

Supporting Information

CdO decorated CdS nanorod with enhanced photocatalytic reduction of CO₂ to CO

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SUPPLEMENTAL MATERIALS

All commercial chemicals were analytical reagents and were used without further purification. P25 were purchased from Alfa Aesar. Glycerol, CH₃CN, and methanol were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. Cadmium nitrate was purchased from Shanghai Macklin Biochemical Co., Ltd. Thiourea was purchased from Tianjin Damao Chemical Reagent Factory. Maltose, xylose, and lactose were purchased from Shanghai Macklin Biochemical Co., Ltd. Other sugars were purchased from Sinopharm Chemical Reagent Co., Ltd, and Aladdin Chemistry Co. Ltd. Bi₂O₃ and Cu₂O were purchased from Aladdin Chemistry Co. Ltd.

SUPPLEMENTAL METHODS

Preparation of catalysts

Preparation of CeO₂

Pristine CeO₂ were prepared by a traditional precipitation process described in the literature.¹ In a typical experiment, Ce(NO₃)₃·6H₂O (5.0 g) was dissolved in deionized water, and then the solution was adjusted to a pH of 11.0 by the addition of NH₃·H₂O under stirring at room temperature. The obtained precipitate was filtered, washed with deionized water, and then dried at 120 °C for 12 h. The obtained solid was calcined at 500 °C under the flow of air (50 mL·min⁻¹) for 4 h.

Preparation of Nb₂O₅

Nb₂O₅ were prepared through the hydrothermal treatment according to a literature procedure.² In a typical experiment, 0.1 g of niobic acid was dispersed into 40 mL of ethanol aqueous solution. The suspension was added in a Teflon-lined stainless-steel autoclave, heated to 180 °C and kept at the temperature for 38 h. After reaction, the mixture was naturally cooled down to room temperature. White precipitate was obtained by centrifugation, rinsed with deionized water and ethanol for several times. The sample was calcined at 600 °C for 5 h in air, obtaining Nb₂O₅.

Preparation of Bi₂WO₆

Bi₂WO₆ was prepared according to a literature procedure.³ Typically, Bi(NO₃)₃·5H₂O (0.98 g) was dissolved in nitric acid (40 mL, 0.3 mol L⁻¹) and ultrasonicated to dissolve it evenly. Next, Na₂WO₄ (20 mL, 0.05 mol L⁻¹) solution was added with vigorous stirring and a white precipitate was formed. Subsequently, NaOH (20 mL, 0.2 mol L⁻¹) aqueous solution was added. After stirring for 24 h, the mixture was transferred to a 130 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. After being washed with water (3 × 25 mL) and absolute ethanol (3 × 25 mL), a yellow solid was obtained after being dried in vacuum at 60 °C for 12h.

Preparation of g-C₃N₄

Melamine (10 g) was directly heated at 550 °C for 4 h (the same heating rate: 2.5 °C/min) in the muffle furnace, giving a pale-yellow solid.

Preparation of Pt/P25

Pt/P25 was prepared by impregnation method by using H_2PtCl_6 and Degussa P25, the Pt content was 0.1 wt%. Typically, P25 (500 mg) was dispersed in Milli-Q water (10 mL) with vigorous stirring, and H_2PtCl_6 (1.011 mL, 7.61 mmol L^{-1}) aqueous solution was added dropwise. After stirring for 6 h, the solution was evaporated on a 100 °C hot plate. The grey Pt/P25 was obtained after reducing at 400 °C by H_2 (30 mL min^{-1}) for 2 h with a ramp rate of 10 °C min^{-1} .

Preparation of Cu/P25

The P25 supported catalyst with 1 wt% weight of copper was prepared by the impregnation method. Typically, 0.5 g of P25 was dispersed in 20 mL of deionized water, into which a certain volume of $\text{Cu}(\text{NO}_3)_2$ aqueous solutions (0.1 mol $\cdot\text{L}^{-1}$) was added. The mixture was stirred for 24 h at room temperature and then heated at 100 °C overnight to remove water. The acquired powders were put in a quartz tube and calcined at 450 °C for 2 h in pipe furnace with a heating rate of 2 °C min^{-1} and 25 mL min^{-1} flow of air.

Preparation of Cu/TNR

Cu/TNR were prepared according to our previous work.⁴ Typically, Cu^{2+} -exchanged hydrogen titanate was prepared by an ion-exchange reaction of NH_4 -TNTs in $\text{Cu}(\text{NO}_3)_2$ aqueous solution. Typically, 0.5 g of NH_4 -TNTs was dispersed in 20 mL of deionized water, into which a certain volume of $\text{Cu}(\text{NO}_3)_2$ aqueous solutions (0.1 mol $\cdot\text{L}^{-1}$) was added. The mixture was stirred for 24 h at room temperature and then heated at 100 °C overnight to remove water. The acquired powders were put in a quartz tube and calcined at 450 °C for 2 h in pipe furnace with a heating rate of 2 °C min^{-1} and 25 mL min^{-1} flow of air.

Preparation of N-TiO₂

The N-TiO₂ were prepared according to our previous work.⁴ Typically, 0.5 g of NH_4 -TNTs was put in a quartz tube and calcined at 400 °C for 2 h in pipe furnace with a heating rate of 2 °C min^{-1} and 25 mL min^{-1} flow of air.

Preparation of In₂S₃

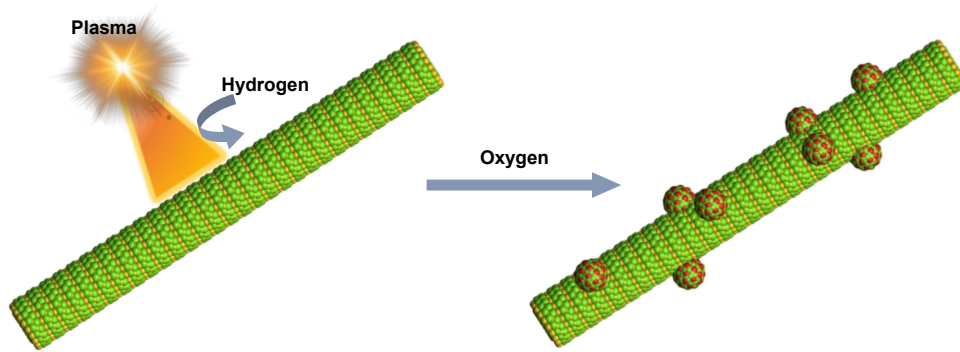
In₂S₃ was prepared by a hydrothermal method. Typically, $\text{InCl}_3\cdot 4\text{H}_2\text{O}$ (936.3 mg) and CTAB (260.6 mg) were dissolved in 20 mL of water in a 100 mL beaker and magnetically stirred for 30 min at room temperature. Thioacetamide (604.8 mg) was then added into the above solution. 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. CAUTION: Toxic H_2S gas is generated. After being washed with absolute ethanol (3 × 25 mL) and ethanol/deionized water (1:3, 3 × 25 mL), a yellow solid was obtained after being dried in vacuum at 60 °C for 12 h. The yield was more than 95%

Lifetime of photogenerated electrons

The calculated lifetime of photogenerated electrons (τ_n) of both samples is based on the following equation:⁵⁻⁶

$$\tau_n = \frac{k_B T}{e_0} \frac{d(V_{oc})}{dt}$$

where τ_n is carriers' lifetime, k_B is Boltzmann's constant ($=1.38 \times 10^{-23}$ J/K), T is the absolute temperature ($=298$ K), e_0 is the elementary charge ($= 1.6 \times 10^{-19}$ C) and $d(V_{oc})/dt$ could be obtained from the time-dependent open-circuit potential plots.



Scheme S1. Schematic synthesis of CdO/CdS.

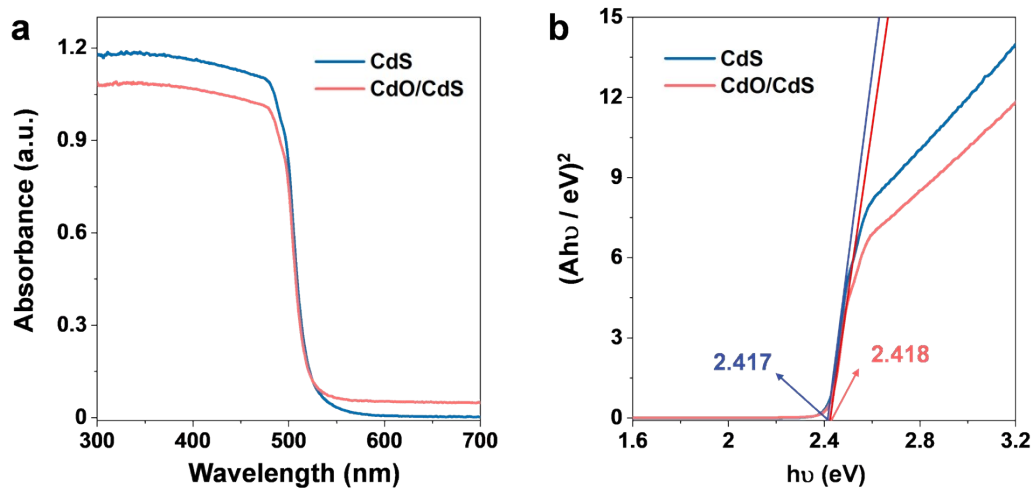


Figure S1. Absorption properties of CdS and CdO/CdS catalysts. (a) UV-vis diffuse reflectance spectra, (b) Tauc plot obtained from UV-vis diffuse reflectance spectra.

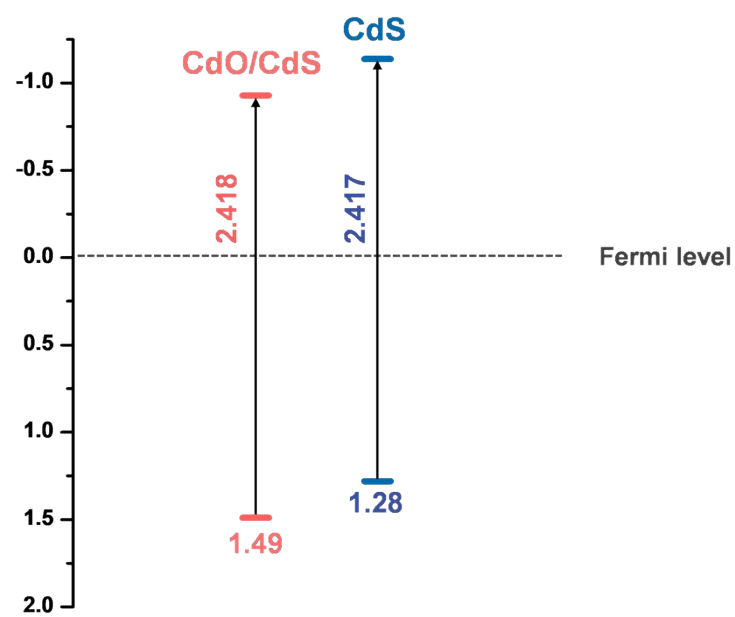


Figure S2. Energy level distributions of CB and VB of CdO/CdS and CdS catalysts.

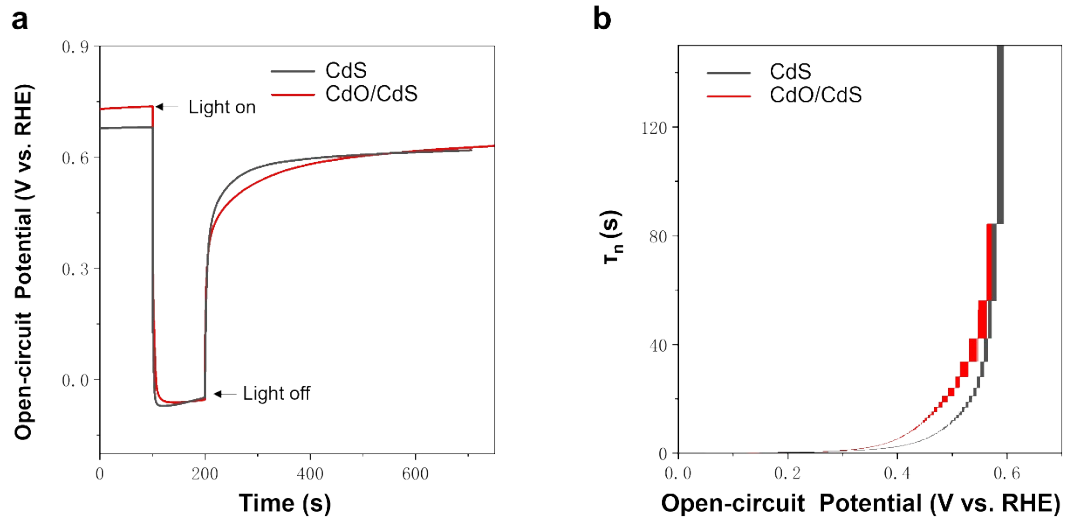


Figure S3. Photoelectrical properties. (a) Time-dependent open-circuit potential plots. (b) The calculated electron lifetimes.

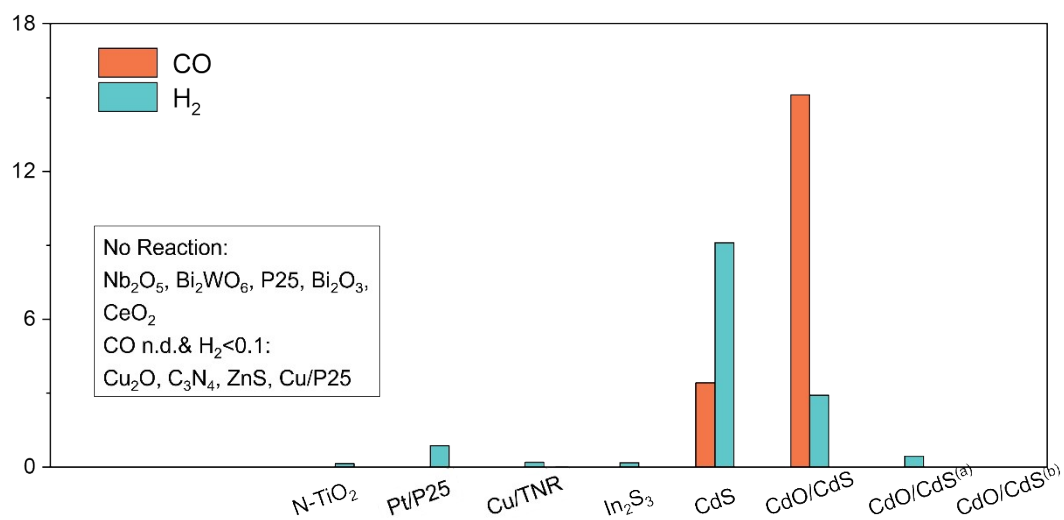


Figure S4. Catalysts screening. Reaction conditions: 5 mg of catalyst, 0.9 mL of CH₃CN, 0.1 mL of H₂O, 0.1 mL of triethylamine, 1 bar of CO₂, 18 W blue LEDs (455 ± 5 nm), 155 mW cm⁻², 12 h

(a) Argon instead of CO₂.

(b) Without illumination.

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