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Supporting Information for

Synergetic enhancement of plasmon-hot-electron injection in Au cluster-nanoparticle/C_3N_4 for photocatalytic hydrogen evolution

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S1. Materials

Au cluster-NP/C_3N_4. The synthesis of Au cluster-NP/C_3N_4 undergoes two well-designed steps: ammonia reduction and post-thermal treatment. Typically, pure g-C_3N_4 was prepared by the commonly used thermal polymerization of urea at 550 °C for 4 h[1,2] and then was treated by 38 vol% ammonia solution maintaining at 80 °C for 6 h. Subsequently, 120 mg ammonia-treatment g-C_3N_4 was ultrasonic dispersion in 100 mL deionized water before dropwise addition of 0.85 mL $HAuCl_4$ (29.5 mM) into the suspension under vigorous stirring. After that, the resultant solution was continuously stirred at room temperature (25 °C) for 8 h and then was centrifugated, washed, and dried to collect the light yellow precipitate. Finally, the resultant precipitate was further thermal treatment in muffle furnace at 400 °C for 2 h. After naturally cooling down to room temperature, the final product of Au cluster-NP/C_3N_4 with dark-red-color was collected and grinded for further characterization.

Au cluster/C_3N_4 and Au NP/C_3N_4. 120 mg ammonia-treatment g-C_3N_4 was ultrasonic dispersion in 100 mL deionized water and then 0.85 mL $HAuCl_4$ (29.5 mM) was added dropwise into the suspension under vigorous stirring. After that, the resultant solution was continuously stirred at room temperature (25 °C) for 8 h and then was centrifugated, washed, and dried to obtain the light yellow Au cluster/C_3N_4. The Au NP/C_3N_4 was gained by annealing the as-obtained Au cluster/C_3N_4 in muffle furnace at 600 °C for 2 h. All the samples were washed several times and dried at 60

°C overnight for further characterization.

Au Particle. Typically, 18 mg $HAuCl_4$ was completely dissolved in 100 mL deionized water under vigorous stirring before the addition of 15mg PVP (Polyvinylpyrrolidone) and then the mixed solution was heated to 100 °C. Subsequently, 5 ml $NaBH_4$ solution (30 mM) was added into the above solution and the resultant solution was continuously stirring at 100 °C for 0.5 h. After that, the precipitate was centrifugated, washed, and dried to obtain the yellow Au particle. The final product was washed several times and dried at 60 °C overnight for further characterization.

S2. Materials characterization

Transmission electron microscopy (TEM) and High-resolution TEM (HRTEM) were performed on a JEM-2100F microscope at an acceleration voltage of 200 kV. Aberration-corrected high angle annular dark field transmission electron microscopy (HAADF-TEM) was conducted on a JEM-ARM200F instrument at 200 kV. The XRD patterns were performed on Philips X'Pert Pro Super X-ray diffractometer with Cu *K*α radiation. The UV-vis spectra (DRS) were recorded on a Shimadzu DUV-3700 spectrophotometer. X-ray photoelectron spectra (XPS) were acquired on an ESCALAB MKII with Mg Kα (*hυ* = 1253.6 eV) as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.5 eV.

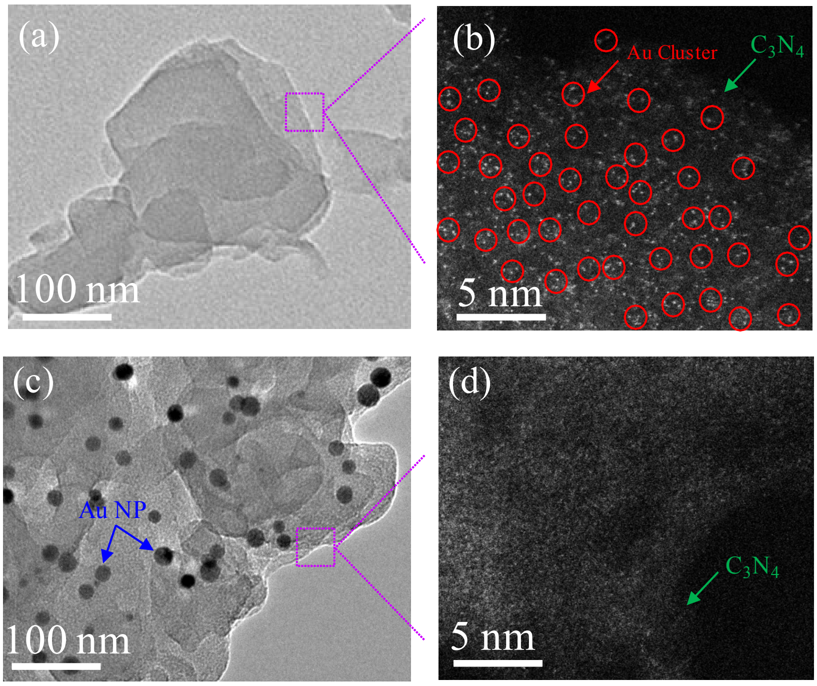

Figure S1. TEM and HAADF-TEM images for (a) Au cluster/C_3N_4, (b) Au NP/C_3N_4.

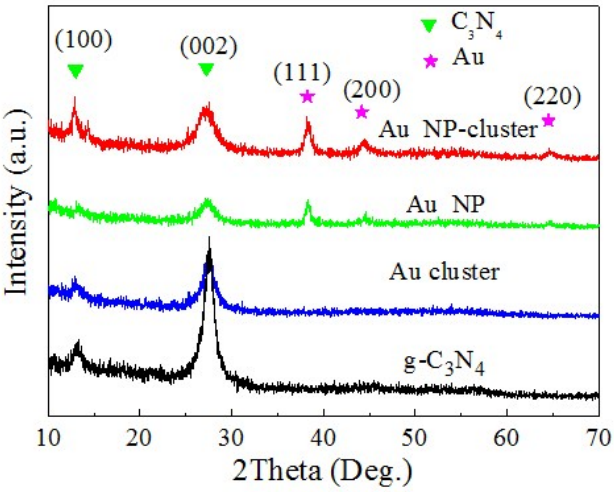

Figure S2. XRD pattern for pure C_3N_4, Au cluster/C_3N_4, Au NP/C_3N_4, and Au cluster-NP/C_3N_4.

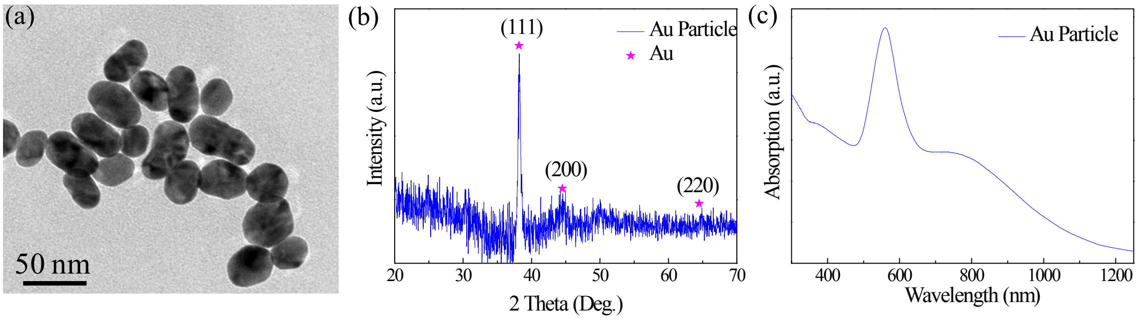

Figure S3. TEM (a), XRD pattern (b), and UV-Visible spectra (c) for Au particle.

Ultraviolet photoemission spectroscopy (UPS) characterization. Photoemission spectroscopy experiments were performed at the photoemission end-station at beamline BL10B in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The beamline is connected to an undulator and equipped with two gratings that offer soft X-rays from 100 to 1000 eV with a typical photon flux of 5×10^{10} photons/s and a resolution ($E/\Delta E$) better than 10^3 at 244 eV. The density of states for valence-band photoelectron spectra by the ultraviolet photoemission spectroscopy (UPS) characterization is applied to explore the chemical state and the information for bonding structure of the solid surface. The Fermi level E_F is located at E=0 which was measured from the Fermi edge of an evaporated Au film. The work function measurements were also conducted with that to allow the observation of the secondary electron cut-off. The sample was biased by −10.0 V in order to acquire distinct the secondary-electron cutoff of the spectrum and Valence band spectrum chosen for 170 eV of synchrotron radiation light excitation energy. During the process of experiment, the standard samples of Au 4f spectral peak and Fermi edge was used for photon energy calibration. The energy differences between the vacuum level (VL) and the Fermi level corresponds to the work function (WF) of the samples which reflect the changes of the fine structure on the surface.

XAFS measurements. The XAFS data were collected at BL14W1 station in SSRF (Shanghai Synchrotron Radiation Facility) and 1W1B station in BSRF (Beijing Synchrotron Radiation Facility). The storage rings of SSRF and BSRF were operated at 3.5 GeV with the current of 300 mA and at 2.5 GeV with a maximum current of 250 mA, respectively. The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The k^3-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k^3-weighted $\chi(k)$ data in the k-space ranging from 2.4–14 Å^{-1} were Fourier transformed to real (R) space using a hanning windows (dk = 1.0 Å^{-1}) to separate the EXAFS contributions from different coordination shells.

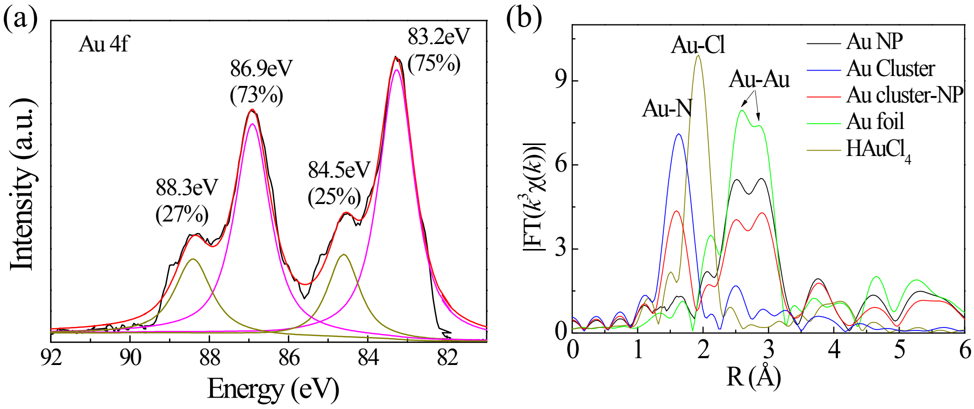

Figure S4. (a) Deconvolution of Au 4f XPS spectra for Au NP-cluster/C_3N_4, (b) Fourier transform curves of Au L_3-edge $k^3\chi(k)$ oscillation for samples.

Electrochemical measurement methods. Electrochemical measurements were performed using an electrochemical workstation (Model CHI760D, CH instruments, Inc., Austin, TX) with a standard three-electrode photoelectrochemical cell and was used to record transient photocurrent behavior of the samples, where the prepared electrodes immersed in a sodium sulfate electrolyte solution (0.5 M), a gauze platinum and Ag/AgCl (saturated KCl) act as the working, auxiliary, and reference electrode, respectively. The working electrodes were prepared as follows: First, fluoride tin oxide (FTO) glass was washed sequentially with acetone, ethanol and DI water in an ultrasonic bath for 30 min. Next, 0.05 g of photocatalyst was ground with 5 uL nafion (5 wt%, Sigma Aldrich) and mixed with 2 mL of acetone under sonication for 30 min to obtain slurry. Then, the slurry was coated onto 1 cm × 2 cm FTO glass electrode by the spin coater. In addition, the three electrodes were immersed in a sodium sulfate electrolyte solution (0.5 M) as conductive media at pH 6.8, which was continuously in an N_2-purged flow to remove O_2 before light irradiation. Photocurrent measurements utilized a 300 W Xe lamp. The working electrode was back-illuminated through the FTO glass in order to minimize absorption by the dark and thick catalyst layer. The photoresponse of the prepared photoelectrodes (I-t) was operated by measuring the photocurrent densities under chopped light irradiation (light on/off cycles: 30s) at a bias potential of −0.3 V vs. Ag/AgCl. A 500 nm cutoff filter was added to remove the light whose wavelength is shorter than 500 nm, and then the visible-light region of ≥ 500 nm was obtained as illumination source to activate photocatalytic reaction

The transient open-circuit voltage decay (OCVD) measurements were taken for 1300 s in all, and the light on and off were controlled at 300 s and 600 s from the start, respectively. The average lifetime of the photogenerated carriers (τ_n) were obtained from the OCVD according to Equation (2):[3]

$$\tau_n = -\frac{k_B T}{q}\left(\frac{dV_{OC}}{dt}\right)^{-1} \tag{1}$$

Where k_B is the Boltzmann constant, T is the temperature (in Kelvin), and q is the unsigned charge of an electron.

Photocatalytic reactions and measurements. Photocatalytic hydrogen evolution performance measurements were carried out in a top-irradiation-type photoreactor (Pyrex glass) connected to a closed gas circulation system. Approximately 30 mg of the photocatalysts were dispersed in 100 ml mixed solution of DI-water and methanol (4:1 in volume ratio). The reactant solution was evacuated several times to remove air thoroughly and irradiated using a 300 W Xe-lamp (PLS-SXE 300, Beijing perfectlight Co. Ltd, China). The generated hydrogen and nitrogen were measured by a gas chromatograph (GC) equipped with a thermal conduction detector (TCD, 5 Å molecular sieve columns with 3 m length) using Ar as carrier gas with flow rate of 20 ml/min. The injection port, column, and detector temperatures are 60, 60, and 130 °C, respectively. The 60 cycles with time interval of 6 hours were performed.

For full spectrum measurement, a 300 W xenon arc lamp (PLS-SXE300/300UV) with a standard AM1.5 filter, outputting the light density of 100 mW/cm^2, was used as illumination source to trigger the photocatalytic reaction for samples. Subsequently, a 420 nm cutoff filter was added to remove the light whose wavelength is shorter than 420 nm, and then the visible-light region of ≥ 420 nm was obtained as illumination source to activate photocatalytic reaction. As for the visible-light irradiation of ≥ 500 nm, a 500 nm cutoff filter was employed. Several band-pass filters (FWHM=15 nm) were employed to achieve a different incident light wavelength under a 300 W Xe lamp for measurement of the photocatalytic activity. The average intensity of each irradiation wavelength was determined by an optical power meter (PM100D, Thermal Powermeter Head, THORLABS).

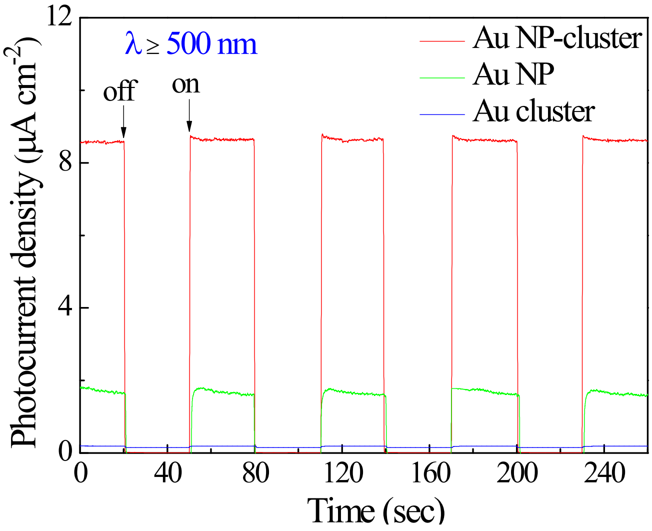

Figure S5. Photocurrent transient measurements under irradiation of λ ≥ 500 nm for C_3N_4, Au cluster/C_3N_4, Au NP/C_3N_4 and Au NP-cluster/C_3N_4, respectively.

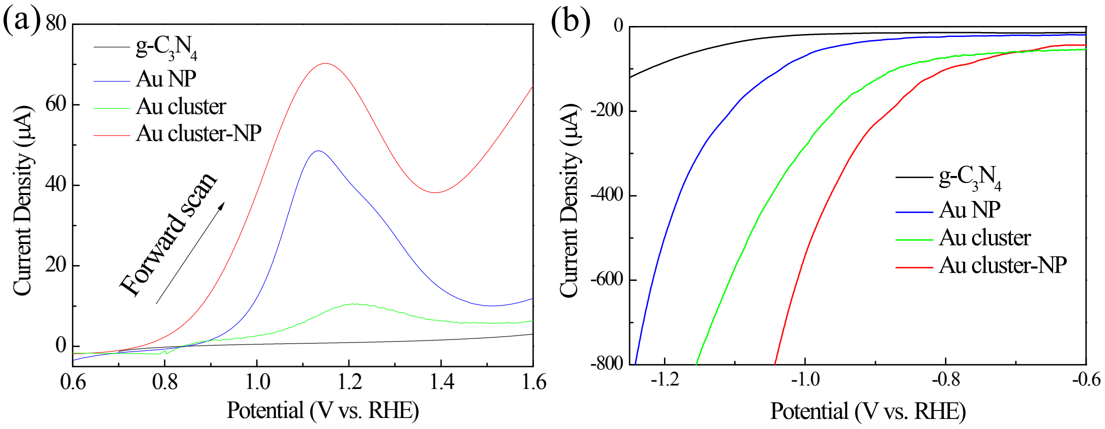

Figure S6. (a) Electrochemical methanol oxidation and (b) hydrogen evolution measurements for g-C_3N_4, Au NP/C_3N_4, Au cluster/C_3N_4, and Au cluster-NP/C_3N_4.

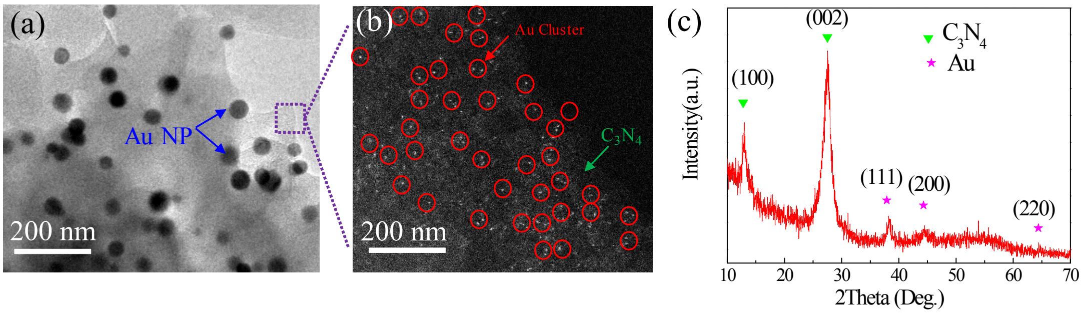

Figure S7. (a) TEM image, (b) HAADF-TEM image and (c) XRD pattern for the Au NP-cluster/C_3N_4 after photocatalytic hydrogen evolution measurement.

Table S1. Summary of Au plasmonic hot electron mediated photocatalytic water splitting

Catalysts	Reaction solution	catalysts mass	Light source	Incident light/nm	H_2 Rate (μmol/h/g)	(Ref.)
Au NR/MoS_2	10 vol% lactive acid aqueous solution	5 mg	LAX-C100 visibie light	>460 nm	18	4
Au NR@Cu_2O	0.0125 M glucose + 0.01 M NaOH	5 mg	300W Xe lamp	AM 1.5	80.2	5
Au NP@TiO_2	10 vol% methanol aqueous solution	3 mg	300W Xe lamp	>420 nm	~58	6
Au NP/N-TiO_2	10 vol% methanol aqueous solution	150 mg	150 W Xe lamp	AM1.5	78	7
Au NP/C_3N_4	10 vol% triethanolamine aqueous solution	20 mg	125W Hg lamp	>400 nm	~177	8
Au NP/C_3N_4	25 vol% methanol aqueous solution	50 mg	350W Xe lamp	>400 nm	32	9
Au NP/PtO-C_3N_4	25 vol% methanol aqueous solution	50 mg	350W Xe lamp	>400 nm	338	9
Au NP/C_3N_4	20 vol% methanol aqueous solution	30 mg	300 W Xe lamp	>420 nm	35	This work
Au cluster-NP/C_3N_4	20 vol% methanol aqueous solution	30 mg	300 W Xe lamp	>420 nm	230	This work

S3. DFT calculation details

The first-principles density functional theory (DFT) calculations were performed using a plane wave basis set with the projector augmented plane-wave (PAW) method.[10,11] The exchange-correlation interaction was described within the generalized gradient approximation (GGA) in the form of PW91.[12] The energy cutoff was set to 400 eV, and the atomic positions were allowed to relax until the energy and force were less than 10^{-4} eV and 10^{-2} eV/Å, respectively. The graphitic carbon nitride was modeled in supercell geometry containing up to four tri-s-triazine units and the graphitic planes were separated by a vacuum region of 15 Å.

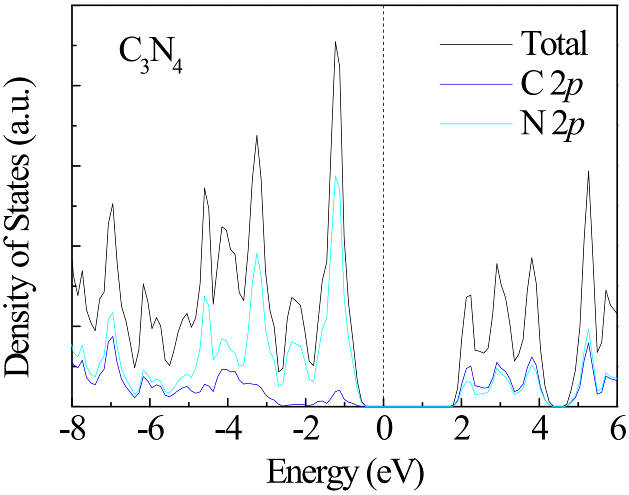

Figure S8. DOS plots of g-C_3N_4.

References

[1] Liu, J.; Liu, Y.; Liu, N.Y.; Han, Y.Z.; Huang, H.; Lifshitz, Y.; Lee, S.T.; ZHONG, J.; Kang, Z.H. Science **2015**, *347*, 970-974.

[2] Hou, Y.; Wen, Z.H.; Cui, S.M.; Guo, X.R.; Chen, J.H. *Adv. Mater.* **2013**, *25, 6291–6297.*

[3] Bai, S.; Yang, L.; Wang, C.; Lin, Y.; Lu, J.; Jiang, J.; Xiong, Y. *Angew. Chem. Int. Ed.* **2015**, *54*, 14810.

[4] Zhang, P.; Fujitsuka, M.; Majima, T. *Nanoscale*, **2017**, *9*,1520-1526.

[5] Yu, X. J.; Liu, F. Z.; Bi, J. L.; Wang, B.; Yang, S. C. *Nano Energy*, **2017**, *33*, 469-475.

[6] Shi, X. W.; Lou, Z. Z.; Zhang, P.; Fujitsuka, M.; Majima, T. *Appl. Mater. Interfaces*, **2016**, *8*,31738-31745.

[7] Naik, B.; Kim, S. M.; Jung, C.; Moon, S. Y.; Kim, S. H.; Park, J. Y. *Adv. Mater.*, **2014**, *1*,1300018.

[8] Samanta, S.; Martha, S.; Parida, K. *ChemCatChem*, **2014**, *6,* 1453-1462.

[9] Jiang J.; Yu, J.; Cao, S. W. J. *Colloid interf. Sci.* **2016***, 461*, 56-63.

[10] Furthmiiller, G. K. J. *Computufional Murerials Scienc***e** **1996***, 6*, 15.

[11] Lebègue, S.; Eriksson, O. *Phys. Rev. B* **2009**, *79*, 1.

[12] Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.