Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

$g\text{-}C_3N_4/WO_3$ Photoanode with Exceptional Ability for Photoelectrochemical Water Splitting

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Experimental section

1.1 Photocatalysts preparation

Preparation of $WO_3 \cdot 0.33\ H_2O$ NRs

The g-C_3N_4 nanosheets/WO_3 nanorods (g-C_3N_4-NSs/WO_3-NRs) were prepared on F-doped SnO_2 (FTO) glass substrates *via* a two-step process (Fig. 1a). Firstly, $WO_3 \cdot 0.33\ H_2O$ NRs were gristly grown on FTO substrates by a facile hydrothermal method reported.[1] In general, the H_2WO_4 precursor solution was prepared by dissolving 1.25 g H_2WO_4 into 20 mL H_2O, following by adding 5 mL of 30 % H_2O_2 with strong stirring for 2 h. The resulting clear solution was heated at 95 ^oC on a hot plate with stirring, and diluted to 25 mL or 0.2 M solution with deionized water. Then, around 4 mL of the precursor solution was mixed with the same amount of NH_4Cl solution (0.2 M, 4 mL). The mixture was diluted to 25 mL with ethanol. Thus solution was placed within a Teflon-lined stainless steel autoclave, holding a vertically oriented FTO glass substrate (without a WO_3 seed layer), which was then sealed and maintained at 180 ^oC for 5 h. The substrate was rinsed with ethanol and deionized water in sequence, and then dried in air for 2 h. After reaction, the autoclave cooled down naturally to room temperature, following by washing with deionized water and ethanol for 3 times to remove ions that possibly remained at the final products, and then dried at

60 ^{o}C for 12 h.

Preparation of bulk g-C_3N_4

The bulk g-C_3N_4 was fabricated by directly heating low-cost melamine (Fig. S1).[2] In detail, 5 g of melamine powder was put into an alumina crucible with a cover, then heated to 500 °C in a muffle furnace for 4 h at a heating rate of 20 °C min^{-1} to obtain the bulk g-C_3N_4. Next, 100 mg of bulk g-C_3N_4 was dispersed in 100 mL isopropyl alcohol at room temperature and exfoliated by ultrasonication for 24 h to obtain g-C_3N_4 nanosheets (g-C_3N_4-NS). The resultant dispersions were centrifuged at 3,000 rpm for 10 min. After centrifugation, the supernatant (exfoliated g-C_3N_4-NS, about top five sixths of the centrifuged dispersion) was collected by pipette. The mass remaining in the supernatant was estimated by drying and weighing the sediments in the centrifugal tube and about one third of the starting material remained in the supernatant. That was to say, the as-obtained exfoliated g-C_3N_4-NS isopropyl alcohol solution possessed a concentration of ~ 300 mg L^{-1}.

Preparation of g-C_3N_4-NSs/WO_3-NRs

The as-prepared $WO_3 \cdot 0.33\ H_2O$ NRs were impregnated in the isopropyl alcohol solution for different time (0.25, 0.5, 1.0, 1.5, 2.0 h) and then annealed at 450 ^{o}C in air (1 h) for combining closely.

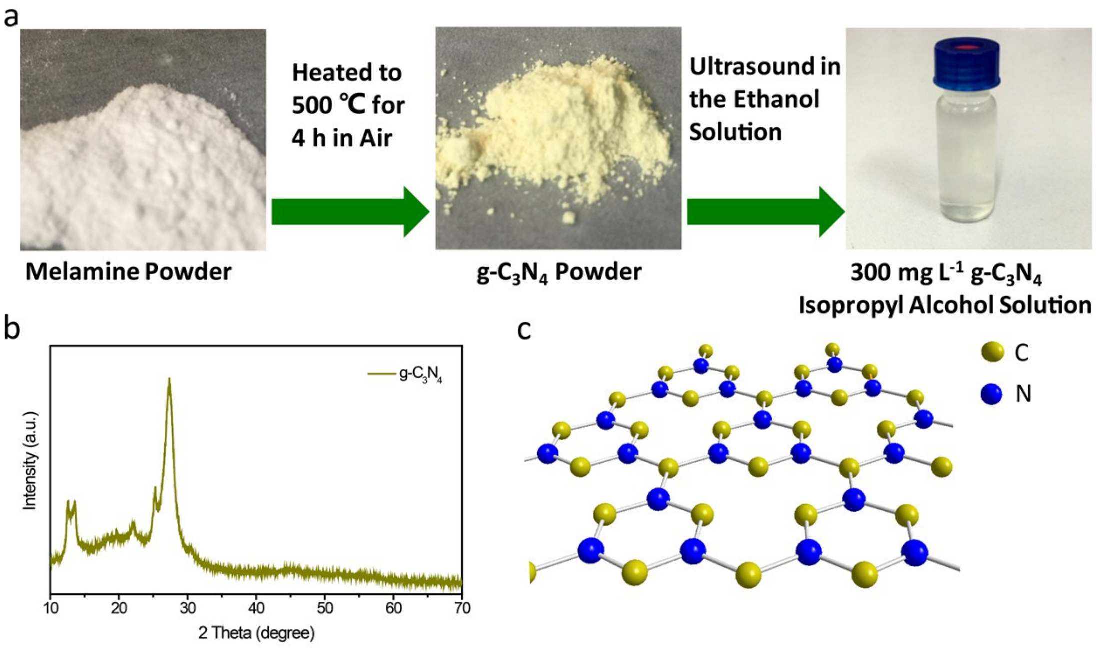

Fig. S1 (a) Schematic illustration of the fabrication procedures for g-C_3N_4 isopropyl alcohol solution. (b) XRD pattern of g-C_3N_4. (c) Schematic drawing of the g-C_3N_4 structure.

1.2 Characterizations and measurements

The morphology, phase and composition of 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), X-ray Photoelectron Spectroscopy (XPS, ESCALab250).The optical properties of the products were measured with UV-Vis-NIR Spectrophotometer (UV-Vis-NIR, Shimadzu UV-2450).

PEC measurements

PEC measurements were carried out in a three-electrode cell with a flat quartz window to facilitate illumination of the photoelectrode surface in 0.1 mol L^{-1} KH_2PO_4 solution (pH=7). The working electrode is the as-synthesized products, while Pt electrode and Ag/AgCl electrode were used as counter and reference electrode, respectively. The illumination source was 300 W Xe arc lamp (Newport, 6255) directed at the quartz PEC cell (100 mW cm^{-2}) with an AM 1.5 global filter (Newport 81094). IPCE were collected by a Solartron 1280B electrochemical station with a solar simulator (Newport 69920, 1000 W xenon lamp), coupled with an infrared water filter (Oriel 6127) and aligned monochromator (Oriel Cornerstone 130 1/8 m). All the electrochemical measurements were performed on a CHI 760D electrochemical workstation (CHI, Shanghai) at RT. IPCE can be expressed as:

$$\mathrm{IPCE}=(1240I)/(\lambda J_{light})$$

where I is the measured photocurrent density at a specific wavelength, λ is the wavelength of incident light, and J_{light} is the measured irradiance at a specific wavelength.

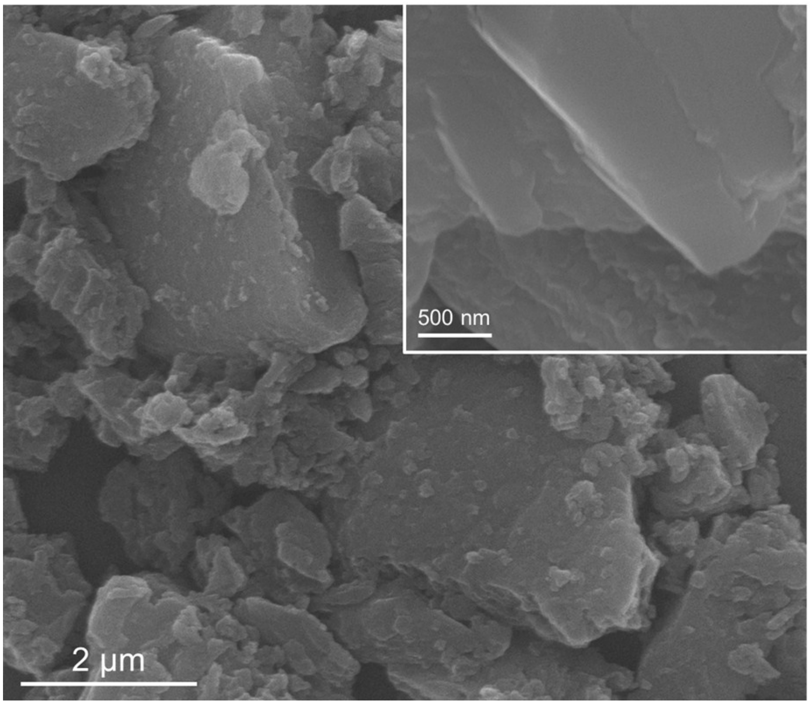

Fig. S2 SEM images of bulk g-C_3N_4.

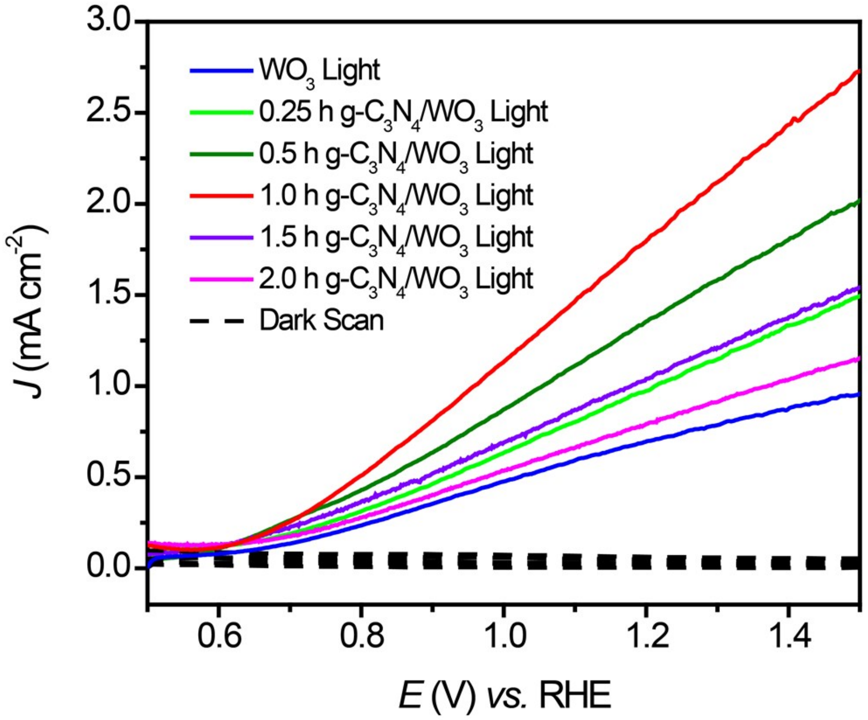

Fig. S3 Linear sweep voltammograms of bare WO_3 and g-C_3N_4-NSs/WO_3-NRs samples with different impregnated time.

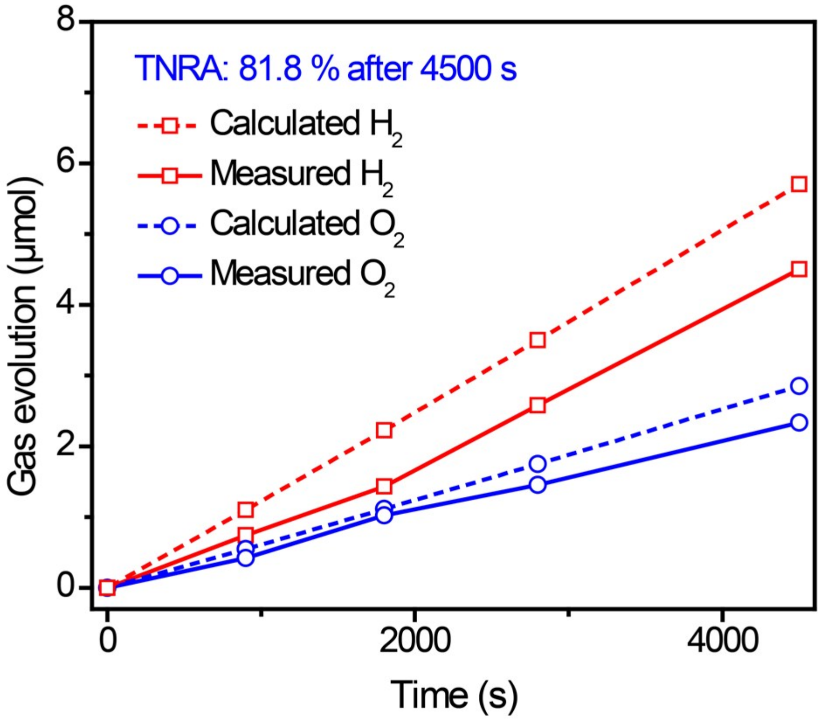

Fig. S4 Time course of the measured and calculated O_2 and H_2 gas evolution from the g-C_3N_4/WO_3 photoanode.

References

1 Y. Liu, S. Xie, C. Liu, J. Li, X. Lu and Y. Tong, *J Power Sources*, 2014, **269**, 98.

2 Y. Hou, F. Zuo, A. P. Dagg, J. Liu and P. Feng, *Adv Mater*, 2014, **26**, 5043.