## **Supporting information**

## Highly efficient photocatalytic hydrogen evolution by nickel phosphide nanoparticles from aqueous solution

## **Experimental Methods**

**1. Chemicals and Materials.** All materials were of analytical grade and used as received without further purification. Cadmium nitrate tetrahydrate  $Cd(NO_3)_2 \cdot 4H_2O$ , thioacetamide, nickel acetylacetonate Ni(acac)\_2, poly(vinylpyrrolidone) (PVP, Mw = 40000) and ethylene glycol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). L-(+)-lactic acid, oleylamine (70%), polyethyleneimine (PEI, M.W. 70000, 50 wt% aq. solution), 1-octadecene (ODE) and tri-n-octylphosphine (TOP) were obtained from Alfa Aesar.

## 2. Material Synthesis

**2.1 Synthesis of CdS nanorods.** CdS NRs were synthesized according to the literature method. In a typical procedure, 0.75 g thioacetamide was dissolved in 10 mL ethylene glycol as sulfur precursor solution (1.0 M). 0.03 g Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.10 mmol), 0.20 g polyethyleneimine (M.W. 70000, 50 wt% aq. solution) and 10 mL ethylene glycol was heated to 120 °C under stirring in a 100 mL 3-necked flask. Then 100  $\mu$ L thioacetamide ethylene glycol stock solution was quickly injected into the hot solution, and the temperature was stabilized at 120 °C for 30 min. The reaction mixture was cooled to room temperature and put through dialysis in distilled water for 24 h to remove the ethylene glycol and excess polymer.

**2.2 Synthesis of Ni<sub>2</sub>P nanoparticles.** 0.50 g (1.95 mmol) nickel acetylacetonate [Ni(acac)<sub>2</sub>], tri-n-octylphosphine (4 mL, 8.80 mmol) and 10.0 mL oleylamine (70%) were added to 9.0 mL of 1-octadecene (ODE, 90%) in a three-necked round-bottomed flask. The solution was degassed under an Ar atmosphere at 120 °C for 60 min then heated to 320 °C and kept at this temperature for 120 min. After the solution cooled to room temperature, n-hexane/ethanol (1:2) was added to form flocculation and centrifuged to separate the black precipitates. The obtained black solid were washed by n-hexane/ethanol (1:3) three times.

**2.3 Capping agent exchange with PVP.** The obtained Ni<sub>2</sub>P nanoparticles were dissolved in 10 mL n-hexane. 200 mL trichloromethane solution containing 2.0 g PVP was added to the n-hexane

solution and then heated to 65 °C for 12 h under an Ar atmosphere. After the mixture was cooled to room temperature, acetone was added to cause flocculation and centrifuged to separate the black precipitates. The obtained black solid were washed by acetone three times. The final product can be dissolved in water easily.

**3.** Photocatalytic activity measurement. The photocatalytic hydrogen-production experiments were performed in a 60 mL quartz tube sealed with a silicone rubber septum. In a typical photocatalytic experiment, the tube containing an aqueous solution of CdS NRs ( $1.75 \times 10^{-4}$  M), Ni<sub>2</sub>P NPs ( $5.0 \times 10^{-5}$  M) and L-(+)-lactic acid (0.5 mL, 5% v/v) was adjusted to pH 3.0 with 1 M NaOH and adjusted the total volume of the mixed solution to 10 mL with distilled water. Then the system was deoxygenated with argon for 30 min. white LED light source ( $30 \times 3$  W,  $\lambda \ge 420$  nm) were used as the irradiation light sources. The LEDs were positioned 2 cm away from the sample which was kept under continuous stirring at room temperature. Hydrogen was measured by a gas chromatograph (GC-14C, Shimadzu, with argon as a carrier gas), which was equipped with a 5 Å molecular sieve column ( $3 \text{ m} \times 2 \text{ mm}$ ) and a thermal-conductivity detector. TON = 2n (H<sub>2</sub>) / n (cat). TOF = 2n (H<sub>2</sub>) / [n (cat) × h].

4. Photoelectrochemical Measurements. Photocurrent measurements were performed on a CHI 660C electrochemical work station (Chenhua Instrument, Shanghai, China) in a conventional three-electrode. The resultant electrode served as the working electrode, with a platinum wire as the counter electrode and an Ag/AgCl (saturated KCl) electrode as the reference electrode. LED light source ( $30 \times 3 \text{ W}$ ,  $\lambda \ge 420 \text{ nm}$ ) were used as the irradiation light sources. A 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: 20 mg of the prepared anhydrous photocatalyst was ground with 30 µL of a Nafion (5.0%) aqueous solution and 100 µL of ethanol to make slurry. The slurry was then spread on a 3.0 ×1.0 cm<sup>2</sup> ITO glass substrate with an active area of about 2.0 cm<sup>2</sup>. The film was dried at 100 °C for 30 min in a flowing N<sub>2</sub> atmosphere. The photoresponses of the samples as light on and off were measured at 0.0 V.

**5. Materials characterization.** The concentration of CdS NRs and Ni<sub>2</sub>P NPs were determined by inductively coupled plasma atom emission spectrometry (ICP-AES, Varian 710-ES, USA). The size, lattice fringes and energy dispersive X-ray (EDX) measurements were analyzed on a transmission electron microscope (TEM) (JEM 2100F) with an accelerating voltage of 200 kV.

Powder X-ray diffraction (XRD) pattern was recorded on a Bruker AXS D8 X-ray diffractometer with Cu K<sub> $\alpha$ </sub> ( $\lambda$  = 1.54056 Å). UV-vis absorption spectrum was recorded on a spectrophotometer (Hitachi U-3010). Fluorescence spectral measurements were carried out with a fluorescence spectrophotometer (Hitachi F-4500) at room temperature. Dynamic light scattering (DLS) measurements were performed with a Dybapro NanoStar instrument (Wyatt Technology).



Figure S1. UV-vis spectrum of the obtained CdS NRs.



Figure S2. Fluorescence spectrum of the CdS NRs excited at 365 nm.



Figure S3. TEM (left) and HRTEM (right) images of the CdS NRs.



Figure S4. XRD pattern of the obtained CdS NRs.



Figure S5. Particle size distribution of Ni<sub>2</sub>P NPs determined by DLS measurements.



**Figure S6.** Transient photocurrent responses of CdS NRs-Ni<sub>2</sub>P NPs (blue line), CdS NRs (red line), Ni<sub>2</sub>P NPs (pink line) and blank ITO glass (black line) in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution under visible-light irradiation at 0.0 V using Ag/AgCl as a reference electrode.