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Facet-selective construction of Cu₂O/Pt/BiVO₄ heterojunction arrays for

photocatalytic H₂ production from water

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Experimental details

1. Preparation of BiVO₄ particles

Monoclinic BiVO₄ was synthesized by a precipitation-hydrothermal process as derived from literature ¹ Bi(NO₃)₃ (99%, Damas-beta) was dissolved in 2 M HNO₃ (65%, Aladdin) solution. And NH₄VO₃ (99.95%, Macklin) was dissolved in 2 M NaOH (98%, Aladdin) solution. The concentration of Bi(NO₃)₃ and NH₄VO₃ were both constrained to 5 mM. Subsequently, 20 mL of each solution was added into same beaker followed by adding 1ml acetic acid (99.8%, Macklin) and stirred for 1 h before it was transferred equally to 50 ml autoclave. After hydrothermal crystallization at 180 °C for 24 h, the yellow BiVO₄ powder was reclaimed by filtration, washed with pure water and dried at 60 °C over night for using.

2. Preparation of Pt/BiVO₄, Cu₂O/Pt/BiVO₄ and Cu₂O/BiVO₄ particles

Pt/BiVO₄, Cu₂O/Pt/BiVO₄ and Cu₂O/BiVO₄ particles were prepared by photodeposition conducted with using an AM1.5 solar simulator (SAN-EI ELECTRIC, XES-40S3-TT) as light source. For Pt/BiVO₄, 0.3 g of the as-prepared BiVO₄ was dispersed in a solution containing 10 ml methanol (99.9%, Aladdin), 90 ml pure water, and 6 ml H₂PtCl₆ (99.9%, Adamas-beta) solution (Pt 1mg/ml) under stirring. The solution was bubbled with argon before and during the reaction. Temperature of solution was constrained to 25 °C by a thermostatic plate. After chopped light (2 s light and 4 s dark) illumination for 3 h, Pt/BiVO₄ powder was reclaimed by centrifugation and then dried at 60 °C in air over night. For the preparation of Cu₂O/Pt/BiVO₄ and Cu₂O/BiVO₄ particles, 0.5 g of Pt/BiVO₄ or BiVO₄ powder was dispersed in an aqueous solution containing 0.48 M CuSO₄ (98%, J&K) and 3 M L-lactic acid (80%, Aladdin). The pH of the solution was adjusted to 9 by 5 M NaOH (98% Aladdin) solution. Under continuous stirring and Ar bubbling, the solution was irradiated for 10 h. The product (Cu₂O/Pt/BiVO₄ or Cu₂O/BiVO₄) was centrifugated and washed with pure water, and then dried at 60 °C in air over light.

3. Characterization

The crystal phases of the obtained powder were confirmed by X-ray diffraction (XRD; Bruker, D8). The morphology and structure were characterized by scanning electron microscope (SEM; JEOL, JEM-7800). The energy dispersive spectrometer (EDS) analysis was performed on the accessory of SEM. The structure of Cu₂O particle was examined by transmission electron microscope (TEM; JOEL, JEM-2100). X-ray photoelectron spectroscopy (XPS) measurement was conducted on an ESCALAB-250Xi using Al K α radiation. For steady-state photoluminescence (PL) spectroscopy, a Fluorlog-3 equipped with 450 W Xenon lamp was employed. Time-resolved photoluminescence spectroscopy was observed on DeltaFlex-011x with 408 nm DeltaDiode as light source. UV-visible absorption spectra were examined by Cary-5000 at ambient atmosphere.

4. Photocatalytic activity measurement

Photocatalytic hydrogen evolution was conducted in a Pyrex top-irradiated vessel connected to a glass circulation system (PerfectLight, LabSolar-IIIAG). A

mixture of 15 ml methanol (99.9%, Aladdin) and 135 ml pure water buffered by 0.2 g La_2O_3 (99.99%, Aladdin) was used as reaction solution. For each trial, 0.15 g catalyst was used for evaluation. Before irradiation, the system was evacuated for 1 h in order to remove the air. A 300 W Xenon lamp (Lamp House, R300-3J) with a cutoff filter (Hoya, L-42: $\lambda > 420$ nm) was employed as light source. Temperature of this system was controlled to 15 °C by a flow of cooling water. The evolved gases were examined by gas chromatography (Agilent: GC-6890, MS-5A column, TCD, Ar carrier).



Fig. S1. (a) Calculated band gaps of $BiVO_4$ and photodeposited Cu_2O .



Fig. S2. SEM images of $Cu_2O/Pt/BiVO_4$ structure at magnifiations of (a) 5 and (b) 30

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Reference

1 Y. Xue, Z. Wu, X. He, Q. Li, X. Yang and L. Li, J Colloid Interface Sci, 2019, 548, 293-302.