Supporting Information

Efficient Photocatalytic Hydrogen Evolution Over Hydrogenated ZnO Nanorod Arrays

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EXPERIMENTAL SECTION

Preparation of the H:ZnO Nanorod Arrays (NRAs):

All reagents used were analytical grade and were used directly without any purification. The electrochemical deposition experiments were performed in a conventional three-electrode glass cell by cathodic electrodepositon. A glass coated with F-doped SnO₂ (FTO) with a sheet resistance of 14 Ω /sq was used as the working electrode, a graphite rod of about 4.0 cm² was used as the auxiliary electrode, and a saturated calomel electrode (SCE) was used as the reference electrode that connect to the cell with a double salt bridge. Prior to electrodeposition, the FTO glass was cleaned ultrasonically in distilled water, ethanol, and acetone and then rinsed in distilled water again. ZnO NRAs were grown on FTO substrate in a solution containing 0.02 M Zn(NO₃)₂, 0.01 ammonium acetate (NH₄Ac) and 0.01 M hexamethylenetetramine (HMT) with a current density of 0.5 mA·cm² at 90 °C for 60 min. The as-prepared ZnO NRAs were thoroughly washed with ethanol and then DI water, and then were annealed at 350 °C for 180 min in air to enhance the mechanical stability and electrical conductivity. Finally, the H:ZnO NTAs were obtained by annealing the ZnO NRAs in hydrogen atmosphere 350 °C for 180 min. The preparation was performed in a home-built tube furnace filled with ultrahigh purity hydrogen gas (Praxair).

Structural Characterization:

The morphology and the microstructure of the products were characterized field emission scanning electron microscope (FE-SEM, JSM-6330F) and transmission electron microscopy (TEM, JEM2010-HR, 200 KV). The phase and composition of the samples were investigated via X-ray diffraction (XRD, Bruker, D8 ADVANCE) with Cu Ka radiation ($\lambda = 1.5418$ Å), X-ray Photoelectron Spectroscopy (XPS, ESCALab250, Thermo VG) with 200 W Al KR radiation in twin anode, and the Raman spectroscopy that performed on a Laser Micro-Raman Spectrometer (Renishaw inVia) at room temperature with Ar⁺ laser of 514.5 nm excitation. For the XPS spectra, the binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference. UV-visible diffusive reflectance spectra of samples were recorded on а VARIAN CARY 5000 UV-Vis-NIR spectrophotometer. Electrochemical impedance measurements were conducted in a Na₂S (0.1 M)-Na₂SO₃ (0.1 M) solution employing a CHI 660D electrochemical workstation. Mott-Schottky plots were generated based on capacitances that were derived from the electrochemical impedance obtained at each potential with 10 kHz frequency in the dark.

Photocatalytic and electrochemical measurements:

The photocatalytic H₂ evolution reaction was performed in a Pyrex reactor with an entry window of optical flat quartz glass, as shown in Fig. S1. Typically, two pieces of the H:ZnO NRA films coated on FTO substrate (geometrical area of each piece is 2 cm²) or 1.64 mg H:ZnO NR powders were placed in the reaction cell with 100 ml of Na₂S (0.1 M)-Na₂SO₃ (0.1 M) solution. The light source was a 300-W Xe lamp (PLS-SXE-300UV, Beijing Changtuo) supplying the full wavelength or visible light (with a UV-cutoff filter $\lambda \ge 420$ nm) illumination. The distance between the light and H:ZnO (or ZnO) films is about 10 cm and the power of light illumination is about 180 mW/cm^2 . The amount of produced H₂ was analyzed using on-line gas chromatography with a thermal conductivity detector and an N₂ carrier. For the stability test, the photocatalytic experiment was stopped for each cycle (5 h) by turn off the light and hydrogen gas in the reactor was evacuated.

The mass of ZnO NRs on the FTO substrate using inductively coupled plasma atomic emission spectroscopy (ICP, SPECTRO). Two pieces of ZnO or H:ZnO NR films (total area: 4 cm²) were completely dissolved into 0.1 M HNO₃ (10 mL), and then the concentration of Zn^{2+} ions was determined by ICP.

Donor densities of ZnO samples were calculated using Mott-Schottky equation:

$$N_{\rm d} = (2/e_0 \varepsilon \varepsilon_0) [{\rm d}(1/C^2)/{\rm d}V]^{-1}$$

where N_d is the donor density, e_0 the electron charge, ε the dielectric constant of ZnO ($\varepsilon = 8$), ¹ ε_0 the permittivity of vacuum, and *V* the applied bias at the electrode. Since ZnO and H:ZnO NRs have similar morphology, a qualitative comparison of carrier densities between them is reasonable, although both the values may be over-estimated compared to bulk ZnO.

 U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho and H. Morkoc, *J Appl Phys*, 2005, 98.



Fig. S1 A schematic diagram of the set up for photocatalytic hydrogen production over ZnO samples in a 100 ml Na₂S (0.1 M)-Na₂SO₃ (0.1 M) solution.



Fig. S2 (a, b) SEM images reveal that the white film is composed of dense and vertically aligned ZnO NRs with an average diameter of ~200 nm and length of ~2 μ m. The inset is the magnified SEM image showing the hexagonal cross-section of ZnO NRs. (c) conventional and (d) lattice-resolved TEM images of ZnO NRs. show that ZnO NRs are single crystals with the same growth direction of [0001]. The inset is the corresponding SAED pattern obtained at the tip of the ZnO NR.



Fig. S3 XRD spectra collected for (a) ZnO and (b) H:ZnO NRAs. Inset is the magnified view of the XRD spectra in the dashed box.



Fig. S4 XPS survey spectrum collected for hydrogenated ZnO nanorod arrays.