Electronic Supplementary Information (ESI)

Enhancing the photocatalytic H_2 evolution activity of red phosphorous by using noble-metal-free $Ni(OH)_2$ under photoexcitation up to 700 nm

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Experimental Section

Synthesis of crystalline red phosphorus (P)

Commercial red phosphorus was ground into a fine, homogeneous powder slightly and then crystallized at 400 °C for 2 h in Ar atmosphere. The crystallized product was washed with distilled water and then dried at 80 °C overnight.

Synthesis of $Ni(OH)_2$/P and Pt/P

$Ni(OH)_2$/P composites were prepared by a simple precipitation method. Typically, 0.5 g of crystalline red P was dispersed in 50 mL of NaOH aqueous solution (0.5 M) under vigorous stirring followed by ultrasonic-dispersion for 1 h. Then 0.005 M $Ni(NO_3)_2$ aqueous solution was added dropwise under vigorous stirring. After the reaction was completed and the suspension was continuously stirred for 1 h, the resulting precipitates were filtered, washed with distilled water several times and dried at 80 °C overnight. By changing the amount of $Ni(NO_3)_2$, samples with various weight percentages (theoretical) of $Ni(OH)_2$ (0, 0.2, 0.5, 1, 3 and 10 wt%) were synthesized, and hereafter were denoted as N0, N0.2, N0.5, N1, N3 and N10, respectively. For comparison, we also prepared pure $Ni(OH)_2$ sample using the same experimental procedures, and the resultant $Ni(OH)_2$ sample was denoted as N100. Various contents of Pt loaded crystalline red P samples (weight ratios: 0, 0.2, 0.5, 0.7, 1.0 and 2.0 wt%) were synthesized by photochemical reduction of H_2PtCl_6 in presence of crystalline red P aqueous suspension. The corresponding samples were denoted as Pt0, Pt0.2, Pt0.5, Pt0.7, Pt1.0 and Pt2.0, respectively.

Characterization

XRD patterns of the samples were collected in a rotation anode X-ray diffractionmeter (D8 Advance, Germany) with Cu-Kα radiation. UV-vis DRS were obtained by using a UV-vis spectrophotometer (U-3010, Hitachi, Japan). XPS (X-ray photoelectron spectroscopy) measurements were recorded on a Kratos Axis Ultra DLD equipped with Al-Kα radiation (hν = 1486.6 eV). Scanning electron microscopy (SEM) images were obtained using a LEO 1530VP field-emission scanning electron microscope. Transmission electron microscopy (TEM) observations were conducted with a JEM-2010F electron microscope (JEOL, Japan).

Photocatalytic H_2 evolution activity

Water splitting reactions were carried out in a top-irradiation quartz reactor connected to a gas-closed circulation system in vacuum. A 300 W Xe lamp (PLS-SXE-300UV, Trusttech) equipped with a cut-off filter (λ< 400 nm) to remove ultraviolet light was used as the light source. 50 mg of the photocatalyst was dispersed in a 100 mL of aqueous solution containing 5 mL of methanol as the sacrificial reagent. The evolved H_2 was analyzed by a gas chromatograph equipped with a thermal conductivity detector (GC9800, N_2 carrier, TDX-01 column).

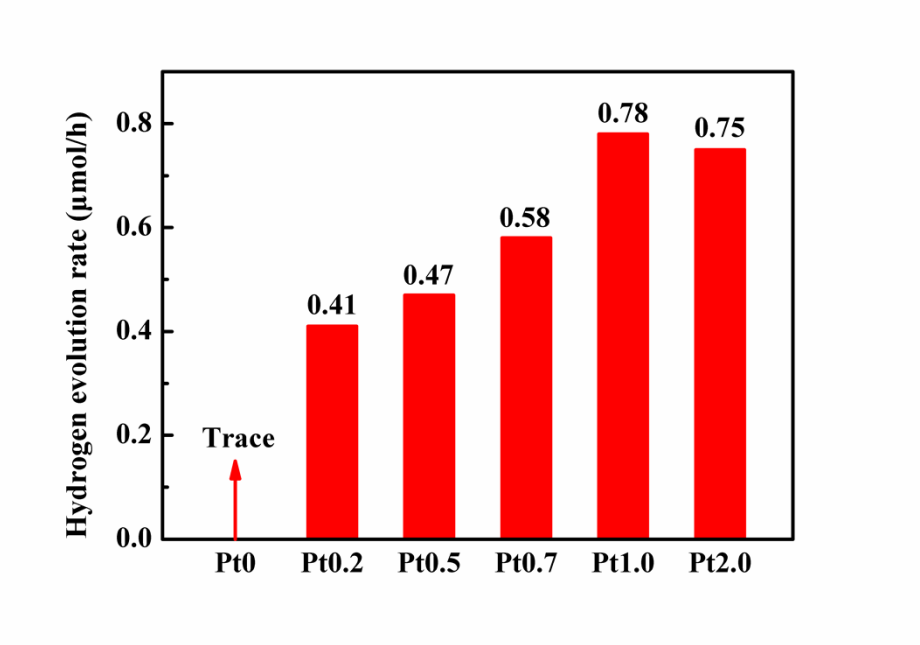

Fig. S1 Effect of Pt content on photocatalytic H_2 evolution activity of red P from methanol aqueous solution under visible light irradiation (λ≧400 nm). (Reaction conditions: photocatalyst, 50 mg; 5 vol% methanol aqueous solution, 100 mL; light source, 300W Xe-lamp equipped with a 400 nm cut-off filter).

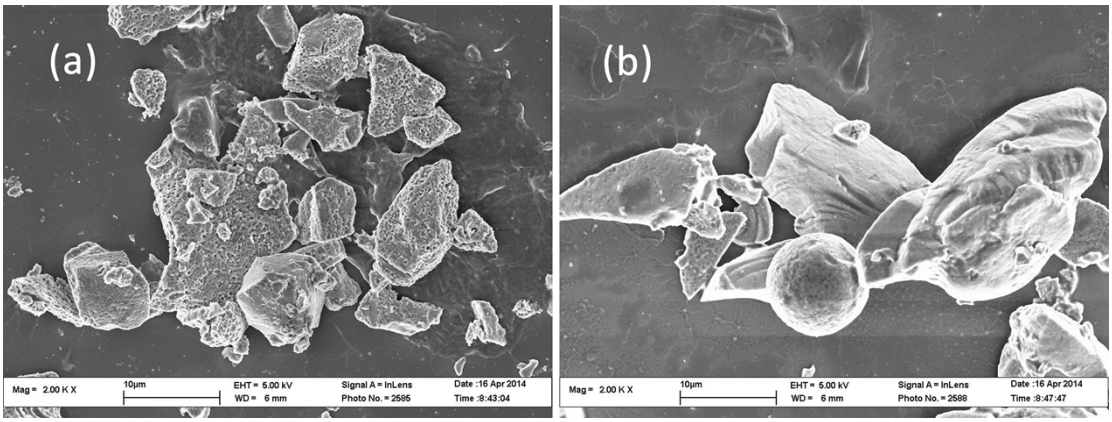

Fig. S2 SEM images of (a) N0 and (b) N0.5 samples.

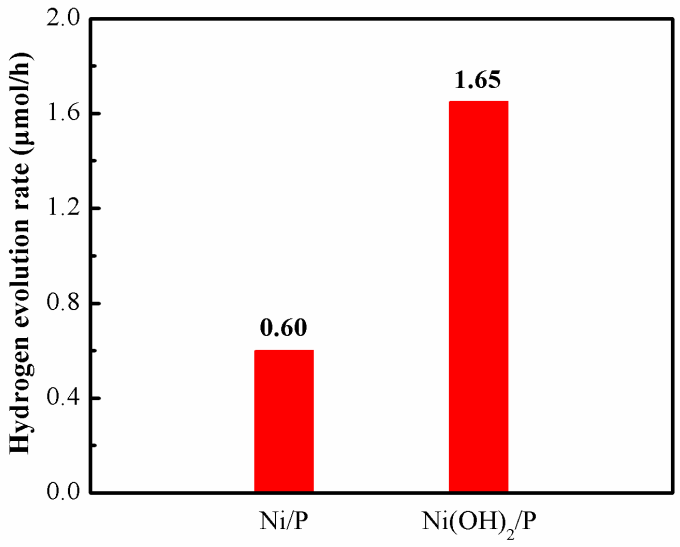

Fig. S3 A comparison of photocatalytic H_2 evolution activity of Ni/P and $Ni(OH)_2$/P samples from methanol aqueous solution under visible light irradiation (λ≧400 nm). Ni atoms-loaded red P sample was synthesised using KBH_4 as reduction reagents. (Reaction conditions: photocatalyst, 50 mg; 5 vol% methanol aqueous solution, 100 mL; light source, 300W Xe-lamp equipped with a 400 nm cut-off filter).