

Supporting Information

Enhanced photoactivity and stability of carbon and nitrogen co-treated ZnO nanorod arrays for photoelectrochemical water splitting

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Experimental Section

Synthesis of ZnO NRAs:

All reagents used were of analytical grade and were used directly without any purification. In a typical synthesis process, the cathodic deposition was performed in a conventional three-electrode glass cell by galvanostatic electrolysis. A F-doped SnO₂-coated glass (FTO) substrate of 1.5 cm × 2 cm and a graphite rod of about 4.0 cm² were used as working electrode and counter electrode, respectively. The reference electrode was an Ag/AgCl electrode. Prior to electrodeposition, the FTO substrate was cleaned ultrasonically in distilled water, ethanol, and acetone and then rinsed in distilled water again. Three types of ZnO nanorods were electrodeposited on FTO

substrates in solution of 0.02 M $\text{Zn}(\text{NO}_3)_2$, 0.01 M NH_4Ac and 0.01 M Hexamethylenetetramine with a current density of 0.5 mA cm^{-2} for 60 min at 90°C .

Then, as-prepared ZnO nanorods were immersed in a 0.01 M glucose aqueous solution at room temperature for 12 h. After the immersion, the product was dried in an oven at 110°C at ambient pressure for 3 h, and was pyrolyzed in NH_3 atmosphere (denoted as CN/ZnO) or Ar (denoted as C/ZnO) at 500°C . Meanwhile, the as-prepared ZnO were annealed in Ar (denoted as ZnO) NH_3 atmosphere (denoted as N/ZnO) at same temperature.

Characterizations:

The as-synthesized products were characterized by field emission scanning electron microscope (FE-SEM, JSM-6330F), X-Ray Diffractometer (XRD, D8 ADVANCE), transmission electron microscopy (TEM, JEM2010-HR) and X-ray Photoelectron Spectroscopy (XPS, ESCALab250). The optical properties of the products were measured with a UV-Vis-NIR Spectrophotometer (UV-Vis, Varian Cary 5000). Raman spectroscopy was performed on a Laser Micro-Raman Spectrometer (Renishaw inVia) using a visible laser ($\lambda = 514.5 \text{ nm}$) with an output laser power of 50 mW as the excitation wavelength at room temperature. Room temperature photoluminescence (PL) spectra were studied using a combined fluorescence lifetime and steady state spectrometer (FLS920, EDINBURGH) and the excitation wavelength was 300 nm.

Photocatalytic and electrochemical measurements:

PEC measurements were carried out in a three-electrode cell with a flat quartz window to facilitate illumination of the photoelectrode surface. The working electrode

is the CN/ZnO, C/ZnO, N/ZnO and ZnO, while a Pt wire electrode and a saturated Ag/AgCl electrode were used as counter and reference electrode, respectively. A 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. The illumination source was a 500W Xe arc lamp (PLS-SXE-300/300UV, Beijing Changtuo) directed at the quartz photoelectrochemical cell. A 1.5 cm² region of the photoelectrode surface was illuminated. The photocurrent densities were recorded with a CHI 760D electrochemical workstation (CHI, Shanghai).

Gas Collection:

Gas generated in water splitting was collected in a home-made device (Fig. S5). The three-electrode cell with a flat quartz window was filled with 0.1 M Na₂SO₄ electrolyte solution, and Ag/AgCl reference electrode and Pt wire counter electrode were inserted into the electrolyte. The Pt electrode positions were sealed with insulating epoxy resin to avoid gas leakage. As shown in the Fig. S5, gas was detected collected by gas chromatography (GC) with a thermal conductivity detector.

Donor density calculation:

The CN/ZnO sample exhibited the smallest slope compared to other samples, suggesting the CN/ZnO sample possess the most donor densities (carrier densities) after CN decorating according to the Mott-Schottky equation:

$$N_d = (2/e_0\epsilon\epsilon_0)[d(1/c^2)/dV]^{-1}$$

where e_0 is the electron charge, ϵ the dielectric constant of ZnO ($\epsilon = 8$), ϵ_0 the permittivity of vacuum, N_d the dopant density and V the electrode applied potential.

1. 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**.

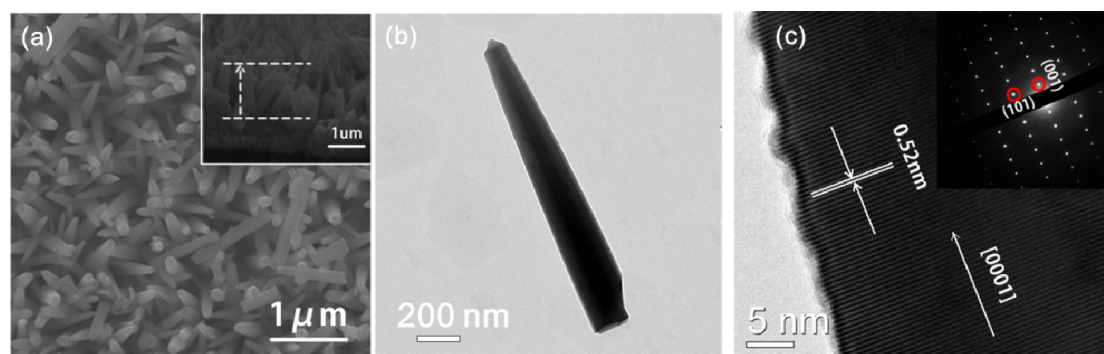


Fig. S1 (a) Top view SEM image of ZnO NRAs. (b) TEM and (c) Lattice-resolved TEM image collected at edge of ZnO NRAs. The inset is the diffraction pattern recorded from the ZnO NRAs.

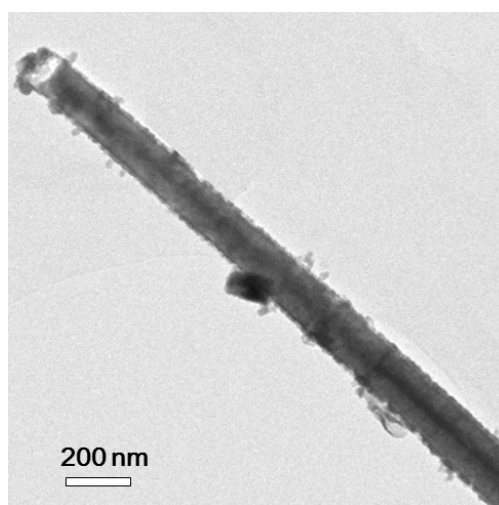


Fig. S2 TEM image of the CN/ZnO nanorod.

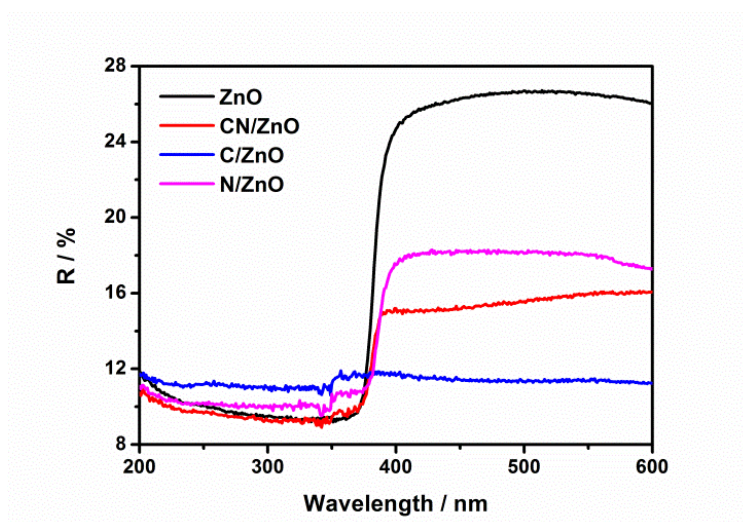


Fig. S3 Diffuse reflectance UV-visible spectra of ZnO, CN-ZnO, N-ZnO and C-ZnO NRAs. All the samples show fairly low reflectance in the UV region (<380 nm) and their reflectance increases rapidly at around 380 nm, which is in accord with the direct band-gap absorption edge of ZnO (3.25 eV). The low reflectance for both the samples in the UV region is mainly attributed to their strong UV light-harvesting ability.

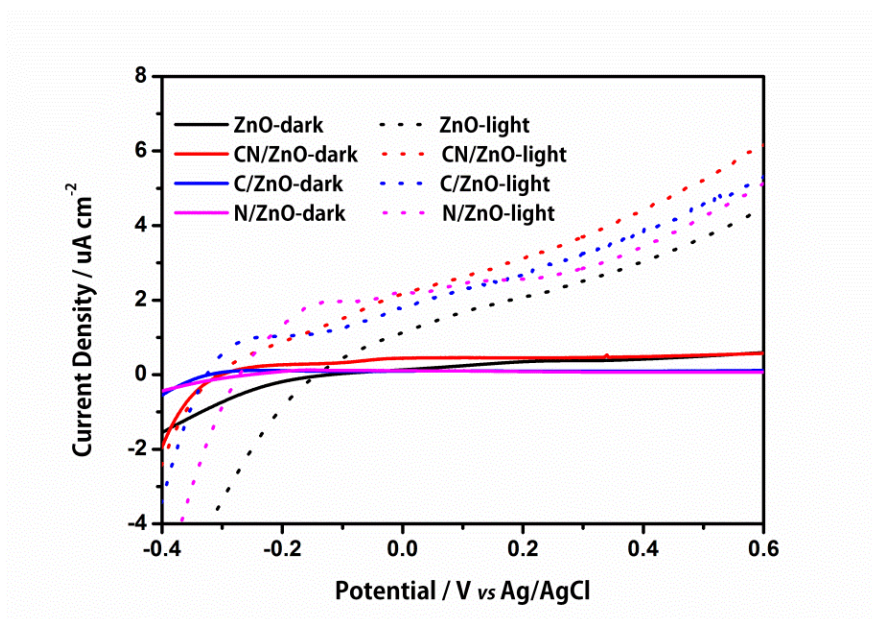


Fig S4 $I-V$ curves recorded under the visible-light irradiation with a UV filter (Changtuo, $\lambda < 420$ nm) of ZnO, N/ZnO, C/ZnO and CN/ZnO with a scan rate of 10 mV/s.