

Electronic Supplementary Information (ESI)

Construction of functional nanonetwork-structured carbon nitride with Au nanoparticle yolks for highly efficient photocatalytic applications

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Experimental

1. Sample preparation

Materials. *tert*-Butyl acrylate (98%, *t*BA) was purchased from Aladdin and purified by passing through a column filled with basic alumina to remove inhibitors. Other commercially available materials were

purchased from Aladdin or J&K Scientific without further treatment.

Preparation of Au@SiO₂. Au@SiO₂ was prepared according to a previously reported method.¹ Typically, a stock solution of Au precursor was prepared by dissolving HAuCl₄ (0.0432 g) into deionized water (475 mL), and heated to boiling with intensive stirring. Trisodium citrate (0.25 g) was dissolved in the mixed solution and heated for 30 min under reflux. After the mixed solution cooled down to room temperature, PVP (0.0084 g) was added and the mixed solution was stirred at room temperature for 24 h. The gold nanoparticles (Au NPs) were obtained via centrifugation (12000 rpm, 20 min) and dispersed in 12 mL deionized water. The Au NPs solution and ethanol (38 mL) were mixed together in a 100 ml 3-neck round-bottomed flask and stirred under ultrasound for 30 min. After NH₃·H₂O (1.6 mL) was added and stirred for another 10 min, TEOS (1.2 mL in 19 mL ethanol) was added to the mixture in 20 min, followed by stirring for 12 h. The product Au@SiO₂ was obtained and redispersed in 30 ml ethanol.

Preparation of Au@SiO₂-Br. KH-550 (0.15 mL in 20 mL ethanol) was added dropwise to the Au@SiO₂ solution and stirred for 38 h. The product Au@SiO₂-NH₂ was obtained via washing by ethanol, water, and CH₂Cl₂, respectively. Au@SiO₂-NH₂ was redispersed and kept in 30 mL anhydrous CH₂Cl₂. Triethylamine (1.4 mL) was added into the Au@SiO₂-NH₂ solution under the N₂ atmosphere. 2-Bromopropionyl

bromide (1 mL in 4 mL anhydrous CH₂Cl₂) was added slowly to the mixture under ice bath and reacted for 3 h. Then the reaction temperature was raised to 25 °C and kept for 48 h. After being filtrated and washed by mixed solution (tetrahydrofuran:H₂O = 1:1, volume ratio) for three times, the product Au@SiO₂-Br was dried in vacuum drying oven at 40 °C for 12 h. The Br content of Au@SiO₂-Br was measured to be approximately 0.684 mmol g⁻¹, according to a reported method.²

Preparation of Au@SiO₂-g-PtBA and Au@SiO₂-g-PAA. The Au@SiO₂-Br initiator (0.1 g) was added to the mixed solution of *tert*-butyl acrylate (*t*BA) monomer, CuBr₂, CuBr, and PMDETA (the molar ratio is [*t*BA]: [Au@SiO₂-Br]: [CuBr]: [CuBr₂]: [PMDETA] = 1000:1:4:0.4:4.4) at room temperature under the N₂ atmosphere. Then the temperature was raised to 65 °C and kept for 48 h. After the reaction stopped, 200 mL ethanol was added to the mixture and the product Au@SiO₂-g-PtBA was obtained by centrifugation (12000 rpm, 5 min).

Au@SiO₂-g-PtBA (0.3 g) was then dissolved in 30 mL CH₂Cl₂, followed by the addition of 10 mL trifluoroacetic acid. The mixture was stirred at room temperature for 24 h. After hydrolysis, the product Au@SiO₂-g-PAA was gradually precipitated in CH₂Cl₂, washed with CH₂Cl₂, and thoroughly dried under vacuum at 40 °C overnight.

Preparation of FNNS-C₃N₄-Au and pristine C₃N₄. Au@SiO₂-g-PAA (0.1 g) and melamine (1 g) were dissolved in deionized water (35 mL),

and the mixture was added to a hydrothermal reactor for 5 h under 100 °C. Then the product Au@SiO₂-g-PAA/MA was obtained by filtration and washed with the deionized water. Au@SiO₂-g-PAA/MA was then heated in a covered quartz container from room temperature to 400 °C with a heating rate of 2.3 °C min⁻¹ in N₂ flow. The temperature was kept at 400 °C for 2 h, and then increased to 550 °C and stabilized for another 3 h. The resulting material was etched by HF for 12 h, leading to formation of FNNS-C₃N₄-Au.

Pristine C₃N₄ was prepared as follows: Melamine was heated in a covered quartz container from room temperature to 400 °C with a heating rate of 2.3 °C min⁻¹ in the N₂ flow. The temperature was kept at 400 °C for 2 h, and then increased to 550 °C and stabilized for another 3 h.

2. Characterization

The powder X-ray diffraction (XRD) patterns were obtained by a D-MAX 2200 VPC diffractometer at 40 kV and 40 mA using Cu Ka radiation ($\lambda = 1.54 \text{ \AA}$). Diffraction patterns were recorded over a 2θ range ($10^\circ < 2\theta < 80^\circ$) with a scan rate of $10^\circ \text{ min}^{-1}$. UV-vis diffuse reflectance spectra were recorded to study the optical absorbance of the photocatalysts using a Shimadzu UV-3100 spectrophotometer in the wavelength range of 200-800 nm with BaSO₄ as a reference. Fourier transform infrared (FTIR) measurements were carried out on Bruker Tensor 27 spectrometer in the frequency range of 4000-500 cm⁻¹ with a

resolution of 4 cm⁻¹ with KBr as the reference diluent. The morphology and structure analysis of the as-synthesized samples were measured by a transmission electron microscopy (TEM, JEM-1400 Plus) at an accelerating voltage of 200 kV and a field emission scanning electron microscopy (FESEM, Hitachi S-4800). Gel permeation chromatography (GPC) was performed using a Waters GPC 2414 with a refractive index detector at 40 °C (mobile phase: tetrahydrofuran).

3. Photocatalysis test

Photocatalytic reaction. The photocatalytic activities of the samples were evaluated by the degradation of methyl orange (MO) (10 mg L⁻¹) solution with a 300 W Xenon lamp (HSX-F300, Beijing NBeT) as the visible light source ($\lambda \geq 420$ nm). In a typical run, 0.04 g of the photocatalysts were added to 50 mL of MO (10 mg L⁻¹) aqueous solution and stirred in the dark for 30 min to reach the adsorption/desorption equilibrium between the dye and the catalyst. Then the mixed solution was exposed to visible light irradiation ($\lambda \geq 420$ nm) under magnetic stirring. At a given time interval of irradiation, 0.3 mL of the solution was withdrawn and removed from the photocatalyst by centrifugation. The concentrations of the residual dye were tested by the UV-vis spectrophotometer at 464 nm.

Photoelectrochemical measurement. The photocurrent response and electrochemical impedance spectra (EIS) of prepared photocatalysts were recorded with an electrochemical station (CHI 660D, Chenhua, Shanghai,

China) in a typical three-electrode system, whose electrolyte was Na_2SO_4 aqueous solution (1 M). A platinum wire and saturated calomel electrode (SCE) were served as the counter electrode and the reference electrode, respectively. The glassy carbon electrodes modified with photocatalysts (pristine C_3N_4 and FNNS- C_3N_4 -Au) were used as the working electrodes.

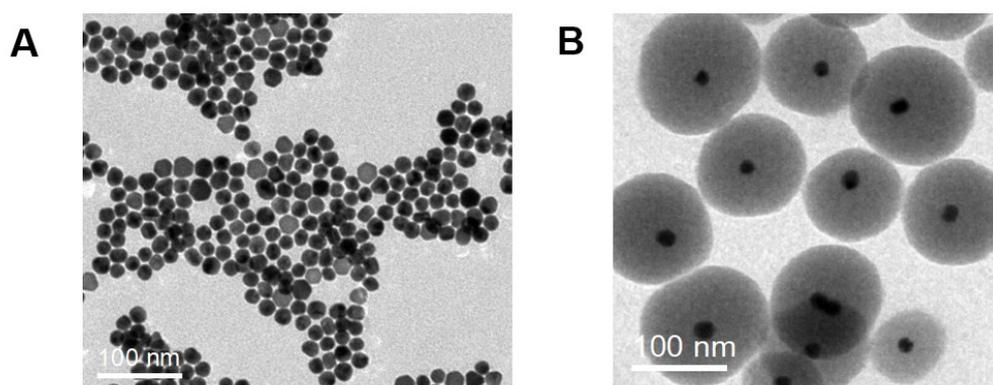


Fig.S1 TEM images of (A) Au NPs and (B) Au@SiO₂ NPs

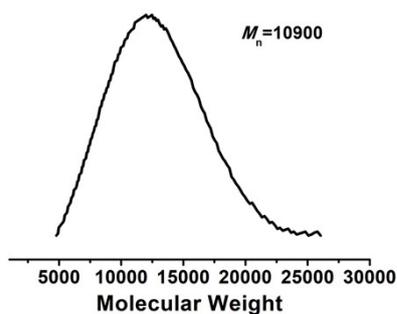


Fig.S2 GPC trace of cleaved PtBA of Au@SiO₂-g-PtBA.

Reference

1. Y. Yao, X. Zhang, J. Peng and Q. Yang, *Chem. Com.*, 2015, **51**, 3750-3753.
2. Y. Liang, L. Chen, D. Zhuang, H. Liu, R. Fu, M. Zhang, D. Wu and K. Matyjaszewski, *Chem. Sci.*, 2017, **8**, 2101-2106.