Boosting the photocatalytic hydrogen evolution activity of g-C₃N₄ nanosheets by Cu₂(OH)₂CO₃-modification and dye-sensitization

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2.2. Characterization

X-ray diffraction (XRD) measurement was performed on Bruker D8-advance X-ray Diffractometer using Cu Kα radiation under 35 kV and 25 mA. Transmission electron microscopy (TEM, JEM2100, JEOL) and scanning electron microscopy (SEM, JSM-6390-LV, JEOL) equipped with energy dispersive X-ray spectrometer (EDS) system were employed to characterize the morphologies, microstructures and the chemical compositions of the products. X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB MKII X-ray photoelectron spectrometer (VG Scientific, UK) using Mg Kα radiation. UV-vis diffuse reflectance spectrum (DRS) was measured by a Cary5000 UV-Vis-NIR spectrophotometer using BaSO₄ as a reference. Photoluminescence (PL) spectra were performed on Shimadzu RF-5301PC fluorescence spectrophotometer with an excitation wavelength of 385 nm. Nitrogen adsorption-desorption isotherms were obtained on a volumetric adsorption apparatus (NOVA Surface Area Analyzer Station A, USA) at 77 K.

The transient photocurrent, electrochemical impedance spectra (EIS), cyclic voltammetry (CV) and Mott–Schottky measurements of g-C₃N₄, Cu₂(OH)₂CO₃ and Cu₂(OH)₂CO₃/g-C₃N₄ samples were performed on an electrochemical analyzer (CHI-660D, CH Instruments Ins.) in a standard three-electrode system, where 0.5 M Na₂SO₄ solution (pH = 7.0) was used as the electrolyte and the as-prepared samples, a standard Ag/AgCl in saturated KCl and a platinum wire were used as the working, reference and counter electrodes, respectively. The EIS measurement was performed under the open circuit voltage without the light irradiation and the frequency range was 0.05-10⁵ Hz with an ac amplitude of 10 mV. The CV curve of the samples was recorded between 0.1 and 1.82 eV at a scan rate of 10 mV s⁻¹ with the negatively initial scan polarity. Linear sweep
voltammetry (LSV) measurement was carried out in 1 M KOH solution (pH = 13.8) with a scan rate of 10 mV s\textsuperscript{-1}. Potentials were referenced to reversible hydrogen electrode (RHE) and/or normal hydrogen electrode (NHE) according to the following formulas:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 \times \text{pH} \quad (1) \]

\[ E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197 \quad (2) \]

The working electrode was prepared as follows: 10 mg sample was dispersed into 0.5 mL ethanol containing 20 \textmu L Nafion and then sonicated for 30 min to form homogenous slurry. The slurry was dip-coated onto a FTO glass electrode with the active area of 1.0 cm \times 1.5 cm. The resulting FTO glass electrode was dried at 60 °C for 30 min to remove the solvent.

To determine the onset reduction potential of fluorescein, cyclic voltammetry measurement was performed in a dry dichloromethane solution (5 ml) containing tetrabutylammonium hexafluorophosphate (180 mg) and fluorescein sample (2 mg) with a scan rate of 100 mV s\textsuperscript{-1} under nitrogen atmosphere. The FTO glass, standard Ag/AgCl electrode calibrated with ferrocene/ferrocenium (Fc/Fc\textsuperscript{+}) as reference and platinum wire were used as the working, reference and counter electrodes, respectively.
Fig. S1. Chemical structure of Fluorescein
Fig. S2. XPS survey spectra of 3Cu/CN sample (a). High resolution XPS spectra of C 1s (b), N 1s (c), O 1s (d) and Cu 2p (e).
Fig. S3. Nitrogen adsorption-desorption isotherms (a) and the corresponding curves of the pore size distributions (b) of CN and 3Cu/CN samples.
Fig. S4. Effect of the amount of FL dye on photocatalytic H₂-evolution of 3Cu/CN composite photocatalyst (irradiation time = 4 h).
**Fig. S5.** Cyclic H$_2$ production for the 3Cu/CN catalyst in the presence of 50 mg of FL dye.
Fig. S6. Cyclic voltammetry curves of 3Cu/CN composite.
Fig. S7. Mott-Schottky plots of bare CN (a) and Cu$_2$(OH)$_2$CO$_3$ (b).
Fig. S8. Cyclic voltammetry curves of FL.
Fig. S9. UV-vis DRS spectrum of FL dye.