

# Template-free preparation and properties of mesoporous g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> nanocomposite photocatalyst

Jianchao Shen,<sup>a</sup> Hui Yang,<sup>a, b</sup> Qianhong Shen,<sup>\*a, b</sup> Yu Feng,<sup>a</sup> and Qifeng Cai<sup>a</sup>

<sup>a</sup> State Key Laboratory of Silicon Materials, Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, P. R. China. E-mail: s\_qianhong@163.com; Fax: +86 571 87953313; Tel: +86 571 87953313

<sup>b</sup> Zhejiang California International NanoSystems Institute, Zhejiang University, Hangzhou 310027, P. R. China

## Electronic Supplementary Information

### Experimental

#### *Preparation*

All of the chemicals were analytical grade and used as received without further purification. Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was synthesized by directly heating Melamine. Typically, 3 g of melamine powder was put into a corundum boat and heated to 380 °C in 10 minutes and then heated to 520 °C in a muffle furnace for 4 h at a heating rate of 2 °C min<sup>-1</sup> in a flowing-argon atmosphere prior to cooling. After the reaction, the resultant yellow product was collected and milled into powder for further use. For the sake of clear presentation, this g-C<sub>3</sub>N<sub>4</sub> was denoted as CN.

The g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composite (denoted as CN-Ti) was prepared according to the following procedure: 0.2g of g-C<sub>3</sub>N<sub>4</sub> was added into 20 mL of ethanol, and the suspension was sonicated for 1 h. Then, 20 mL of Ti(SO<sub>4</sub>)<sub>2</sub> aqueous solution with concentration about 0.037 M was added into the suspension, and the mixture was

stirred magnetically for 18 h. The obtained solution was then pre-heated at 80 °C for 4h under stirring and transferred to a Teflon-lined stainless steel autoclave of 50 mL capacity and maintained at 150 °C for 20 h. After cooling to room temperature naturally, the precipitate was collected, washed with deionized water and absolute ethanol several times, and then dried in air at 60 °C for 24 h. The pure g-C<sub>3</sub>N<sub>4</sub> modified in the ethanol-water solution (denoted as CN-H) and H<sub>2</sub>SO<sub>4</sub> solution (denoted as CN-S for the solution has the same pH value as that of the g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> preparation system, and denoted as CN-SS for the solution added three times amount of sulfuric acid as many as that of CN-S) were also prepared by the similar procedure for reference, respectively.

### ***Characterization***

The crystal structure was characterized by an X-ray powder diffractometer (XRD, APEXII, Bruker, Germany) using Ni-filtered Cu K<sub>α</sub> radiation ( $\lambda = 1.542 \text{ \AA}$ ) at 40 kV and 40 mA, and a scan rate of  $3^\circ \text{ min}^{-1}$  was applied to record the patterns in the range of  $2\theta = 10^\circ - 80^\circ$  at a step of  $0.02^\circ$ . Structure and morphology were investigated using transmission electron microscopy (TEM, TECNAI-10, Hitachi, Japan) at an accelerating voltage of 160 kV and field emission scanning electron microscope (FE-SEM, SU-70, Hitachi, Japan) at 3 kV. FTIR spectra were recorded in transmission mode from 4000 to  $400 \text{ cm}^{-1}$  on a FTIR spectrometer (Avatar 360, Nicolet, USA) using the standard KBr disk method. Nitrogen adsorption - desorption isotherms were collected on an adsorption analyzer (Quantachrome Ins, ASIC-2, USA) at 77 K after the sample had been degassed at 200 °C for 5 h. The BET surface area

was calculated from the linear part of the BET plot ( $P/P_0 = 0.1 - 0.3$ ). Particle size distribution was determined by a laser particle size analyzer (LS-230, Coulter, USA). Laser particle size analysis uses a 750 nm laser scattering and the Fraunhofer model to measure particles in the size range 0.04-2000  $\mu\text{m}$ . UV-vis diffuse reflection spectra (DRS) were performed on a UV-vis spectrophotometer (UV-3150, Hitachi, Japan) using  $\text{BaSO}_4$  as the reference, and absorption spectra were calculated from the reflectance data with the Kubelka-Munk function. Photoluminescence (PL) spectra were detected on a fluorescence lifetime and steady state spectrometer (FLS920, Edinburgh, UK) with excitation wavelength of 325 nm at room temperature. Before measurement, the powder was filled into the glass groove, and then gently flattened by a glass plate.

### ***Photocatalysis evaluation***

The photocatalytic activity of obtained samples was evaluated by degrading methyl orange (MO) in aqueous solution under visible light irradiation. A 35 W CDM-T Philips metal halide lamp with a 420 nm UV-cutoff filter was used as the visible light source. In each experiment, 50 mg of photocatalyst powder was suspended into 100 mL MO solution with a concentration of 10 mg/L. Prior to irradiation, the suspensions were magnetically stirred in the dark for 2 h to establish adsorption-desorption equilibrium. At irradiation time intervals of every 30 min, approximately 4 mL of mixture was collected and then the slurry sample was centrifuged (9000 rpm, 5 min) to remove the photocatalyst particles. The resulting supernatant was analyzed using a UV-vis spectrophotometer (Lambda20, PerkinElmer, USA) and the characteristic

absorption peak of MO at 464 nm was used to determine the extent of its degradation.

The intermediates of MO after different irradiation time of photocatalytic degradation were analyzed by high-performance liquid chromatography (HPLC, Agilent Series 1100, Agilent Technologies, USA). A Zorbax SB-C18 column was equipped with the instrument and an acetonitrile–10.0 mM ammonium formate (30/70, v/v) solution was used as the mobile phase at a flow rate of 0.14 mL/min at room temperature. The injection volume was 10  $\mu$ L and the UV–vis detector was operated at 425 nm to detect the MO dye and its degradation intermediates.

### ***Results***

Fig. S1 shows the typical SEM images of various as-prepared samples of CN, CN-H, CN-S and CN-SS. An aggregated morphology and layered structure of CN sample with relatively smooth and flat surface is exhibited (Fig. S1a). However, the surface of CN-H sample appears some sporadic pores and cracks after hydrothermal treatment (Fig. S1b). Furthermore, when adjusting the pH value of ethanol-water solution by adding H<sub>2</sub>SO<sub>4</sub>, the porosity of CN-S and CN-SS sample is significantly increased (Fig. S1c and 1d).

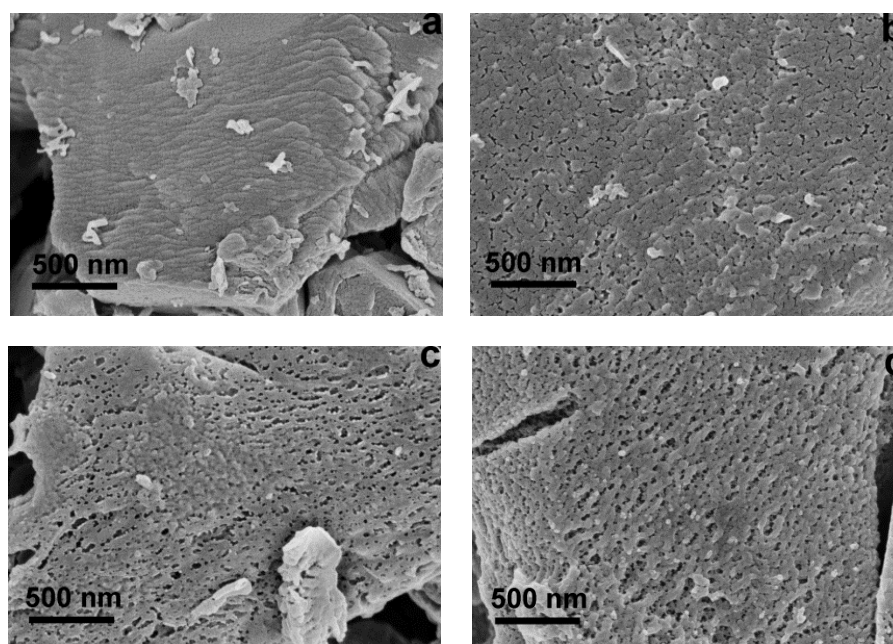


Fig. S1 SEM images of various as-prepared samples of CN (a), CN-H (b), CN-S (c), CN-SS (d)

Fig. S2 shows nitrogen adsorption-desorption isotherms of as-prepared samples. The BET surface area of CN, CN-H, CN-Ti samples are 3.53, 4.74 and 21.21  $\text{m}^2 \text{g}^{-1}$ , respectively. Moreover, the isotherm of CN-Ti sample exhibits typical type IV behavior, indicating its mesoporous nature, which is also demonstrated by the corresponding pore size distribution (The inset of Fig. S2).

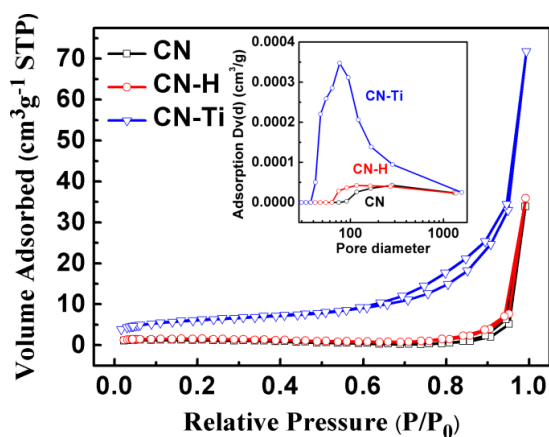


Fig. S2 Nitrogen adsorption-desorption isotherms of various as-prepared samples of CN, CN-H, CN-Ti. The inset shows the corresponding pore size distribution of as-prepared samples

Fig. S3 shows the change in particle size distribution of various samples. The mean particle size of CN sample is 15.9  $\mu\text{m}$  and it originally exhibits a bimodal distribution with the main peaks at 9.8  $\mu\text{m}$  and 57.8  $\mu\text{m}$ . The CN-H sample exhibits similar particle size distribution with CN sample, while its main peaks shift to smaller values and the mean particle size becomes 8.3  $\mu\text{m}$ . As for CN-Ti sample, multi-peaks of particle size distribution is observed and the mean particle size is 7.4  $\mu\text{m}$ .

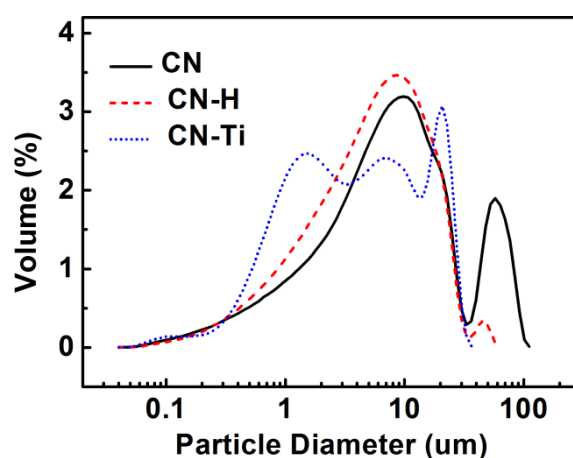


Fig. S3 Particle size distributions of various as-prepared samples of CN, CN-H and CN-Ti

The FTIR spectra of various as-prepared samples of CN, CN-H and CN-Ti imply the existence of condensed CN heterocycles, as they feature characteristic stretching bands of aromatic CN heterocycles at 1200-1600  $\text{cm}^{-1}$  and the breathing mode of the triazine units at 800  $\text{cm}^{-1}$ . Also, the broad band centered at 3150  $\text{cm}^{-1}$  can be assigned to the stretching mode of the N-H bond as the residual hydrogen atoms bind to the edges of the graphene-like C-N sheet. In the case of pure  $\text{TiO}_2$ , the broad band centered at 3400  $\text{cm}^{-1}$  and the band at 1630  $\text{cm}^{-1}$  are due to the absorbed water. Moreover, the broad band centered at 500  $\text{cm}^{-1}$ , which is also observed in the CN-Ti

sample, can be contributed to Ti-O bond.

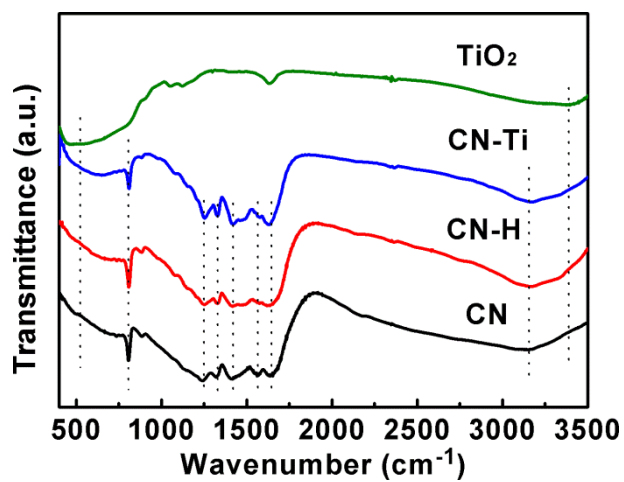


Fig. S4 FT-IR spectra of various as-prepared samples of CN, CN-H, CN-Ti and TiO<sub>2</sub>