

# Ultrafast Spectroscopic Study of Plasmon-induced Hot Electron Transfer under NIR Excitation in Au Triangular Nanoprisms/g-C<sub>3</sub>N<sub>4</sub> for Photocatalytic H<sub>2</sub> Production

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## Section 1. Experimental Details

### 1.1 Synthesis

**Materials.** Materials used were melamine ( $\geq 99.0\%$ ), hexadecyltrimethylammonium chloride (CTAC,  $\geq 95\%$ ), hydrogen tetrachloroaurate(III) trihydrate (HAuCl<sub>4</sub>·H<sub>2</sub>O,  $\geq 99.999\%$ ), hydrogen hexachloroplatinate- (IV) hydrate (H<sub>2</sub>PtCl<sub>6</sub>·nH<sub>2</sub>O,  $\geq 99.9\%$ ), L-ascorbic acid ( $\geq 99.5\%$ ), potassium iodide ( $\geq 99.5\%$ ), sodium borohydride (NaBH<sub>4</sub>,  $\geq 99\%$ ), and silver nitrate ( $\geq 99\%$ ). All chemicals were used after purchased without further purification.

**Synthesis of g-C<sub>3</sub>N<sub>4</sub>.** The bulk g-C<sub>3</sub>N<sub>4</sub> was prepared by thermal condensation as follows: 5 g melamine was put into an alumina crucible with a cover and heated to 773 K for 2 h at a heating rate of 2 K min<sup>-1</sup> in a muffle furnace, then rising the temperature to 793 K at the same heating rate for another 2 h. The resulted product was collected and grounded into powder for further use. The g-C<sub>3</sub>N<sub>4</sub> nanosheet were prepared as follows: 0.45 g of bulk g-C<sub>3</sub>N<sub>4</sub> was uniformly dispersed into a alumina ark with dimensions of 50×30×10 mm to make sufficient contact between bulk g-C<sub>3</sub>N<sub>4</sub> and air, and then heated to 773 K in an open system at a heating rate of 2 K min<sup>-1</sup> for 3 h in a muffle furnace. Thus g-C<sub>3</sub>N<sub>4</sub> nanosheet was obtained.

**Synthesis of Gold Triangular Nanoprisms (Au TNPs).** Au TNPs were synthesized by seed-growth method, following previous publications from our group. Typically, Au seed was prepared firstly as follows: 25 μL 50 mM HAuCl<sub>4</sub> solution was added into 4.7 mL 0.1 M CTAC solution and then 300 μL 10 mM NaBH<sub>4</sub> solution was added under vigorous stirring. The mixture solution was kept for stirring for 2 h at room temperature.

The Au seed solution was diluted 10 times in 0.1 M CTAC solution for further use. Next, two kinds of growth solutions were prepared. 1.6 mL 0.1 M CTAC solution, 80  $\mu\text{L}$  10 mM  $\text{KI}_3$ , 40  $\mu\text{L}$  50 mM  $\text{HAuCl}_4$  and 40  $\mu\text{L}$  0.1 M L-ascorbic acid were added step by step into 8 mL of Milli-Q water which was labeled as A solution. 400  $\mu\text{L}$  10 mM  $\text{KI}_3$ , 500  $\mu\text{L}$  50 mM  $\text{HAuCl}_4$  and 400  $\mu\text{L}$  0.1 M L-ascorbic acid were added step by step into 40 mL 50 mM CTAC solution which was labeled as B solution. Then, 200  $\mu\text{L}$  diluted Au seed solution was added into A solution with shaking and 3.2 mL A solution was added into B solution quickly. The mixture solution was shaken for several seconds and then left undisturbed at room temperature for 1 h for complete growth of Au TNPs. Purification of Au TNPs was done as follows: 200  $\mu\text{L}$  25 wt% CTAC was added into above-mentioned solution and then the solution was left alone for overnight. After that, suspension liquid of solution was removed and precipitate was left on the bottom. 10 mL 20 mM CTAC was added into the bottle and green solution was obtained after ultrasonic treatment. 0.33 mg  $\text{Au}^0$  was obtained (calculated by the results of ICP measurement).

**Synthesis of Au TNPs/g- $\text{C}_3\text{N}_4$ .** 50 mg g- $\text{C}_3\text{N}_4$  was dispersed in 10 mL aqueous solution containing 100  $\mu\text{L}$   $\text{NH}_3\cdot\text{H}_2\text{O}$  and 200  $\mu\text{L}$  3-mercaptopropionic acid (3-MPA), and then was kept for stirring for 12 h. Au TNPs solution was washed with  $\text{H}_2\text{O}$  thoroughly to remove the CTAC and then dispersed in aqueous solution for the further use. A calculated volume of Au TNPs solution was added into above g- $\text{C}_3\text{N}_4$  solution. After ultrasonic treatment for 30 min and stirring for 12 h, the mixture was centrifuged, washed with water and ethanol, freeze dried to obtain the final product.

## 1.2 Characterizations

The samples were characterized by X-ray diffraction (XRD, Rigaku, Rint-2500, Cu  $\text{K}\alpha$  source), and TEM (JEOL JEM-2100, operated at 120 kV). UV-vis diffuse reflectance spectra were obtained on a JASCO V-770 UV-vis/NIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was measured on a JEOL JPS-9010 MC spectrometer.

## 1.3 Photocatalytic $\text{H}_2$ production tests.

Typically, 50 mg samples were dispersed in 50 mL aqueous solution containing 20 vol % methanol as the sacrificial electron donor. The suspension was thoroughly degassed under Ar gas flow and irradiated by a xenon lamp (Asahi Spectra, LAX-C100) with magnetic stirring at room temperature. A 780-nm cutoff filter was used to remove the UV-visible light. The volume of H<sub>2</sub> was measured by using Shimadzu GC-8A gas chromatograph equipped with an MS-5A column and a thermal conductivity detector.

#### **1.4 Finite-difference-time-domain (FDTD) calculations.**

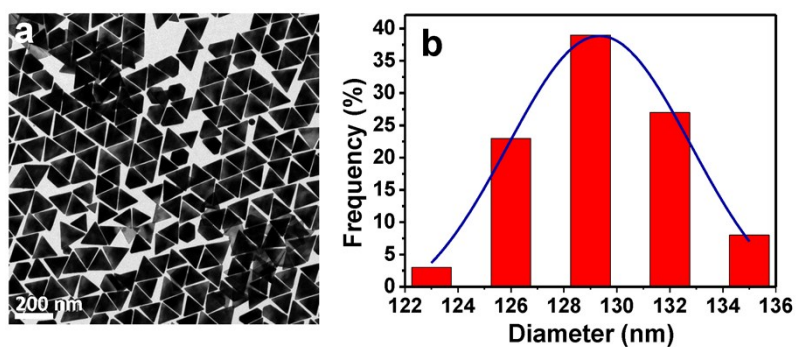
The computational simulations were performed by using the method of finite-difference-time-domain (FDTD), a software package, FDTD Solutions 8.19 (Lumerical Solutions, Inc.). The override mesh cell size was  $1 \times 1 \times 0.1 \text{ nm}^3$ . The optical constant of Au was adopted from tabulated values for bulk gold measured by Johnson and Christy. During the calculation, an electromagnetic pulse in the wavelength range from 780 to 1600 nm was launched into a box containing a target nanostructure. The size of TNPs was modeled as a triangular nanoplate with length of 140 nm and thickness of 6 nm. The refractive index of the medium (water) was set to be 1.33.

#### **1.5 Time-resolved transient absorption measurements.**

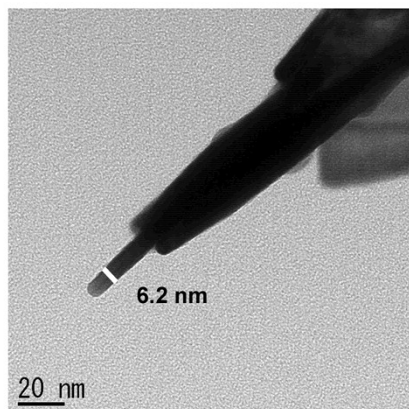
The femtosecond transient absorption spectra were measured by the pump and probe method using a regenerative amplified titanium sapphire laser (Spectra-Physics, Spitfire Pro F, 1 kHz) pumped by a Nd:YLF laser (Spectra-Physics, Empower 15). The seed pulse was generated by a titanium sapphire laser (Spectra-Physics, Mai Tai VFSJW; FWHM 80 fs). The output of the optical parametric amplifier was used as the excitation pulse. A white light continuum pulse, which was generated by focusing the residual of the fundamental light on a sapphire crystal after the computer controlled optical delay, was divided into two parts and used as the probe and the reference lights, of which the latter was used to compensate the laser fluctuation. Both probe and reference lights were directed to the sample and the transmitted lights were detected by a linear InGaAs array detector equipped with the polychromator (Solar, MS3504). The pump pulse was chopped by the mechanical chopper synchronized to one-half of the laser repetition rate, resulting in a pair of spectra with and without the pump, from which the absorption change (% absorption) induced by the pump pulse was estimated.

All measurements were carried out at room temperature.

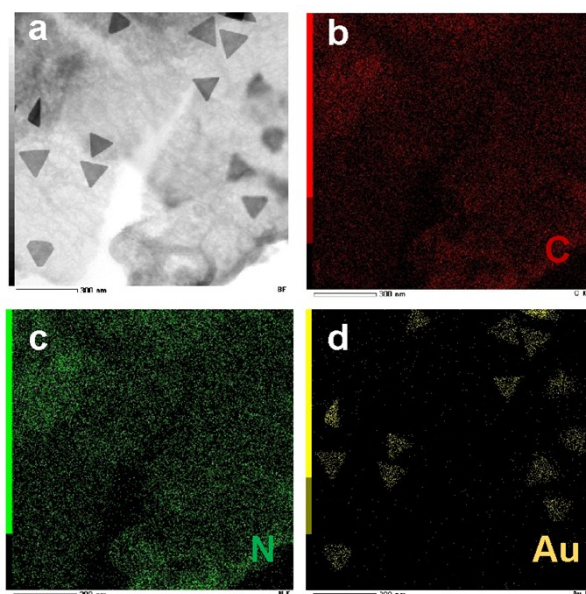
## Section 2. Supplementary Data



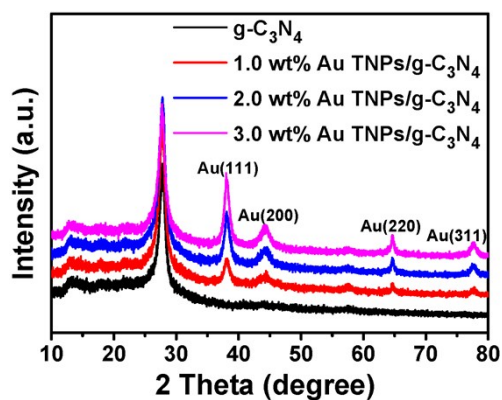
**Figure S1.** TEM image of Au TNPs (a) and size distribution of Au TNPs (b).



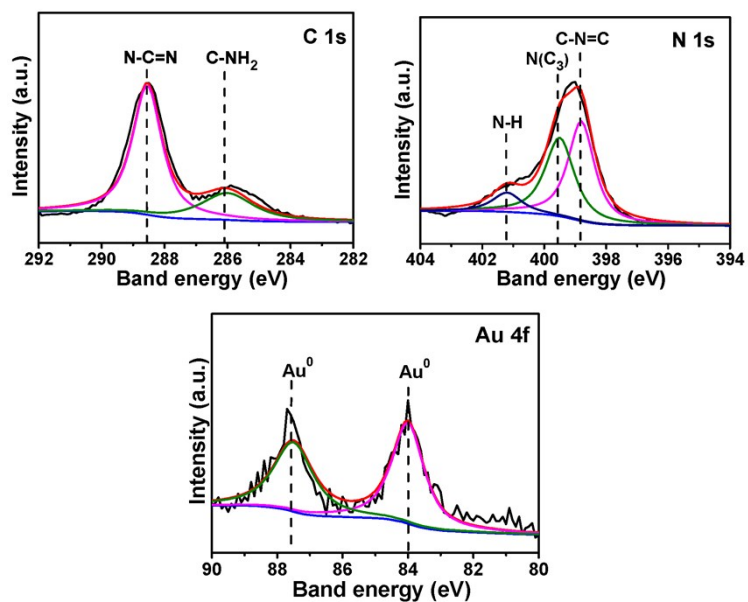
**Figure S2.** TEM image of Au TNPs with vertical view.



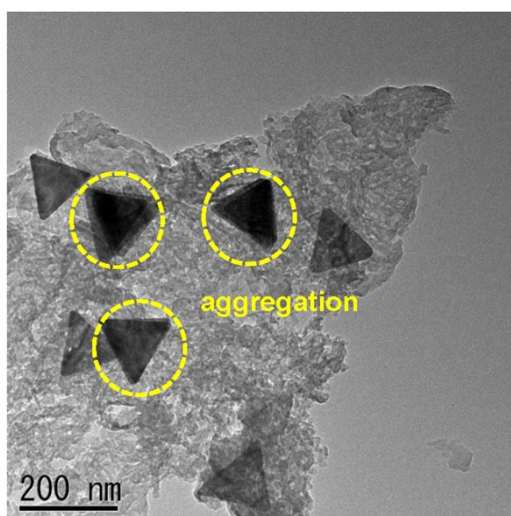
**Figure S3.** TEM image of Au TNPs/g-C<sub>3</sub>N<sub>4</sub> (a). Elemental mappings of C (b), N (c), and Au (d). Scale bar: 300 nm.



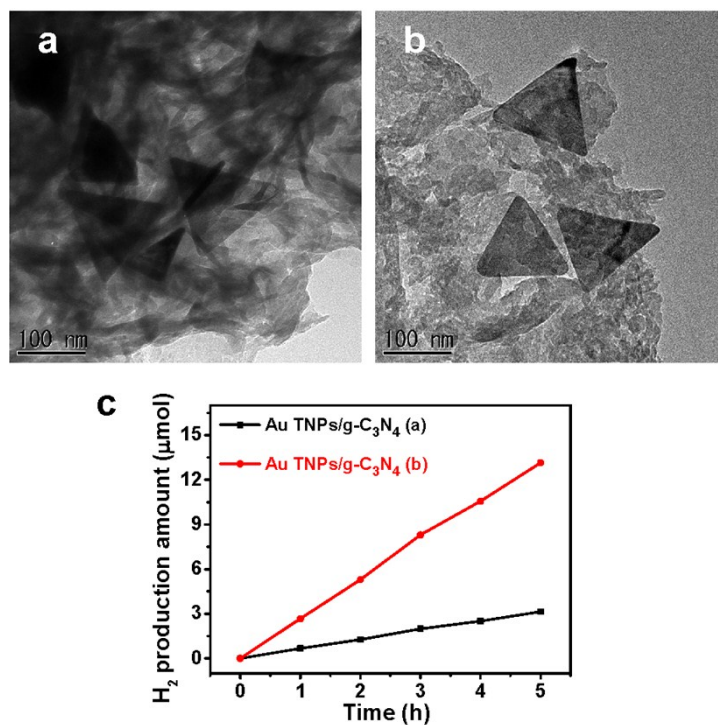
**Figure S4.** XRD patterns of  $g\text{-C}_3\text{N}_4$  and Au TNPs/ $g\text{-C}_3\text{N}_4$ .



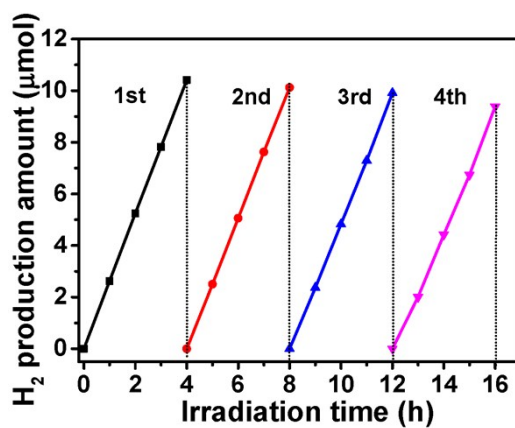
**Figure S5.** XPS spectra of C 1s, N 1s and Au 4f of Au TNPs/ $g\text{-C}_3\text{N}_4$ .



**Figure S6.** TEM image of 3.0 wt% Au TNPs/g-C<sub>3</sub>N<sub>4</sub>.



**Figure S7.** TEM images of Au TNPs loaded on g-C<sub>3</sub>N<sub>4</sub> synthesized by a traditional method (a) and g-C<sub>3</sub>N<sub>4</sub> prepared with better exfoliation (b). Time courses photocatalytic H<sub>2</sub> production over two samples under NIR light irradiation.



**Figure S8.** Recyclability of Au TNPs/g-C<sub>3</sub>N<sub>4</sub> for photocatalytic H<sub>2</sub> production under NIR light irradiation.

## References

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