High-efficiency photocatalytic water splitting by N-doped porous g-C_3N_4 nanosheets polymer photocatalyst derived from urea and N,N-dimethylformamide

Supporting Information

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1. Characterization methods

Powder X-ray diffraction (XRD) data were performed on an X'Pert-Pro MPD (Holand) D/max-γA X-ray diffractometer with Cu Kα radiation (λ=0.154178 nm), Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet-360 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements and valence-band XPS were carried out on an ARL Quant X-ray photoelectron spectrometer using Al Kα X-ray (hv = 1486.6 eV). The morphologies and microstructures of the composites were examined by field emission scanning electron microscopy (FESEM, JSM-6360LV) and Transmission electron microscopy (TEM, FEI-Tecnai F20). Solid-state 13C magic angle spinning (MAS) NMR measurements were carried out on a Bruker AVANCE III 400 MHz WB solid-state NMR spectrometer at room temperature. The Raman spectra were tested on (HR 800 Raman). The room-temperature electron paramagnetic resonance (EPR) spectra were conducted on Electron Paramagnetic Resonance Spectrometer (BRUKER A300-10/12). The optical properties of samples were tested by a UV-vis spectrophotometer (UV-2450). Photoluminescence (PL) spectra of samples were tested by a RF-5301PC luminescence spectrometer with emission wavelength of 325 nm. The Time-resolved transient PL decay measurements were carried out by a fluorescence spectrophotometer (FLSP-920, Edinburgh Instruments). The specific surface area and pore-size distribution test were performed a Micromeritics ASAP-2050 porosimeter. The surface photovoltage (SPV) measurement was carried out on a surface photovoltage spectroscopy (CEL-SPS 1000, Beijing

Perfect Light Technology Co., Ltd). The photocurrent and the electrochemical impedance spectra (EIS) were tested using CHI 660b workstation in a 0.5 M Na_2SO_4 solution with a typical three-electrode system.

2. Computational methods

All calculations were carried out using first-principles study based on the DFT within the projector augmented wave method (PAW), as implemented in Vienna ab initio simulation package (VASP) [S1, 2]. The generalized gradient approximation (GGA) with the functional of Perdew-Burke-Ernzerh of (PBE) was employed to describe the electron exchange-correlation interactions with the vdw-DF approach to take into account the long-range van der Waals interaction [S3, 4]. In this case, a supercell of 2×2×1 was used to simulate 2D g-C_3N_4 monolayers. The slab was built along the *z*-axis and a vacuum spacing of 20 Å was used to avoid the interaction between the sheets. The structures were relaxed without any symmetry constraints with a cutoff energy of 500 eV. The convergence criteria of energy and force were set to 1×10^{-5} eV and 0.01 eV/Å, respectively. Reciprocal space was represented by a Monkhorst-Pack special *k*-point scheme with 5 × 5 × 1 for geometry optimization.

3. Figures and Tables

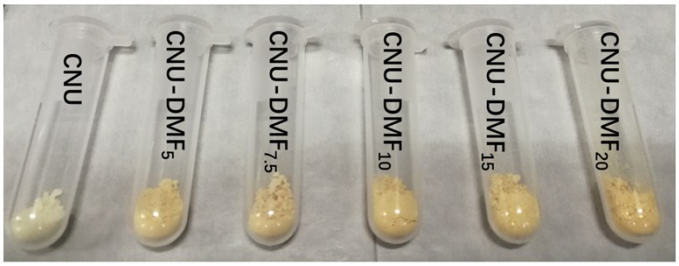

Fig.S1 Digital photograph of as-prepared photocatalysts grains.

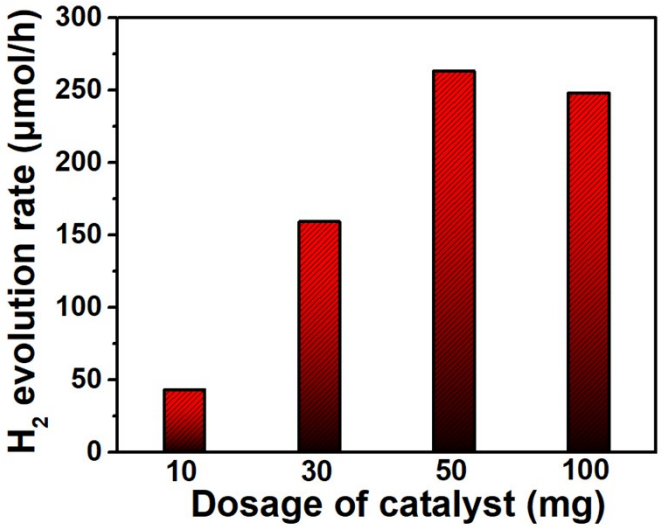

Fig.S2 The weight-dependent hydrogen evolution reaction of CNU-DMF_{10}.

Table S1 N 1s peak area ratio of N-N, C-N=C, N3c and N-H_2 in the CNU and CNU-DMF_{10}

	C-N=C (%)	**N_{3C}-low binding energy (%)**	**N_{3C}-high binding energy (%)**	**-NH_2/N-N (%)**
CNU	57.78	26.82	12.53	2.87
CNU-DMF_{10}	57.19	24.89	14.06	3.86

Table S2 Peak area of XPS spectra N and C of and CNU CNU-DMF.

	CNU			
	Area (P) CPS. eV	Area (N) TPP-2M	Atomic %	N/C ratio
C 1s	19502.6	0.25	42.65	1.34
N 1s	42452.1	0.33	57.35	
	CNU-DMF_{10}			
	Area (P) CPS. eV	Area (N) TPP-2M	Atomic %	N/C ratio
C 1s	19248.4	0.24	37.19	1.69
N 1s	52621.8	0.41	62.81	

Table S3 Hydrogen evolution rate of various N-doped g-C_3N_4 photocatalysts.

Photocatalysts	Light source	Reaction conditions	H_2 evolution rate (μmol/g/h)	Ref

CNU-DMF_{10}	300W Xe lamp, $\lambda > 400$ nm	3 wt% Pt, TEOA (10 vol%)	5268	**This work**
Ultrathin porous N/g-C_3N_4	300W Xe lamp, $\lambda > 420$ nm	1 wt% Pt, Lactic acid (20 vol%)	3579	[S5]
C_3N_{4+x}	300W Xe lamp, $\lambda > 400$ nm	3 wt% Pt, TEOA (10 vol%)	553.5	[S6]
porous nitrogen–rich g-C_3N_4	300W Xe lamp, $\lambda > 420$ nm	3 wt% Pt, TEOA (20 vol%)	2700	[S7]
nitrogen-rich g-C_3N_4 nanosheets	50.0 mW cm^{-2} LEDS $\lambda > 420$ nm	1 wt% Pt, Lactic acid (20 vol%)	310	[S8]

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