

Supporting Information

Over two-orders enhancement of photocatalytic hydrogen evolution of carbon nitride *via* mediator-free decorating gold-organic microspheres

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Experimental Section

Materials

Chloroauric acid hydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, $\geq 47.8\%$), cyanoguanidine ($\text{C}_2\text{H}_4\text{N}_4$, $\geq 98\%$), triethanolamine ($\text{C}_6\text{H}_{15}\text{NO}_3$, $\geq 99.8\%$) and *N,N*-dimethylformamide (DMF , $\geq 99.8\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. They were used without further purification. High-purity water with the resistivity of $\geq 18.2 \text{ M}\Omega \cdot \text{cm}$ was used in the experiments.

In situ preparation of AuNPs/g- C_3N_4 photocatalysts.

The gold-cyanoguanidine microspheres (GCMs) were prepared by mixing HAuCl_4 and cyanoguanidine in deionized (DI) water at $60 \text{ }^\circ\text{C}$ for ~ 30 min. The concentrations of HAuCl_4 and cyanoguanidine are 2 mmol/L and 6 mmol/L , respectively. After the reaction, the precipitates were collected by centrifuge, and then rinsed with DI water for 3 times to remove unreacted HAuCl_4 and cyanoguanidine. The GCMs were then dried under vacuum at room temperature. To fabricate AuNPs/g- C_3N_4 hybrids, the as-prepared GCMs were

mixed with cyanoguanidine in DI water, which was then freeze-dried, placed in crucible and annealed at 550 °C for 4 h with a ramp of 1 °C min⁻¹ in Ar flow. The weight ratios of GCMs relative to cyanoguanidine were 1.6%, 2.1%, 3% and 6.1%. For comparison, pure g-C₃N₄ was prepared by directly heating cyanoguanidine at the same condition without adding GCMs. Note: The weight fractions of Au in text refer to the amount of Au in AuNPs/g-C₃N₄ hybrids, which were determined by ICP-AES.

ICP-AES measurement of Au content

The AuNPs/g-C₃N₄ samples of known weights were dissolved in 2 mL freshly made aqua regia in screw capped glass bottles (5 mL) under sonication and heating for 24 h, followed by diluting the solution to 10 mL in a volumetric flask, which was then centrifuged (2300 g, 5 min) to remove all precipitates. After that, the supernatant solution was further diluted in the volumetric flask. The resulted samples were analyzed by a PerkinElmer Optima 7300 DV DRC Emission Spectrometry.

Electrochemical Characterization

The transient photocurrent was conducted in H₂SO₄ (0.5 M) using an electrochemical instrument (Gamry Interface 1000) with three-electrode system under light irradiation (300 W Xe-lamp, $\lambda > 420$ nm) and an applied bias of 0.3 V. The working electrodes were the FTO separately coated with g-C₃N₄ and AuNPs/g-C₃N₄ solutions (4 mg/mL in DMF) and dried at 120 °C for 2 h respectively. The Ag/AgCl was used as reference electrode and platinum as counter electrode.

Photocatalytic Activity Test

The photocatalytic performance was evaluated by hydrogen production. The photocatalytic H₂ evolution reactions were carried out in a Pyrex reactor with reflux water at room temperature. The photocatalyst AuNPs/g-C₃N₄ (10 mg) was dispersed in a mixture of 80 mL DI water and 20 mL triethanolamine aqueous solution, and the mixed suspension was agitated magnetically. Subsequently, the above suspension was irradiated by a 300 W xenon-lamp (CEL-HXF 300) with a cut-off-filter (400 nm), which was employed for light

source. For comparison, the photocatalytic experiment of bulk g-C₃N₄ and 3 wt% Pt involved g-C₃N₄ were also carried out under the identical conditions.

Characterization

The Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and chemical element mapping analysis were performed on a field emission transmission electron microscope (Tecnai G2F30 S-TWIN, FEI) at an acceleration voltage of 300 kV. The X-ray diffraction (XRD) measurements were performed on an X-ray diffractometer (D8 Advance, BRUKER-AXS) with Cu K α radiation. Fourier transform infrared spectra (FT-IR) of the samples were recorded from 400 to 4000 cm⁻¹ on a Bruker spectrometer (Tensor 27) using KBr pellets. X-ray photoelectron spectroscopy (XPS) data were obtained with an electron spectrometer (ESCALAB250 Xi, Thermo Scientific). Photographs were taken by a digital camera (COOLPIX S8100, Nikon). The UV-vis diffuse reflectance spectra (DRS) were obtained using a UV-Vis-NIR spectrophotometer (Cary-5000, Varian). The Time-resolved fluorescence were performed with time-resolved spectrum (FLSP20, Edinburgh Instruments). The photoluminescence (PL) spectra were measured on a spectrofluorometer (F-4500, Hitachi), using a Xe lamp as light source. The Brunauer-Emmett-Teller (BET) specific surface area (SBET) was determined by nitrogen adsorption-desorption isotherm measurements (ASAP 2020 HD88, Micromeritics).

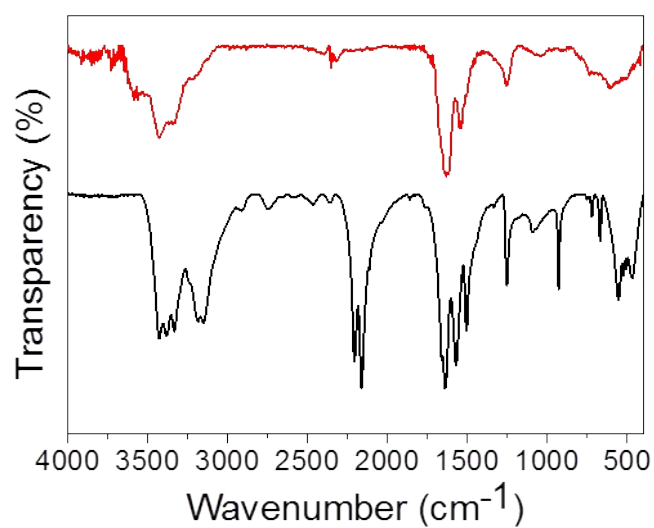


Fig. S1 FT-IR spectra of pure CGN (black) and AuNPs/CGN (red).

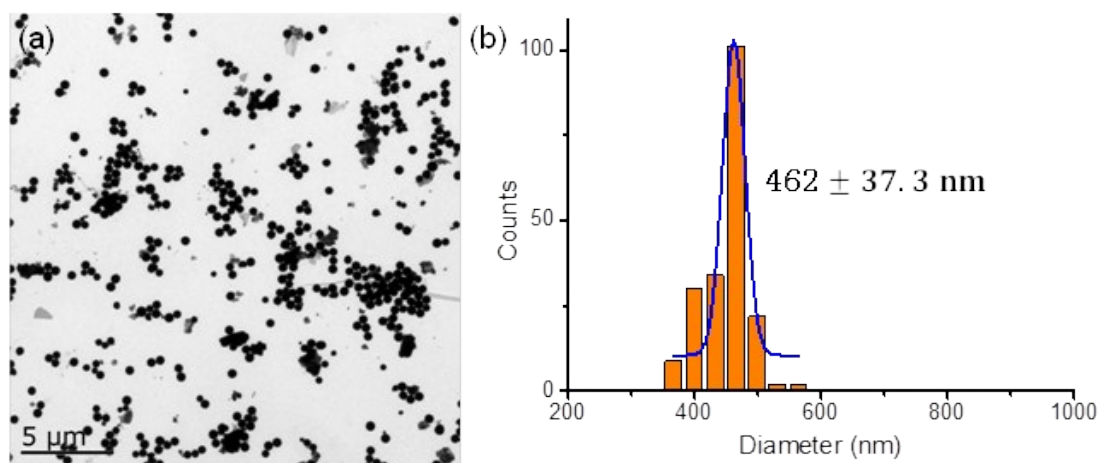


Fig. S2 (a) TEM image of gold-cyanoguanidine microspheres (GCMs). (b) Diameter distribution of GCMs determined by TEM image of Figure S2a. The data were obtained from software for diameter analysis on picture. (Department of Chemistry, Fudan University, version 1.1.0.33).

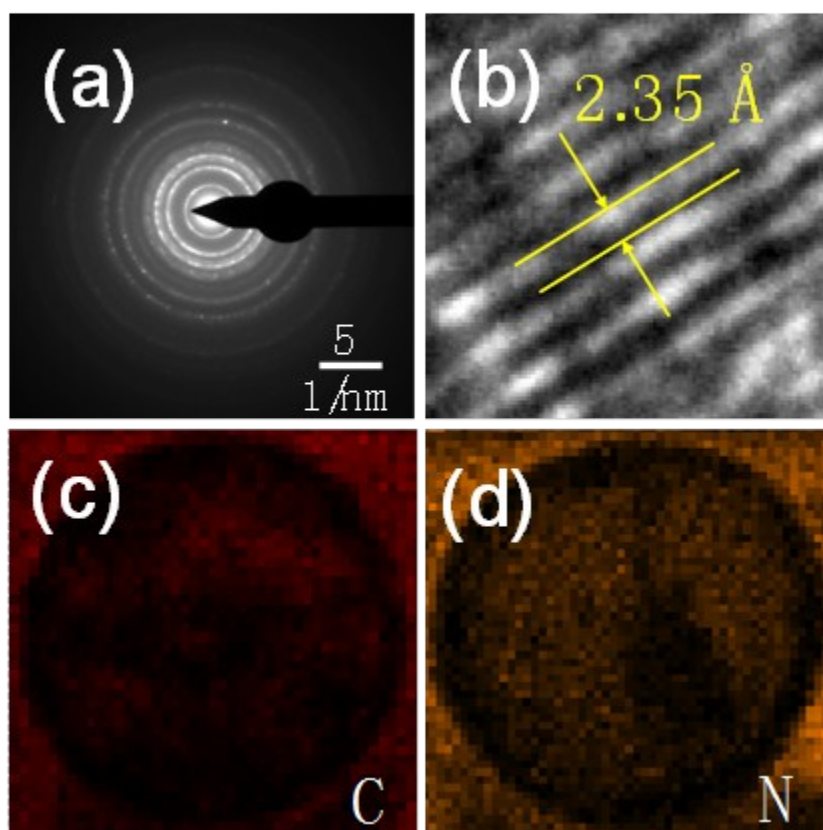


Fig. S3 (a) Selected area electron diffraction (SAED) pattern and (b) lattice spacing from HRTEM of AuNPs in GCM. (c-d) The elemental mapping images of C and N for GCM. Note: the background also displays color can be attributed to C and N elements in the polymer support film on TEM grid.

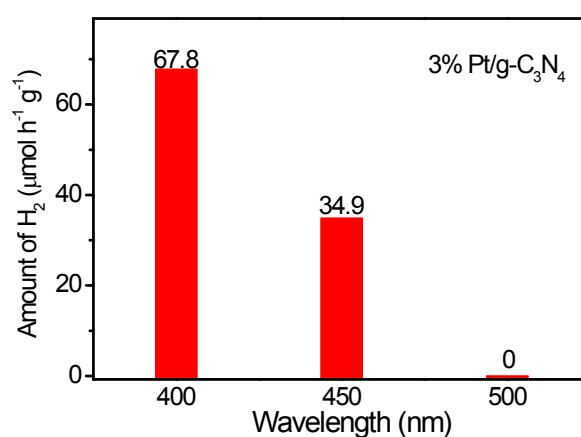


Fig. S4 Photocatalytic H₂ generation rates of 3 wt% Pt involved g-C₃N₄ photocatalyst under different light irradiation.

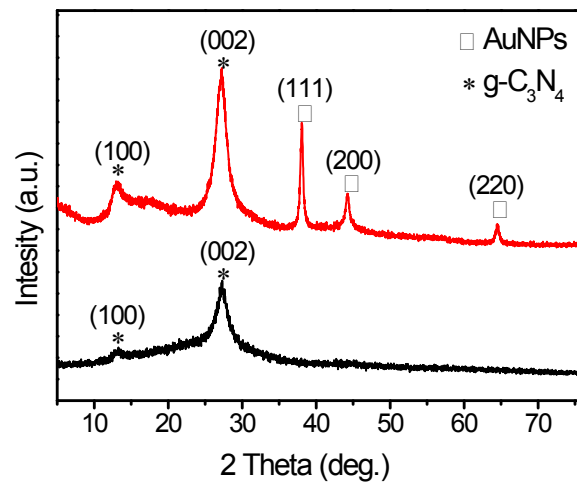


Fig. S5 XRD patterns of the pure g-C₃N₄ (black) and 2.1 wt% AuNPs/g-C₃N₄ hybrids (red).

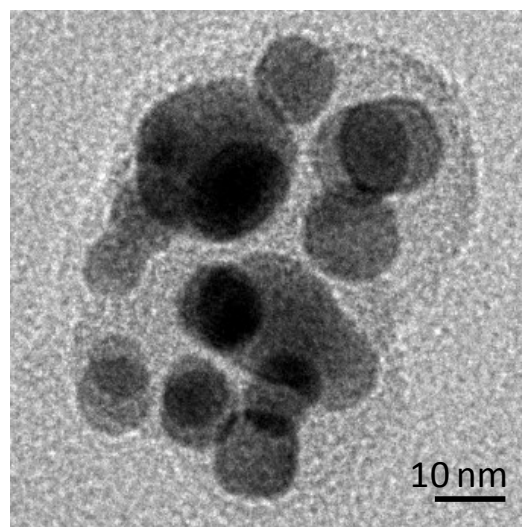


Fig. S6 TEM image of the evolution process of AuNPs from small to large scale.

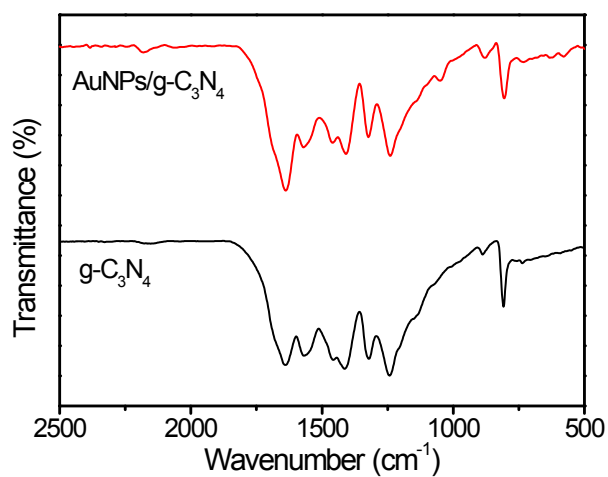


Fig. S7 FT-IR spectra of bulk $g\text{-C}_3\text{N}_4$ (black) and $\text{AuNPs}/g\text{-C}_3\text{N}_4$ (red). The peak at $\sim 808\text{ cm}^{-1}$ is due to the breathing mode of tri-s-triazine.

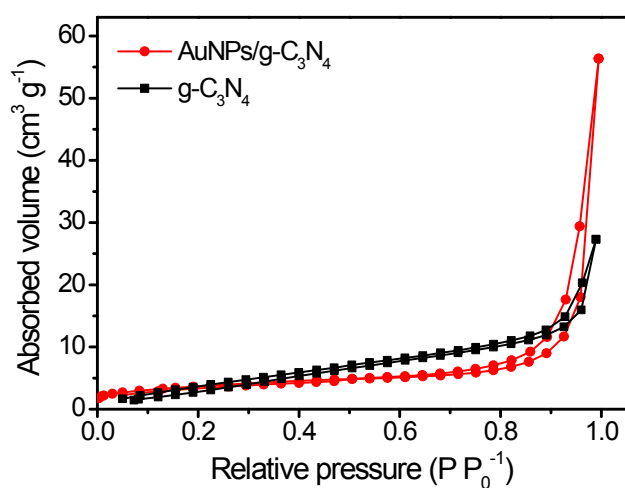


Fig. S8 Nitrogen adsorption of pure $g\text{-C}_3\text{N}_4$ and $\text{AuNPs}/g\text{-C}_3\text{N}_4$.

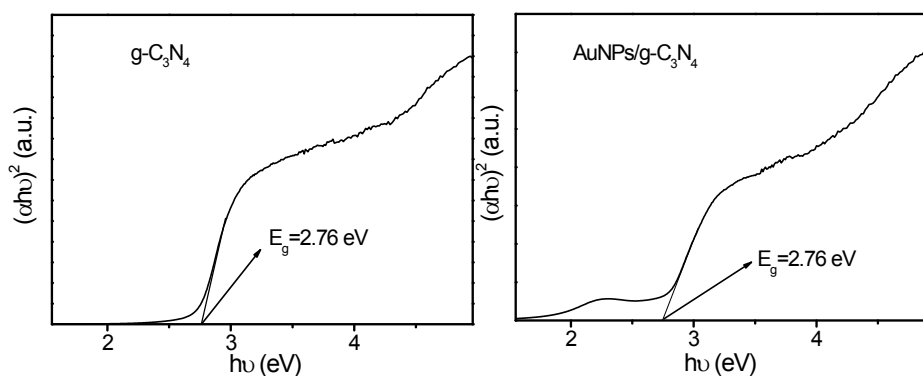


Fig. S9 Transformed Kubelka-Munk function vs. the light energy curves of bulk $g\text{-C}_3\text{N}_4$ and $\text{AuNPs}/g\text{-C}_3\text{N}_4$.

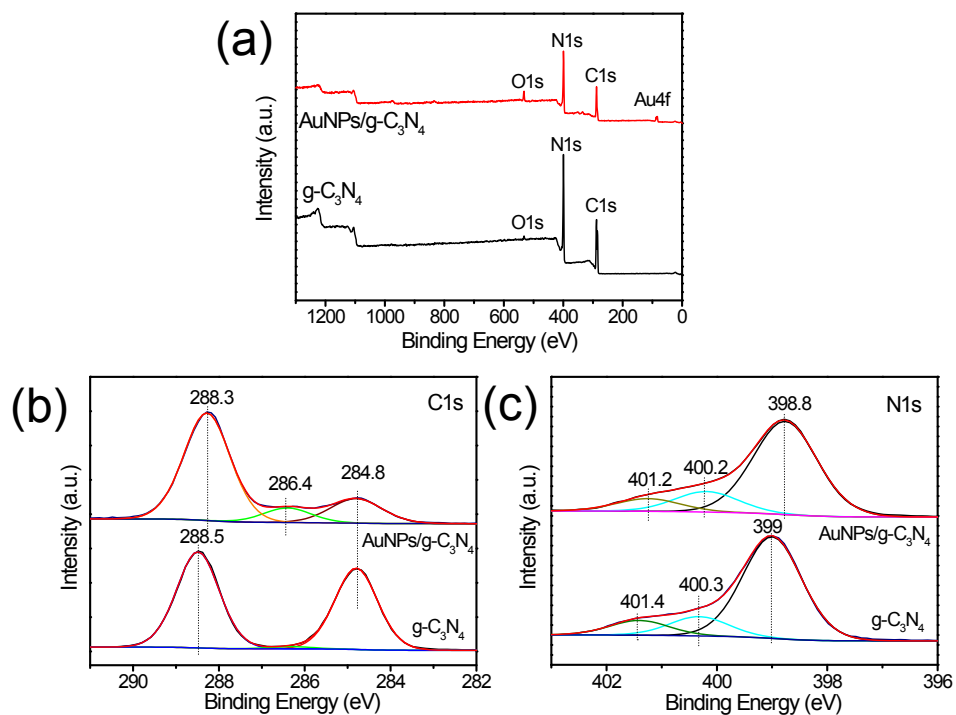


Fig. S10. XPS spectra of (a) survey scan, (b) C1s, (c) N1s of bulk g-C₃N₄ and AuNPs/g-C₃N₄ hybrids.