode. To prepare working electrode, photocatalyst sample (50 mg) was dispersed in ethanol (35 mL), and then the suspension was sprayed onto the FTO glass, and then the FTO glass was calcined at 200 °C for 2 h in Ar. Furthermore, a 300 W xenon lamp with UVIRCUT filter (420-780 nm) was used as visible-light source. Electrochemical impedance spectroscopy was measured with amplitude of 5 mV and frequencies varying from 0.01 to 10000 Hz.

Photothermal test

The photothermal test of as-prepared samples was carried out as follow. 0.1 g of samples was loaded on a white paper and the initial temperature was controlled at room temperature. The temperature of the sample was measured using the Testo 865 infrared thermograph. A 300 W xenon lamp was used as a light source.

Hydroxyl radical (•OH) production test

Through the photoluminescence (PL) method with terephthalic acid (TA) as probe molecule, the generation of •OH radical was tested to confirm the relationship between the generation of •OH in the prepared samples and the photocatalytic performance. Specifically, TA can react with •OH to form 2-hydroxylterepthalic acid which can be detected by PL. The PL signal intensity of 2-hydroxylterepthalic acid is in proportion to the concentration of •OH generated in the aqueous media. In a typical •OH production test, 30 mg of prepared samples were put into 30 mL of TA solution (1×10^{-3} M). After achieving adsorption-desorption equilibrium between prepared samples and TA, a 300 W Xe lamp was turned on to irradiate the samples continuously. 3 mL of solution was taken every 15 min and measured using fluorescence spectrophotometer (RF-5301PC).

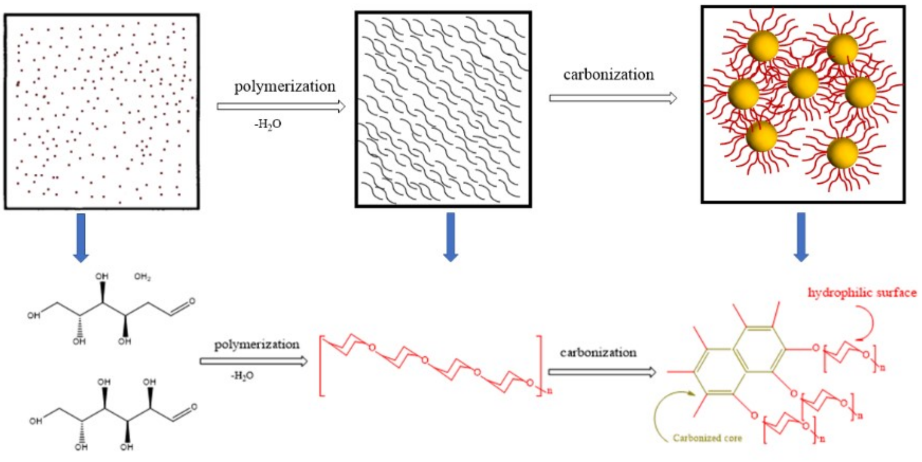

Fig. S1. The formation of carbon colloid sphere.

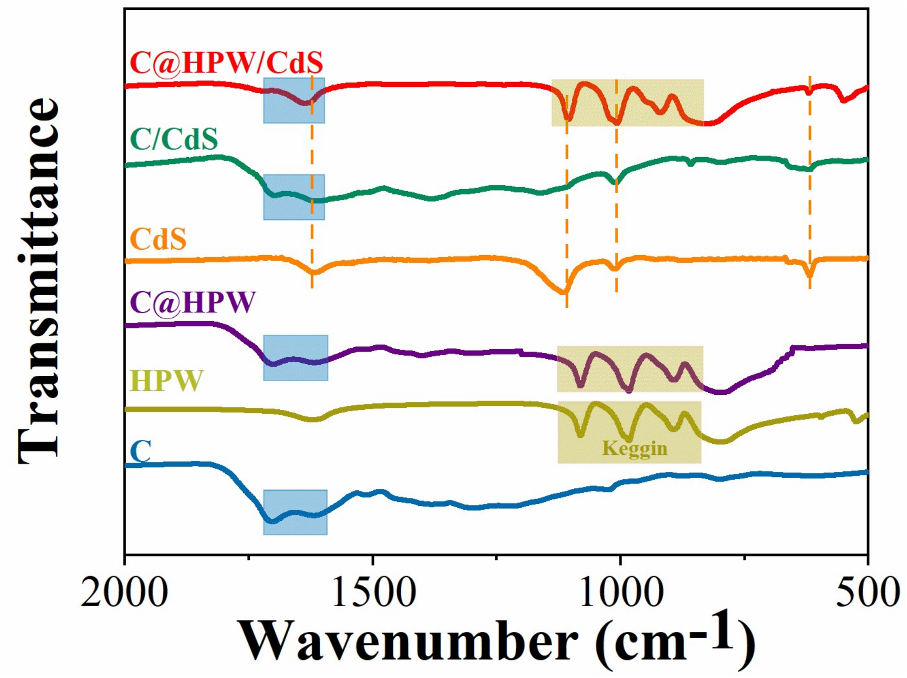

Fig. S2. Partially enlarged FT-IR spectra of C, HPW, CdS, C@HPW, C/CdS and C@HPW/CdS.

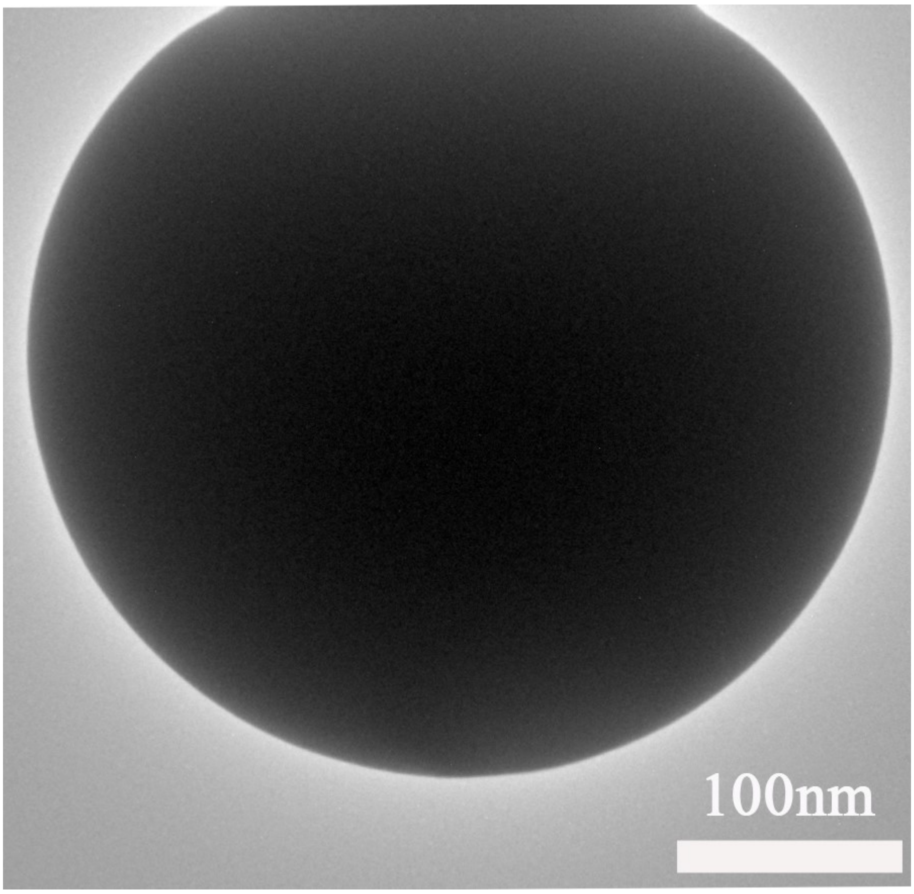

Fig. S3. TEM image of carbon colloid sphere.

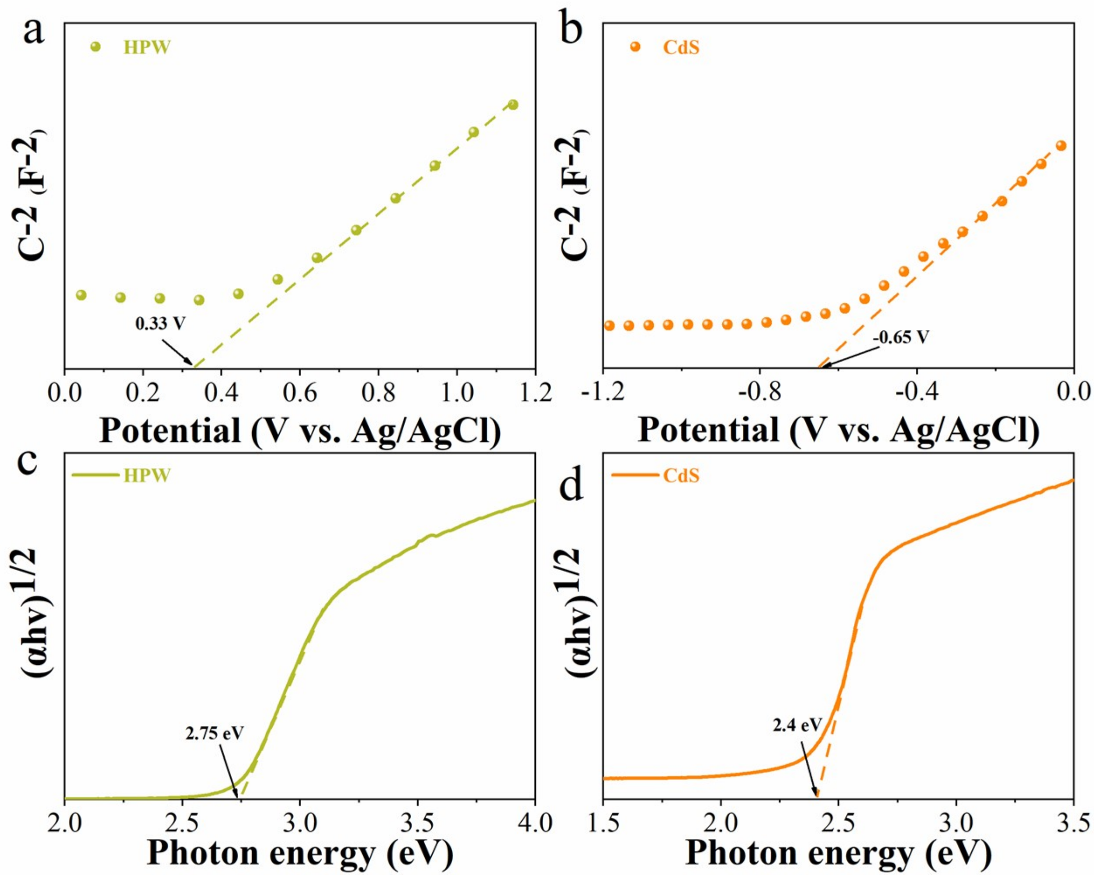

Fig. S4. Mott-Schottky curves (a, b) and Tauc plots (c, d) of HPW and CdS.

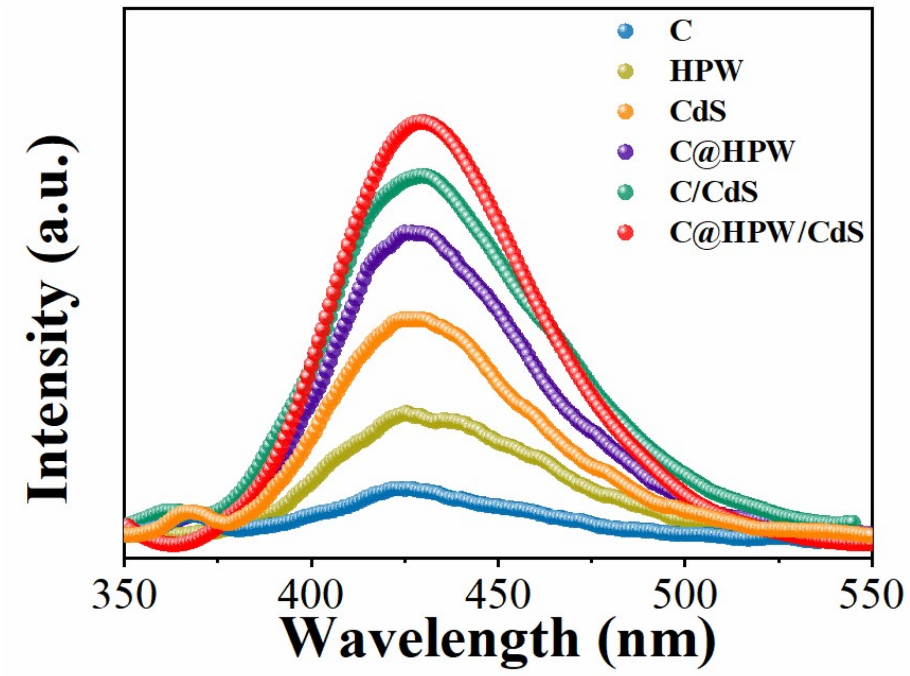

Fig. S5. Fluorescence spectra related to the amount of produced •OH of HPW, CdS, C@HPW, C/CdS and C@HPW/CdS.

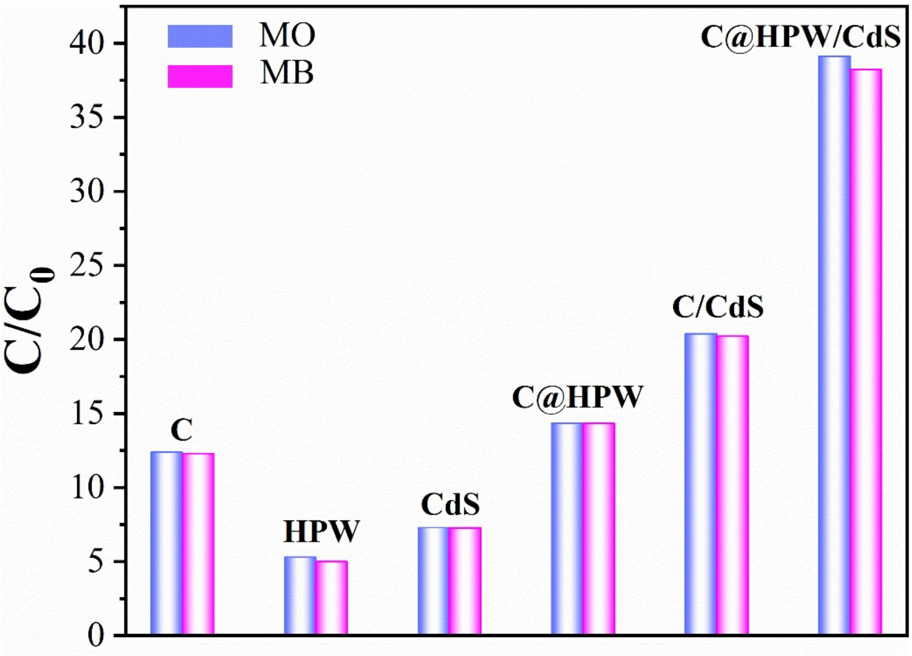

Fig. S6. Dark adsorption of MO and MB of as-prepared samples.

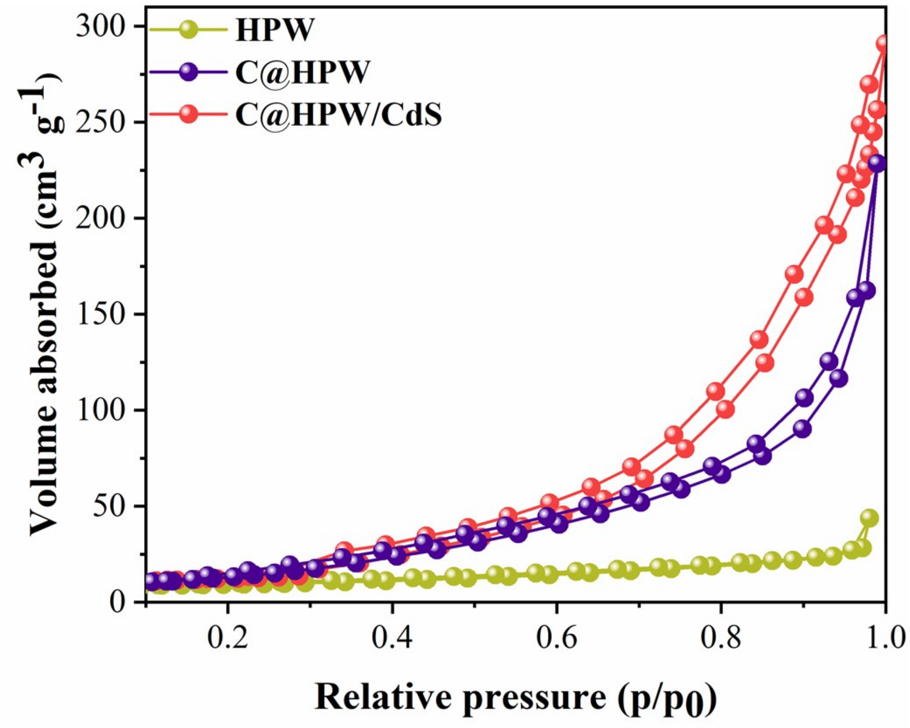

Fig. S7. N_2 adsorption/desorption isotherms for as-prepared HPW, C@HPW and C@HPW/CdS heterojunctions.

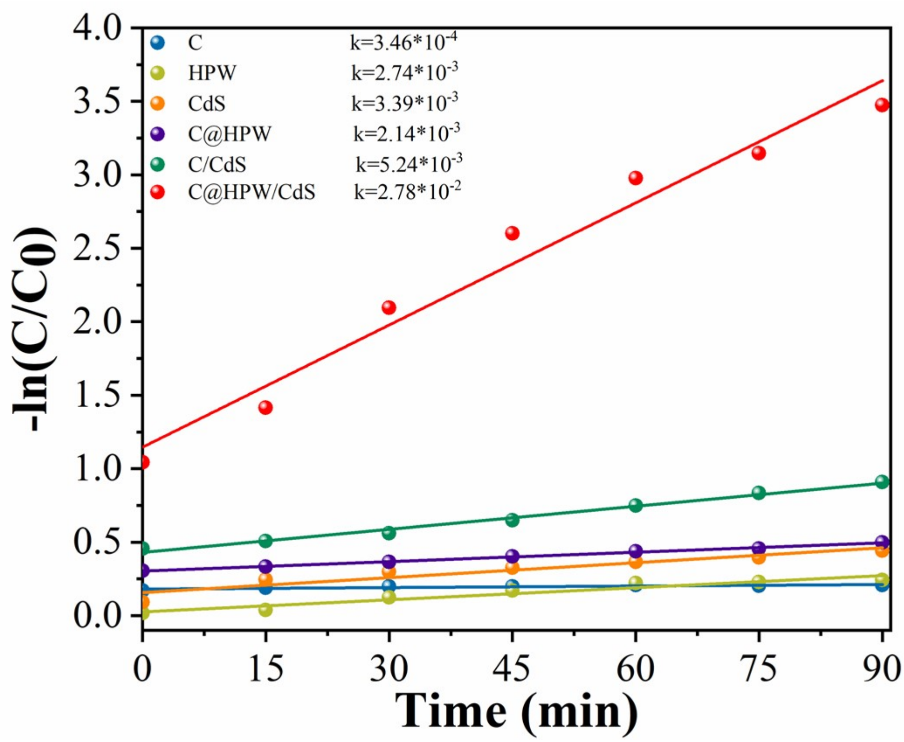

Fig. S8. Photodegradation plots with the apparent reaction rate constants k for the photocatalytic degradation of 2,4-DCP under visible light irradiation.

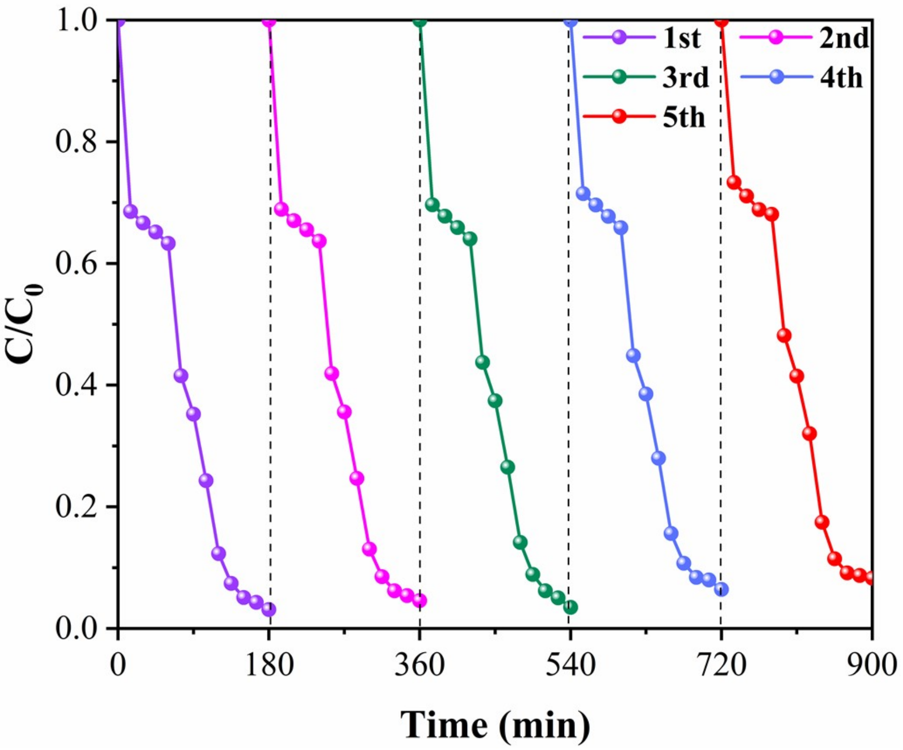

Fig. S9. The recycling runs of C@HPW/CdS for degrading 2,4-DCP.

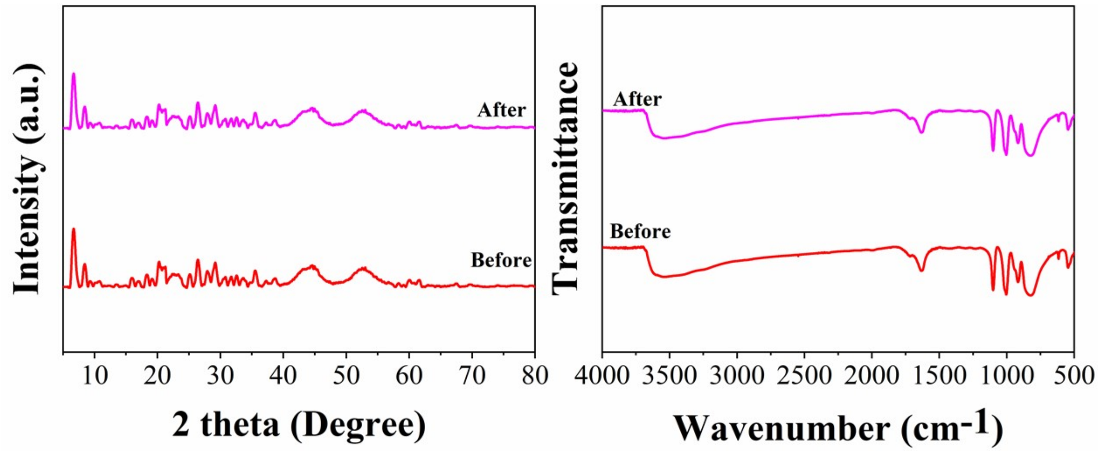

Fig. S10. XRD patterns (a) and FT-IR (b) of C@HPW/CdS before and after photocatalytic removal of 2,4-DCP under visible-light irradiation.

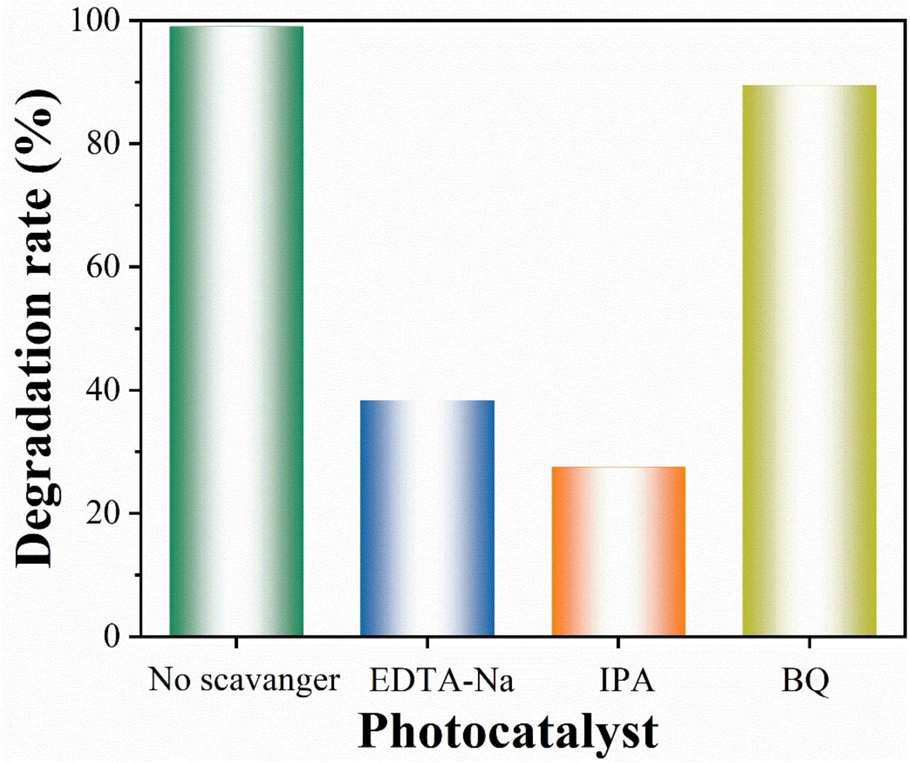

Fig. S11. The species trapping experiments for degradation of 2,4-DCP over C@HPW/CdS photocatalyst under visible light irradiation.

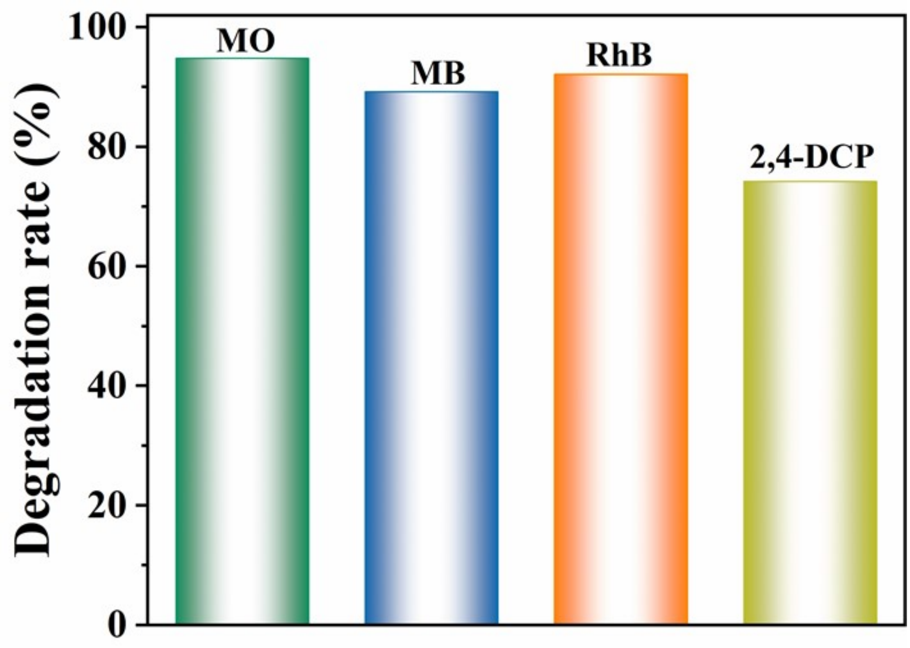

Fig. S12. Photocatalytic degradation rate of C@HPW/CdS for different pollutants within 60 min.

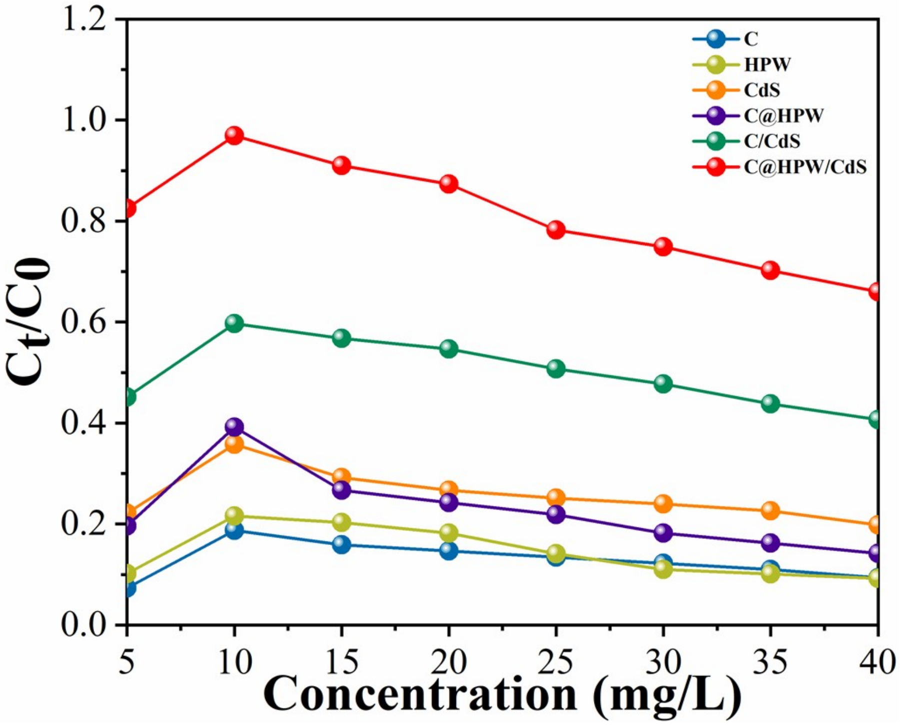

Fig. S13. Effect of different concentrations of 2,4-DCP solution on photocatalytic degradation performance.

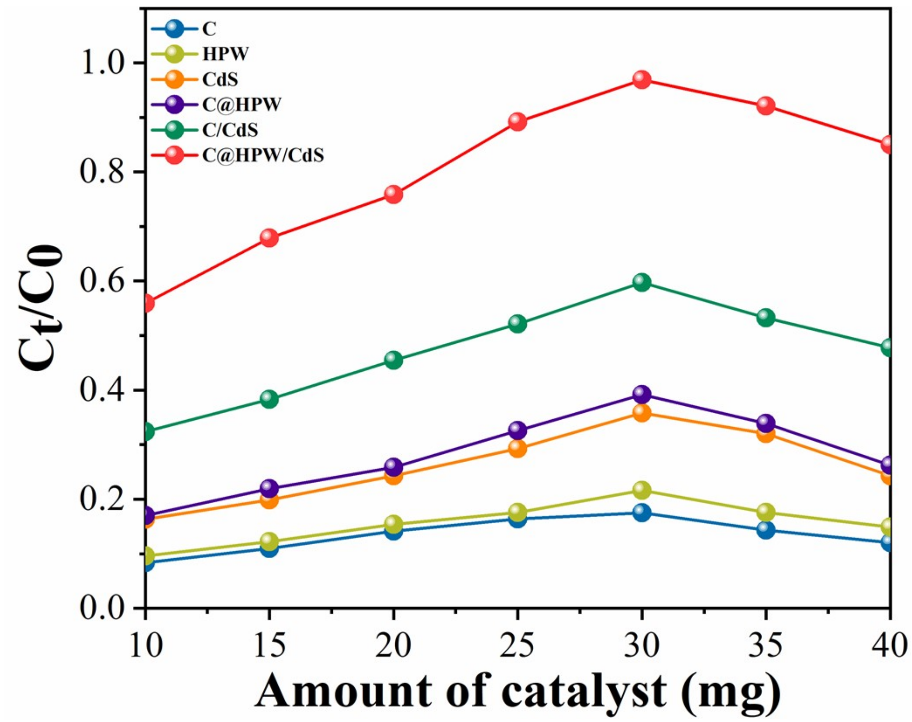

Fig. S14. Effect of different catalyst amounts on photocatalytic degradation performance of 2,4-DCP.

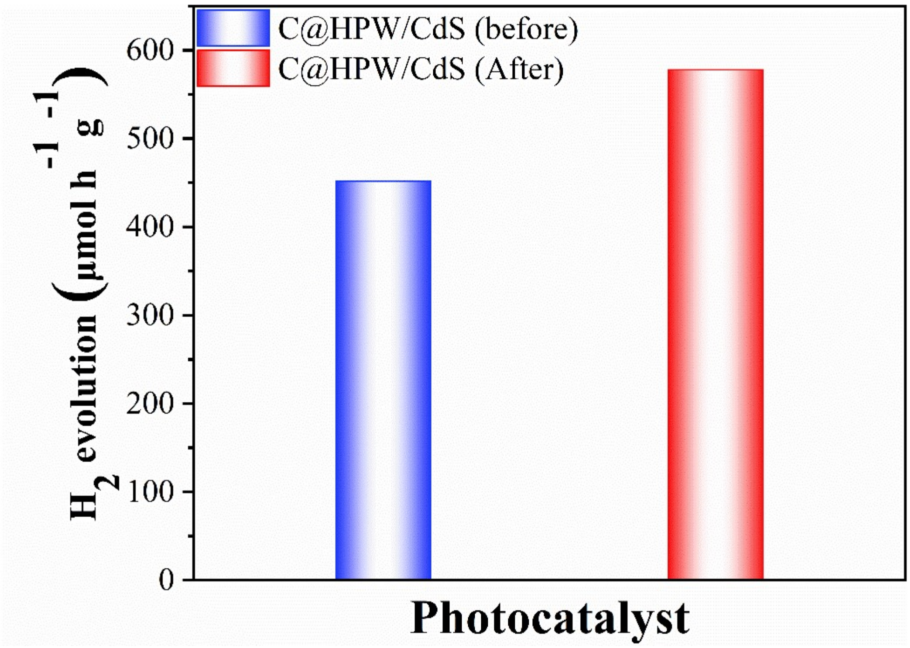

Fig. S15. Photocatalytic H_2 evolution of C@HPW/CdS before and after calcination.

Table S1. List of main chemicals and manufactures.

Chemicals	Molecular formula	Buy manufactures
Glucose	$C_6H_{12}O_6$	Tianjin Kermel Chemical Reagent Co. Ltd, China
Phosphotungstic acid	$H_3PW_{12}O_{40}$	Aladdin Reagent Company
Acetic acid	CH_3COOH	Aladdin Reagent Company
Deionized water	H_2O	Aladdin Reagent Company
Ethanol	C_2H_6O	Aladdin Reagent Company
Cadmium acetate dihydrate	$Cd\ (AC)_2 \cdot 2H_2O$	Tianjin Guangfu chemical Regent Company
Sodium sulfide nonahydrate	$Na_2S \cdot 9H_2O$	Tianjin Hengxing Chemical Reagent Company

Table S2. The band gap energies, conduction band (CB) and valence band (VB) potentials for HPW and CdS.

photocatalysts	Band gap (eV)	CB (eV)	VB (eV)
HPW	2.75	0.33	3.08
CdS	2.4	-0.65	1.75