

Supporting Information

Facile preparation of yttrium and aluminum co-doped ZnO via sol-gel route for photocatalytic hydrogen production

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Experimental section

Materials

Zinc acetate (99.9%), yttrium nitrate (99.9%), aluminum nitrate (99.99%), glycol ether ($\geq 98.0\%$) and ethanolamine ($\geq 99.5\%$) were purchased from Aladdin Co. Ltd, and used as received without further purification. Besides, TiO₂ (P25) was purchased from J&K Chemical Ltd. Ethanol (AN, analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Laboratory deionized (DI) water was obtained from an ultrapure water system, leading to a resistivity $>18 \text{ M}\Omega \text{ cm}$, and it was also used to prepare all aqueous solutions.

Instruments

The crystallinity of as-prepared samples were characterized by Bruker D8 Advance X-ray diffractometer (XRD, Bruker, Germany) with Cu K_{α} radiation ($\lambda = 0.15406 \text{ nm}$). The diffraction patterns were measured over the 2θ angle range from 10° to 80° with a scanning rate of $8^{\circ} \cdot \text{min}^{-1}$ and a step size of 0.01° .

The surface morphology and composition of samples were characterized by scanning electron microscopy (SEM, JSM-6510A) and energy dispersive X-ray spectroscopy (EDS, JEM-2100), respectively.

The Brunauer-Emmett-Teller (BET) specific surface area of samples was evaluated on the basis of nitrogen adsorption isotherms measured at 77 K using a Quantochrome NOVA 1200e instrument.

UV-visible (UV-vis) spectra were recorded on a UV-vis spectrometer (Hitachi U-3010). Photoluminescence (PL) spectra were measured at room temperature under 260 nm excitation (F-4500, Hitachi).

Synthesis of ZnO nanoparticles (NPs)

ZnO NPs was synthesized by sol-gel method according to previously reported procedures.^{1, 2} A mixture of zinc acetate (0.04 mol, 7.34 g) and glycol ether (0.8 mol, 98 mL) were stirred at room temperature in 20 minutes, and it turned into a white solution. Then ethanolamine (0.04 mol, 2.44 g) and zinc acetate (0.04 mol, 7.34 g) were added with continuous stirring. Subsequently, the mixed solution was slowly heated to 70°C and maintained at this temperature for 4 h. Afterward, the product was washed with DI water and ethanol three times. The sample was calcined at 450 °C for 12 h with a heating rate of 5 °C·min⁻¹ to produce the ZnO NPs.

Synthesis of AZO NPs

For a typical preparation, zinc acetate (0.08 mol, 14.68 g) and ethanolamine (0.04 mol, 2.44 g) were added into glycol ether (0.8 mol, 98 mL) with vigorous stirring to obtain a clear solution. Then, aluminum nitrate solution having 0.4 M concentration in DI water (100 mL) was separately prepared for the doping, and introduced at room temperature. The molar ratio of Al in the product was selected as 3% to afford the material. Upon further stirring for 4 h at 70°C under refluxing, and then the mixture was washed with DI water and ethanol three times. Finally, the product was calcined at 450°C for 12 h with a heating rate of 5 °C·min⁻¹ and obtained AZO NPs.

Synthesis of Y-ZnO NPs

Similarly, for the preparation of Y-ZnO NPs, a mixture of zinc acetate (0.08 mol, 14.68 g), ethanolamine (0.04 mol, 2.44 g) and glycol ether (0.8 mol, 98 mL) were stirred at room temperature. On the other hand, for the preparation of 0.4 M of yttrium nitrate were dissolved in 100 mL of DI water using a 200 mL beaker. After that, yttrium nitrate (0.4 M) was added with continuous stirring in sequence. The mixture was gradually heated to 70°C, and held at that temperature for 4 h. The molar

ratio of Y in the product were maintained at 3% and the prepared sample was designated as Y-ZnO NPs. Again it was filtered, washed with DI water and ethanol three times. Then it was dried at 450°C for 12 h with a heating rate of 5 °C·min⁻¹ and obtained Y-ZnO NPs.

Synthesis of Y-AZO NPs

To this AZO sol, zinc acetate (0.08 mol, 14.68 g) and aluminum nitrate (0.24 mol, 51.12 g) with the molar ratio of 1 : 3 were dissolved in glycol ether (0.8 mol, 98 mL), and ethanolamine (0.04 mol, 2.44 g) was added slowly under stirring. Meanwhile, yttrium nitrate solution having 0.4 M concentration in DI water (100 mL) was separately prepared for the doping. However, for the preparation of Y-AZO, the molar amount of Y-doping (from 1% to 9%) along with AZO sol were dissolved in glycol ether. The above reaction mixture was heated at 70°C for 4 h to form a yellow gel. The Y-AZO NPs was treated at 450 °C for 12 h with a heating rate of 5 °C·min⁻¹. The non-doped AZO NPs was denoted as 3%Al-ZnO, and the Y doped AZO samples were denoted as 1%Y-AZO, 3%Y-AZO, 5%Y-AZO, 7%Y-AZO and 9%Y-AZO, respectively.

Synthesis of Al-Y-ZnO NPs

Al-Y-ZnO NPs was also synthesized by a similar sol-gel method. Zinc acetate (0.08 mol, 14.68 g) dissolved in glycol ether (0.8 mol, 98 mL) is mixed on a magnetic stirrer until the solution starts to turn milky. In order to stabilize the solution, ethanolamine (0.04 mol, 2.44 g) was added dropwise under stirring, so that the solution became transparent again. A 3% doping concentration was achieved by adding 0.4 M of aqueous yttrium nitrate solution. For the preparation of Al-Y-ZnO NPs, different molar concentrations of aluminum nitrate with Al³⁺ from 1% to 9% were put into 3%Y-ZnO solution separately. The rest steps of the preparation remain as the same as that of Y-AZO NPs introduced

above. The obtained samples at different concentration of Al³⁺ of 1%, 3%, 5%, 7% and 9% were named 1%Al-3%Y-ZnO, 3%Al-3%Y-ZnO, 5%Al-3%Y-ZnO, 7%Al-3%Y-ZnO and 9%Al-3%Y-ZnO, respectively.

Photocatalytic hydrogen production³⁻⁶

Photocatalytic experiments for hydrogen evolution were performed in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. It was carried out by taking 0.05 g of the target photocatalyst in 70 mL of an aqueous solution containing 15 vol% of lactic acid solution for H₂ evolution. A high-pressure Xe lamp (300 W) through a UV-cutoff filter was used as a visible light source for the photocatalytic reactions, which was positioned on the side of photoreactor. The as-prepared sample was continuously suspended in the aqueous solution with a magnetic stirrer during the irradiation. The temperature of the suspension was maintained at 25 °C by a flow of cooling water during the reaction. Prior to illumination, the reactant solution was de-aerated thoroughly for 1 h by nitrogen gas purging. The amount of H₂ generated was analyzed by online gas chromatography (GC7900, Tian Mei, Shanghai), using a 5 Å molecular sieve column with a thermal conductivity detector (TCD), as shown in **Figure S1**.

Determination of QE values⁷

Apparent quantum efficiency (QE) was measured under identical photoreaction conditions except that the incident monochromatic light with a band-pass filter ($\lambda = 420$ nm, half width =15 nm) and an irradiometer. The hydrogen yields of 1 h photocatalytic reaction in one continuous reaction under visible light with the wavelength of 420 nm were measured. The incident photon number was

determined by a calibrated Si photodiode (SRC-1000-TC-QZ-N, Oriel), and the QE value was calculated using eqn (1).

$$QE\% = \frac{2 \times \text{Number of evolved H}_2 \text{ molecules}}{\text{Number of incident photons}} \times 100\% \quad (1)$$



Figure S1. Photocatalytic hydrogen production testing system.

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