Electronic Supplementary Information for

g-C₃N₄/nanocarbon/ZnIn₂S₄ nanocomposite: Artificial Z-Scheme visible-light photocatalysis system using nanocarbon as the electron mediator

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Experimental section

1. Catalyst preparation

Preparation of CN/C/ZIS and C/ZIS nanocomposites

g-C₃N₄ nanosheets were prepared according to the previously reported method.¹ In a typical procedure for the synthesis of CN/C/ZIS composite, 0.013 g of g-C₃N₄ was dispersed into a mixed alcoholic solution that contained glycerol (5 mL) and deionized water (15 mL) by ultrasonication for 30 min. Then, 0.1910 g of In(NO)₃·4.5H₂O, 0.0414 g of Zn(AC)₂·2H₂O and 0.1818 g of L-cysteine (C₃H₇NO₂S) was added into the above solution under stirring one by one, followed by ultrasonication for another 30 min. Finally, the obtained solution was transferred to a 50 mL Teflon-lined stainless steel autoclave, which was heated to 180 °C and maintained for 9 h. After cooling, the as-synthesized products were collected by centrifugation, washed with distilled water and absolute ethanol, and dried at 60 °C overnight. For comparison, C/ZIS binary nanocomposite was obtained under the same experimental condition as the CN/C/ZIS but without adding CN.

Preparation of ZIS and CN/ZIS nanocomposite

The pure ZIS was prepared according to the literature of Chen *et al.*² In a typical synthesis, 0.136 g of ZnCl₂ and 0.586 g of InCl₃·4H₂O were added by stoichiometric ratio, and excessive thioacetamide (TAA, 0.45 g) was dissolved in a Teflon liner with 100 mL capacity containing 80 mL of deionized water. The pH was adjusted to 2.5 by hydrochloric acid (0.1 mol/L), and then the Teflon liner was sealed in the stainless steel autoclave and maintained at 80 °C for 6 h. After the reaction was completed, the as-synthesized product was collected by centrifugation, washed with distilled water and absolute ethanol, and dried at 60 °C overnight.

CN/ZIS composite were obtained under the same experimental conditions except with adding of CN. In a typical synthesis, 0.047 g of g-C₃N₄, 0.136 g of ZnCl₂ and 0.586 g of InCl₃·4H₂O, and excessive thioacetamide (TAA, 0.45 g) was dissolved in a Teflon liner with 100 mL capacity containing 80 mL of deionized water. The pH was adjusted to 2.5 by hydrochloric acid (0.1 mol/L), and then the Teflon liner was sealed in the stainless steel autoclave and maintained at 80 °C for 6 h. After the reaction was completed, the as-synthesized product was collected by centrifugation, washed with distilled water and absolute ethanol, and dried at 60 °C overnight.

Preparation of C/CN nanocomposite

In a typical synthesis, 0.013 g of g-C₃N₄ was dispersed into a mixed alcoholic solution that contained glycerol (5 mL) and deionized water (15 mL) by ultrasonication for 30 min. Then, 0.1818 g of L-cysteine (C₃H₇NO₂S) was added into the above solution, followed by ultrasonication for another 30 min. Finally, the obtained solution was transferred to a 50 mL Teflon-lined stainless steel autoclave, which was heated to 180 °C and maintained for 9 h. After cooling, the as-synthesized products were collected by centrifugation, washed with distilled water and absolute ethanol, and dried at 60 °C overnight.

2. Characterization

The phase purity and crystal structure of the obtained samples were examined by X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer) with Cu-K α radiation (λ =1.5406 Å). Infrared spectra were obtained on KBr pellets on a Nicolet NEXUS470 FTIR in the range of 4000-500 cm⁻¹. Field emission scanning electron microscopy (FESEM) measurement was performed by JSM-6700F instrument operated at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and EDX line-scanning element mapping were recorded on a JEOL-JEM-2010 (JEOL, Japan) operating at 200 kV. Surface analysis of the sample was examined by X-ray photoelectron spectroscopy (XPS) using a ESCA PHI500 spectrometer. The surface areas of the samples were measured by a TriStar II 3020-BET/BJH Surface Area. UV-vis diffuse reflectance spectra (DRS) were performed on a Shimadzu UV-2401 spectrophotometer equipped with spherical diffuse reflectance accessory. The photoluminescence (PL) spectra of the photocatalyst were obtained by a Varian Cary Eclipse spectrometer with an excitation wavelength of 230 nm. The electrochemical impedance spectroscopy (EIS) measurements were carried out in a conventional three-electrode, single-

compartment quartz cell on an electrochemical station (CHI 660D).

3. Photocatalytic hydrogen production

The photocatalytic hydrogen production experiments were carried out in a 100 mL Pyrex flask connected to a closed gas circulation and evacuation system. Four low power UV-LEDs (3 W, 420 nm) (Shenzhen LAMPLIC Science Co. Ltd. China), used as light sources to trigger the photocatalytic reaction, were positioned 1 cm away from the reactor in four different directions. The focused intensity and areas on the flask for each UV-LED was ca. 80.0 mW·cm⁻² and 1 cm², respectively. Typically, 0.05 g of photocatalyst was dispersed by magnetic stirrer in 80 mL of aqueous solution containing 0.5 M Na₂S and 0.5 M Na₂SO₃. Prior to irradiation, the suspension of the catalyst was dispersed by an ultrasonic bath for 10 min, and then purged with nitrogen for 20 min to completely remove the dissolved oxygen and ensure the reactor was in an anaerobic condition. A 0.4 mL gas was intermittently sampled through the septum, and the amount of H₂ was determined by gas chromatography (GC-14C, Shimadzu, Japan, TCD, with nitrogen as a carrier gas and 5 Å molecular sieve column).



Figures

Fig. S1 (a) XRD pattern and (b) Raman spectra of CN/C/ZIS nanocomposite.



Fig. S2 (a) XPS survey spectra, (b-f) high-resolution XPS spectra of C 1s, N 1s, S 2p, In 3d and Zn 3d of CN/C/ZIS nanocomposite.



Fig. S3 TG curves of the samples: (a) ZIS, CN/ZIS, C/ZIS and CN/C/ZIS; (b) CN and C/CN.



Fig. S4 (a) Ultraviolet-visible diffusive absorption spectra of CN, ZIS, CN/ZIS, C/ZIS, C/CN and CN/C/ZIS samples. (b) plot of $(\alpha hv)^{1/2} vs. hv$ for the band gap energy of CN and plot of $(\alpha hv)^2 vs. hv$ for the band gap energy of ZIS.

According to the UV-vis DRS spectras, the band gaps of ZIS and CN are calculated to be 2.43 and 2.69 eV, respectively. It should be noted that the Eg value of ZIS is in agreement with the range of 2.2–2.8 eV due to the different phases, morphologies, particle size, and fabrication method of this compound.³⁻⁷

The band edge potentials of semiconductors were estimated according to the empirical equation below:

$$E_{CB} = X - E^{e} - 0.5E_{g}$$
 (1)

where E_{CB} is the conduction band edge potential, X is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, E^e is the energy of free electrons on the hydrogen scale (about 4.5 eV), E_g is the band gap energy of the semiconductor. The VB and CB position of ZIS are estimated to be 1.63 and -0.80 eV, while those of CN are estimated to be 1.57 and -1.12 eV, which are similar with previous results.^{6,8}



Fig. S5 XRD patterns of CN, ZIS, CN/ZIS, C/ZIS, and C/CN samples.

The CN sample has a characteristic peak at 13.04° and 27.47°, which can be indexed as the (100) and (002) diffraction plane, respectively. It is observed clearly that the bare ZIS is hexagonal phase (JCPDS No. 65-2023).



Fig. S6 Photos and SEM images of (a) CN, (b) ZIS, (c) CN/ZIS, (d) C/ZIS, and (e) C/CN samples. The colour of the pristine CN is pale yellow, and the colour of the pristine ZIS is bright yellow.When CN was combined with ZIS, the colour of the sample is lighter than pure ZIS. After the nanocarbon coating on the surface of ZIS, the colour of the sample become black.



Fig. S7 N₂ adsorption-desorption isotherms of CN, ZIS, CN/ZIS, C/CN, and CN/C/ZIS samples.

The BET surface areas of CN, ZIS, CN/ZIS, C/ZIS, C/CN and CN/C/ZIS samples are 31.03, 76.59, 16.82, 27.92, 4.16 and 38.92 m²/g, respectively.



Fig. S8 (a) PL spectra and (b) EIS spectra of CN, ZIS, CN/ZIS, C/CN, and CN/C/ZIS

samples.

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