

Electronic Supporting Information

3D ordered macroporous TiO₂-supported Pt@CdS core-shell nanoparticles: Design, synthesis and efficient photocatalytic conversion of CO₂ with water to methane

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Experimental Section

Synthesis of monodispersed PMMA microsphere and assembly of template

Non-crosslinked, monodispersed PMMA microspheres were synthesized using a modified emulsifier-free emulsion polymerization technique with water-oil biphasic double initiators. All water in the forthcoming synthetic steps was distilled and deionized to a resistivity of at least 12 M Ω ·cm. Methyl methacrylate (MMA, 80 ml) was washed in a separatory funnel three times with 50 ml of 1 M NaOH, then washed three times with 50 ml of water. And it was refined by reduced pressure distillation. A four-necked, 2000 ml round-bottomed flask was filled with the mixture of acetone (100 ml) and water (300 ml) and heated to 70 °C by a hot water bath, following the addition of the refined monomers. An electric motor was attached to the flask and to drive a Teflon stirring paddle and N₂ was bubbled to deaerate the air for 2 h. In a separate 160 ml polyethylene bottle, 0.31 g of 2, 2'-azobis (2-methylpropionamide) dihydrochloride (AIBA, water phase initiator) and 0.18 g of azodiisobutyronitrile (AIBN, oil phase initiator) were added into 150 ml of water, and then the solution was heated to 70 °C and added to mixture solutions. Under constant stirring (380 r/min) and with N₂ bubbling, the mixture was kept at 70 °C for 2 h. After the reaction was finished, the colloid sol was naturally cooled to room temperature, and obtained the homogenous latex with nearly monodispersed PMMA microspheres through filter paper with pores size of 1 μ m. In the present studies, the average diameters of the obtained microspheres were 350 nm which were estimated by using Laser particle size analyzer. The latex was centrifuged at 3000 r/min for 10 h to form colloidal crystal templates (CCT). The clear liquid was decanted and the solid block was dried in centrifugal tubes at room temperature. Finally, the highly ordered PMMA templates were obtained.

Preparation of 3DOM TiO₂ support

3DOM TiO₂ support was prepared by colloidal crystal template method using tetrabutyl titanate as precursor solution, and the schematic is shown in Figure S1. The 50mL of tetrabutyl titanate solvent were poured into a 100 ml beaker at room temperature. And the colloidal crystal template is immersed into the solvent which permeated the voids between the close-packed spheres and then condensed into a hard inorganic framework upon drying. Excessive liquid was removed from the impregnated microspheres template via a Buchner funnel connected to vacuum. The infiltrated template was allowed to dry in a drying oven with constant temperature at 50 °C for 24 h. The dried sample was calcined to remove the CCT at an air flow of 80 ml min⁻¹ in a tube furnace. The temperature-rising rate was 1 °C min⁻¹ from room temperature to 600 °C, and the calcination at 600 °C was kept for 5 hours. Finally, 3DOM TiO₂ support was obtained.

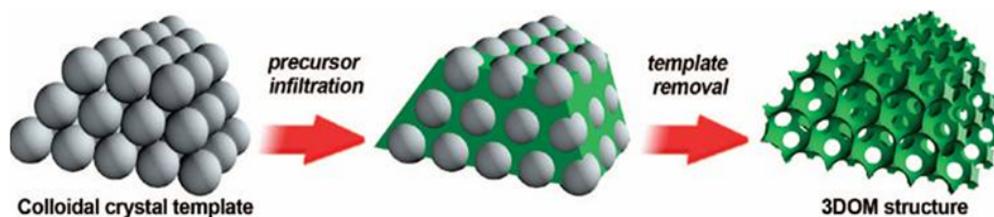


Fig. S1: The schematic for preparing periodic macroporous structures by colloidal crystal template method [1].

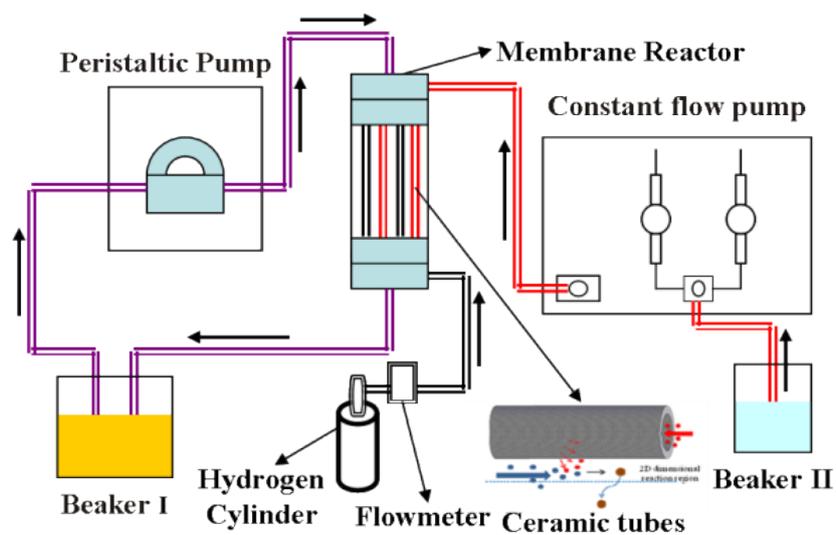


Fig. S2 Schematic of the gas bubbling-assisted membrane reduction-precipitation (GBMR/P) device for synthesis of 3DOM TiO_2 -supported Pt@CdS core-shell nanoparticle catalysts. ^[2]

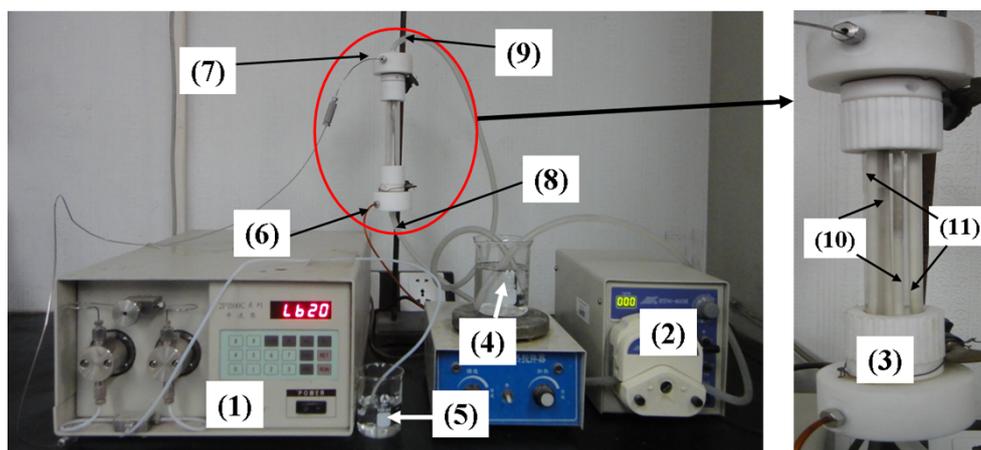


Fig. S3 The digital photos of GBMR/P device. The right photo is the ceramic membrane reactor composed of four ceramic membrane tubes, which is the core of the device of GBMR/P method. [2]

- (1) The constant flow pump (HLB-2020, Satellite Manufactory of Beijing, P.R. China).
- (2) The peristaltic pump (BT00-600M, Baoding Lange Co., Ltd, P.R. China).
- (3) The ceramic membrane reactor consisted of four ceramic membrane tubes (Φ 3 mm \times 160 mm, Hyflux Group of Companies, Singapore), which is the core of the device of GBMR method.
- (4) Beaker 1 filled with mixture solution (H_2PtCl_6 , 3DOM TiO_2 support and PVP).
- (5) Beaker 2 filled with reductant/precipitant solution (NaBH_4 or NH_4OH).
- (6) The inlet of hydrogen.
- (7) The inlet of reductant/precipitant solution (NaBH_4 or NH_4OH).
- (8) The inlet of mixture solution.
- (9) The outlet of mixture solution and hydrogen.
- (10) Two ceramic membrane tubes used for the dispersion of reductant solution (NaBH_4).
- (11) Two ceramic membrane tubes used for the dispersion of hydrogen bubbling.

Results Section.

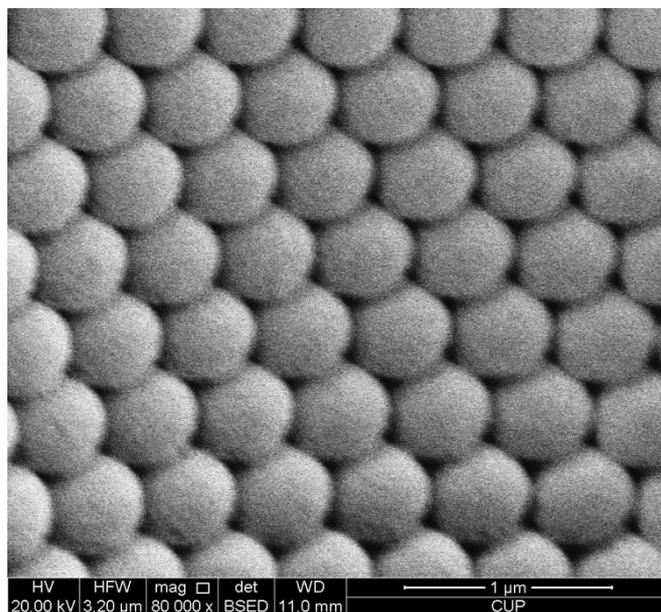


Fig. S4 SEM image of the three-dimensional ordered PMMA colloidal crystal template.

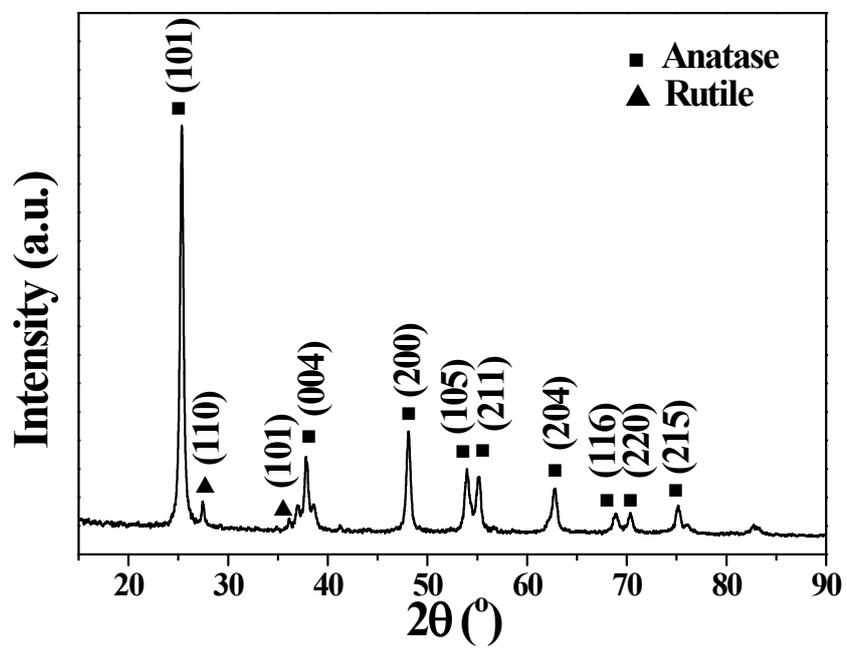


Fig. S5 XRD patterns of commercial P25 catalysts.

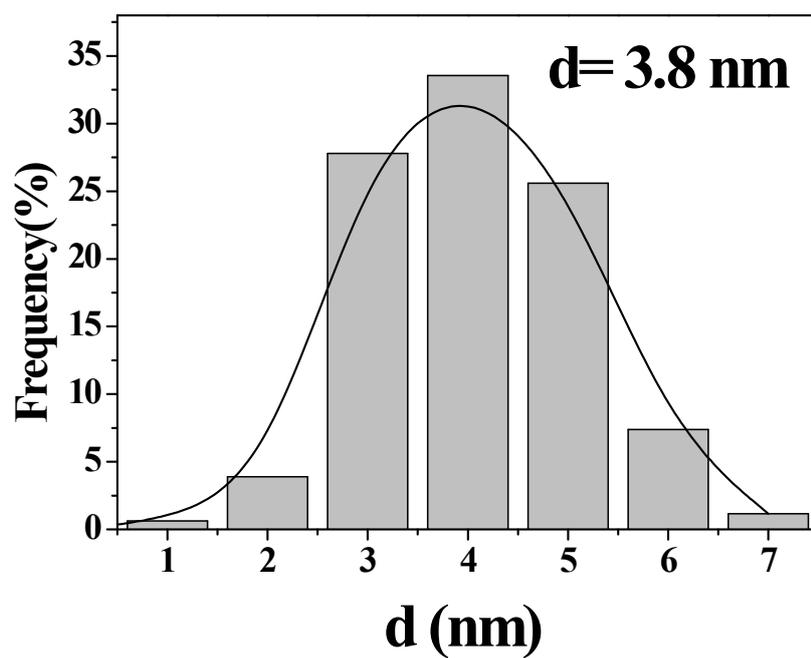


Fig. S6 The size distribution of Pt nanoparticles over 3DOM Pt/TiO₂ catalyst.

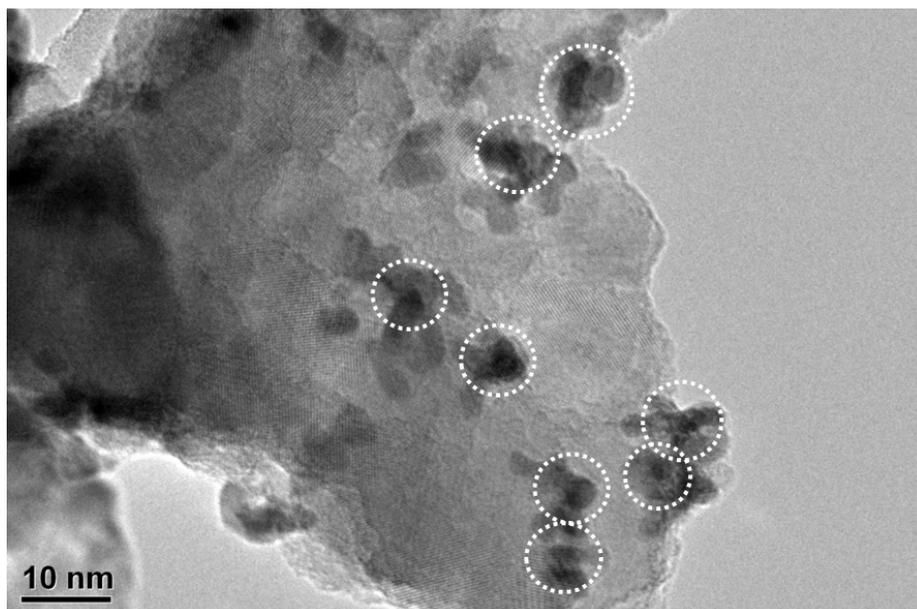


Fig. S7 TEM images of 3DOM Pt@CdS/TiO₂-2 catalysts.

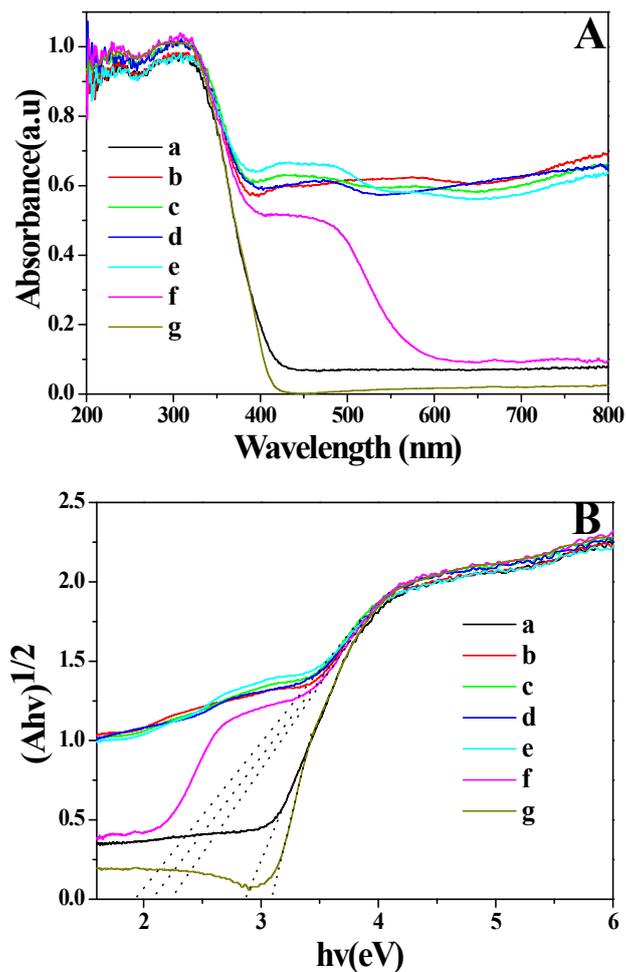


Fig. S8 UV-Vis DRS (A) and Kubelka-Munk transformed reflectance spectra to estimate optical absorption band gap (B) of P25, 3DOM TiO_2 , Pt/TiO_2 , CdS/TiO_2 and $\text{Pt}@/\text{CdS}/\text{TiO}_2$ catalysts. a. TiO_2 ; b. Pt/TiO_2 ; c. $\text{Pt}@/\text{CdS}/\text{TiO}_2$ -1; d. $\text{Pt}@/\text{CdS}/\text{TiO}_2$ -2; e. $\text{Pt}@/\text{CdS}/\text{TiO}_2$ -4; f. CdS/TiO_2 ; g. Commercial P25

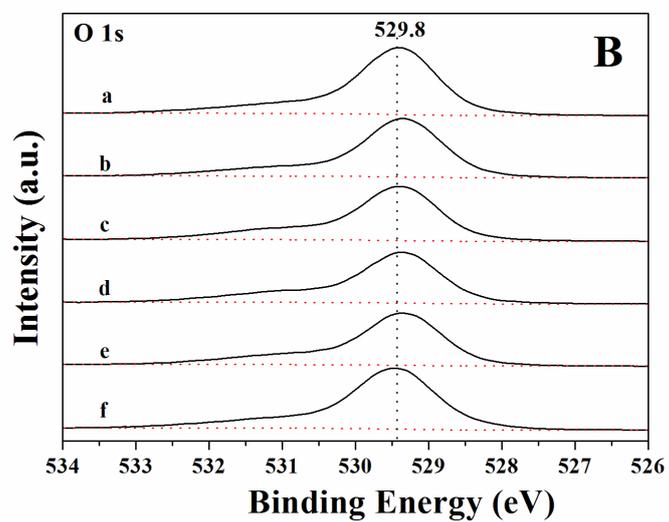
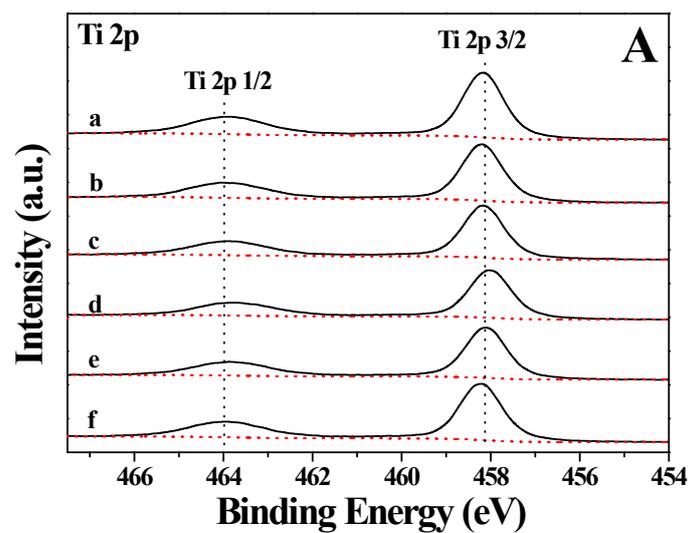


Fig. S9 Ti 2p (A) and O 1s (B) XPS spectra of 3DOM TiO₂, Pt₄/TiO₂, Pt@CdS/TiO₂ and CdS/TiO₂ catalysts. a. TiO₂; b. Pt/TiO₂; c. Pt@CdS/TiO₂-1; d. Pt@CdS/TiO₂-2; e. Pt@CdS/TiO₂-4; f. CdS/TiO₂

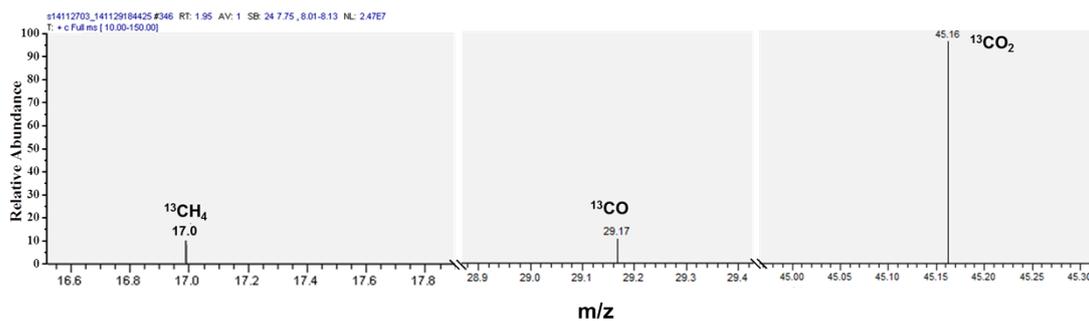


Fig. S10 The analysis results of ^{13}C isotopic tracing vis GC-MS for the products of photocatalytic $^{13}\text{CO}_2$ reduction over 3DOM Pt@CdS/TiO₂-1 catalyst after 20 h irradiation. The injected volume of the photocatalytic products was 20 μL . Helium was used as a carrier gas at a flowing rate of 0.5 mL/min. The MS presents the designated m/z signals. As observed from the mass spectra, the peak with m/z of 17 could be recognized as $^{13}\text{CH}_4$. The peak with m/z of 29 could be attributed to ^{13}CO . The isotopic ^{13}C tracer experiment results show that the C element in the product of CO and CH₄ comes from CO₂ reactant.

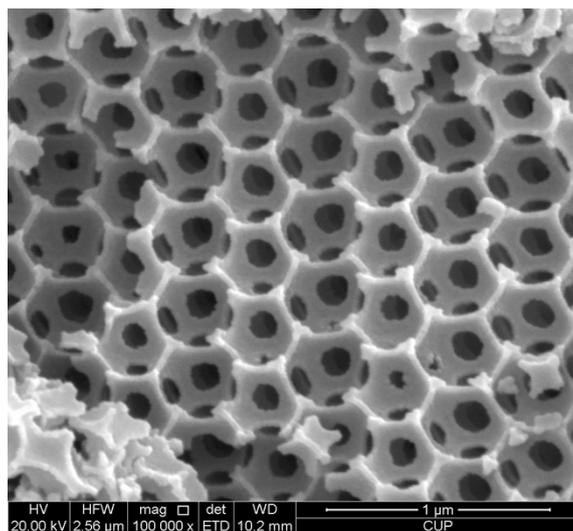


Fig. S11 SEM images of 3DOM Pt@CdS/TiO₂-1 catalysts after the six test cycles of photocatalytic reduction of CO₂ with H₂O.

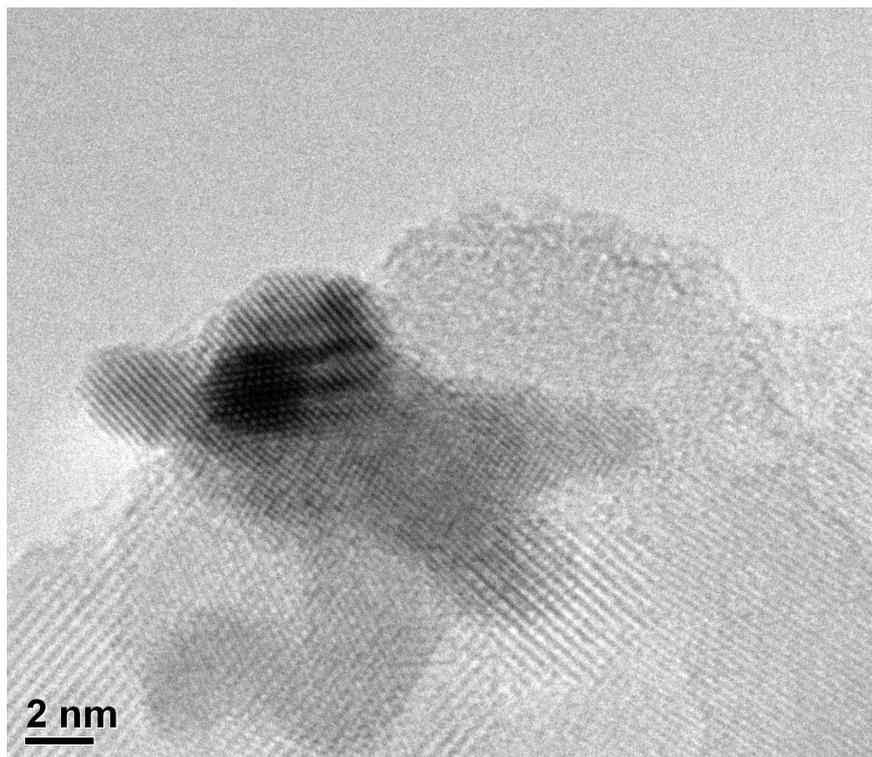


Fig. S12 TEM images of 3DOM Pt@CdS/TiO₂-1 catalysts after the six test cycles of photocatalytic reduction of CO₂ with H₂O.

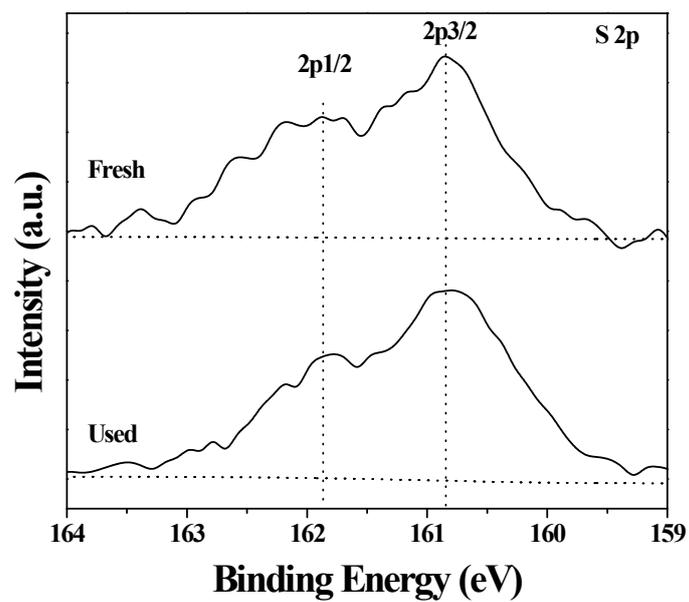


Fig. S13 S2p XPS spectra of the fresh 3DOM Pt@CdS/TiO₂-1 catalyst and used one after the six test cycles of photocatalytic reduction of CO₂ with H₂O.

[1] A. Stein, F. Li and N. R. Denny, *Chem. Mater.* 2008, **20**, 649.

[2] Y. Wei, J. Liu, Z. Zhao, A. Duan, G. Jiang, C. Xu, J. Gao, H. He, X. Wang, *Energy Environ. Sci.*, 2011, **4**, 2959.