Supplementary Material (ESI) for Chemical Communications

A new type of carbon nitride-based polymer composite for

enhanced photocatalytic hydrogen production

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1. Experimental details

1.1 Preparation of C₃N₄-PEDOT composites

The g-C₃N₄ powders are prepared via polycondensation of dicyandiamide according a reported method.¹ In a typical synthesis, dicyandiamide powder was placed in an alumina crucible, covered with cap and heated at 550 °C for 4 h in a muffle furnace with a ramp rate of 2.3 °C/min and in the cooling process the ramp rate was maintained at 1 °C/min. The obtained yellow agglomerates were ground to fine powders in an agate mortar for later use.

To prepare the C_3N_4 -PEDOT composites, the g- C_3N_4 powders were mixed with commercial PEDOT-PSS "solution" containing 0.5 wt%, 1 wt%, 2 wt% and 5 wt% of PEDOT-PSS respectively. The suspension was then evaporated under vigorous stirring via heating. To make the PEDOT insoluble, the dried powders were subsequently soaked in ethylene glycol (EG) and stirred for 1 hour. After treatment with EG, the C_3N_4 -PEDOT composites were centrifuged, washed with deionized water and ethanol for several times and dried in a 100 °C oven. The final products were ground again after being dried, and different composites were denoted as C_3N_4 -0.5 wt% PEDOT, C_3N_4 -1 wt% PEDOT, C_3N_4 -2 wt% PEDOT and C_3N_4 -5 wt% PEDOT, respectively.

1.2 Characterization of photocatalysts

The prepared C₃N₄-PEDOT composites were comprehensively characterized by powder X-ray diffraction (XRD, Rigaku Miniflex) with Co K α (λ = 1.78897 Å)

radiation, UV-Vis spectrometer (Shimadzu 2200), X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, a monochromatic Al KR x-ray source), Fluorescence spectrometer (FLS 920, Edinburgh Instruments), and transmission electron microscopy (TEM, Philips Tecnei F20).

1.3 Photocatalytic reactions

The photocatalytic reactions were carried out in a quartz reactor connected to a closed gas circulation and evacuation system. In a typical reaction, 100 mg catalyst was suspended in 300 mL aqueous solution containing 30 mL triethanolamine (TEA) solution, and H₂PtCl₆ solution containing 1 wt% of Pt was added. Before the reaction started, the whole system was thoroughly degassed. The quartz reactor was then irradiated by a 300 W Xe lamp (Beijing Trusttech Co. Ltd., PLS-SXE-300UV) equipped with an optical cut-off filter ($\lambda > 400$ nm) to remove ultraviolet light and a water filter to eliminate infrared light. The temperature of the reactor was maintained at 293±5 K by a cooling water cycle system during the reaction. The amount of H₂ produced was analyzed using gas chromatography (GC) with Ar as the carrier gas.



2. Results of Characterizations

Fig. S1 X-ray diffraction patterns of (a) pure $g-C_3N_4$, (b) C_3N_4 -0.5 wt% PEDOT, (c) C_3N_4 -1 wt% PEDOT, (d) C_3N_4 -2 wt% PEDOT and (e) C_3N_4 -5 wt% PEDOT.





Fig. S2 Left: UV-visible absorption spectra of (a) pure $g-C_3N_4$, (b) $C_3N_4-0.5$ wt% PEDOT, (c) C_3N_4-1 wt% PEDOT, (d) C_3N_4-2 wt% PEDOT, (e) C_3N_4-5 wt% PEDOT and. Right: UV-visible absorption spectra of commercial PEDOT-PSS "solution". The photos of all samples above the spectra on the left show the gradual colour changes when the amount of PEDOT is increased.



Fig. S3 TEM image of C_3N_4 -5 wt% PEDOT.



Fig. S4 High-resolution XPS spectra for S 2p measured on (a) C_3N_4 -0.5 wt% PEDOT, (b) C_3N_4 -1 wt% PEDOT, (c) C_3N_4 -2 wt% PEDOT, and (d) C_3N_4 -5 wt% PEDOT.

References:

1. P. Niu, L. L. Zhang, G. Liu and H. M. Cheng, Adv. Funct. Mater., 2012, 22, 4763-4770.