## **Electronic Supporting Information**

# Isolation of Single Pt Atom in a Sliver Cluster: Forming Highly Efficient Silver-based Cocatalysts for Photocatalytic

### **Hydrogen Evolution**

Xu Lei Du,<sup>a,†</sup> Xue Lu Wang,<sup>a,†</sup> Yu Hang Li,<sup>a</sup> Yu Lei Wang,<sup>a</sup> Jun Jie Zhao,<sup>a</sup> Li Jun Fang,<sup>a</sup> Li Rong Zheng,<sup>b</sup> Hua Tong,<sup>c</sup> and Hua Gui Yang<sup>a,\*</sup>

<sup>a</sup> Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China

<sup>b</sup> Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup> School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China

\*Corresponding Author

E-mail for H. G. Yang: <u>hgyang@ecust.edu.cn.</u>

#### **Experimental Section:**

#### 1. Synthetic procedures

**Synthesis of pristine g-C<sub>3</sub>N<sub>4</sub>.** The g-C<sub>3</sub>N<sub>4</sub> was synthesized following a reported protocol.<sup>1</sup> 18 g of urea was heated at 600 °C (ramp rate, 5 °C min<sup>-1</sup>) for 2 h in a 50 mL closed alumina crucible placed inside muffle furnace.

Synthesis of Ag<sub>25</sub>(SPhMe<sub>2</sub>)<sub>18</sub>PPh<sub>4</sub>. Ag<sub>25</sub>(SPhMe<sub>2</sub>)<sub>18</sub>PPh<sub>4</sub> was prepared via the reported method by Bakr et al.<sup>2</sup> AgNO<sub>3</sub> (37 mg, 0.22 mmol) was dissolved in 2.5 mL methanol and 17 mL DCM (Dichloromethane) with sonication. Then, 2,4-dimethylbenzenethiol (90  $\mu$ L, 0.66 mmol) was added under vigorously stirred (~ 1200 rpm), and the solution turned from a colorless transparent solution to a yellow turbid liquid. Next, a freshly prepared solution of PPh<sub>4</sub>Br (~ 6 mg, 0.014mmol) in methanol (0.5 mL) was added. The solution was stirred for 20 minutes under ice-bath. After that, 0.5 mL freshly prepared ice-cold aqueous NaBH<sub>4</sub> (30 mg/mL) was added drop-wise. The reaction was allowed to proceed overnight. After that, the aqueous layer was removed, and the DCM solution was centrifuged and the obtained supernatant was concentrated by evaporating solvents. Then 20 mL methanol was used to precipitate the synthesized nanoclusters (NCs). The methanol that contains the redundant SPhMe<sub>2</sub> and by-products was discarded. The precipitate obtained was then dissolved into DCM that produced Ag<sub>25</sub>(SPhMe<sub>2</sub>)<sub>18</sub>PPh<sub>4</sub> NCs.

**Synthesis of**  $[Pt_1Ag_24(SPhMe_2)_{18}](PPh_4)_2$ . The synthesis of  $[Pt_1Ag_{24}(SPhMe_2)_{18}](PPh_4)_2$  was carried out as literature.<sup>3</sup> About 30 mg of AgNO<sub>3</sub> and 4 mg of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O were dissolved in a solvent mixture of 5 mL of methanol and 15 mL of ethylacetate with sonication. After that, 2,4-dimethylbenzenethiol (90 µL, 0.66 mmol) was added. Subsequently, after 15 minutes of reaction, ice-cold aqueous NaBH<sub>4</sub> (20 mg/mL) was added. The whole reaction was continued for 24 hours in nitrogen environment. The solvents were evaporated using a rotary evaporator. The product of NCs was extracted into methanol, which was subsequently precipitated by the addition of PPh<sub>4</sub>Br. The precipitate of NCs was collected by centrifugation and dissolved in DCM.

Synthesis of Ag<sub>25</sub>/g-C<sub>3</sub>N<sub>4</sub> and Pt<sub>1</sub>Ag<sub>24</sub>/g-C<sub>3</sub>N<sub>4</sub>. Typically, g-C<sub>3</sub>N<sub>4</sub> bulk (0.1 g) were added into the mixed solution of DCM and toluene (v : v = 1:1, total volume is 10 mL) followed by sonication for 2 h.  $M_1Ag_{25}(SR)_{18}$  (M=Ag or Pt) (metal content, measured by ICP-AES, is about 0.2 mg) was added in the above mixture. After stirring for 12 h

at room temperature, the supernatant became colorless. The catalysts were collected by centrifugation (3000 rpm, 1 min), and was dried at room temperature in vacuum, followed by annealing at 150 °C for 2 h in Ar atmosphere. ICP-AES analysis indicates that the loading amount of the metal on the support is about 0.2 wt%.

Synthesis of Ag/g-C<sub>3</sub>N<sub>4</sub>. Appropriate amount of AgNO<sub>3</sub> aqueous solution was added into the pristine g-C<sub>3</sub>N<sub>4</sub> powder and maintained at 80 °C for 1 h. After being dried, the products were calcined at 150 °C for 2 h in Ar atmosphere.

Synthesis of Pt/g-C<sub>3</sub>N<sub>4</sub>. The photodeposition process was carried out as literature.<sup>4</sup> Typically, 100 mL of deionized water, a certain amounts of catalyst and metal precursor (H<sub>2</sub>PtCl<sub>6</sub>) were added into the solution. The system was evacuated several times to completely remove the dissolved air, and it was irradiated under UV-Vis ( $\lambda > 300$  nm) for 4 hours to sufficiently reduce the metal cations. After that, the samples were filtered and washed with deionized water. The solids were obtained after dried in a vacuum oven at 60 °C for 12 h.

#### 2. Characterization methods

All NCs were analyzed in the negative ionization mode in electrospray ionization mass spectrometry (ESI-MS) by a ThermoFisher Q Exactive mass spectrometer. The morphologies and structures of the samples were analyzed by transmission electron microscopy (TEM, TECNAI 30, 300 kV). The crystal structure of catalysts was studied by X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer with Cu K<sub>a</sub> radiation). Infrared transmission was measured using a Fourier transform infrared (FT-IR) spectrophotometer Spectrum (Nicolet). The C 1s peak at 284.9 eV was adopted as an internal reference in this work. UV-vis diffuse reflection spectra were carried out with a UV-vis spectrophotometer (CARY 500). The Pt and Ag contents in the samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian 710ES). X-ray photoelectron spectroscopy (XPS, ESCALAB250, Al Ka radiation) measurements were used to study the surface binding elements and element content. Pt L<sub>3</sub>-edge absorption spectra (extended X-ray absorption fine structure spectroscopy, EXAFS) were performed on the 1W1B beamline of the Beijing Synchrotron Radiation Facility, China, operated at ~ 200 mA and ~ 2.5 GeV.

#### 3. Photoelectrochemical measurements

Electrochemical measurements were performed using an electrochemical workstation

(CHI 660E) with a standard three-electrode photoelectrochemical cell. The Pt foil and Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The working electrodes were prepared as follows: Fluoride tin oxide (FTO) conductor glass with 1.0 cm<sup>2</sup> exposing area was used to prepare the working electrode. 10 mg catalyst was well dispersed in 50 µL naphthol and 200 µL dimethyl formamide (DMF). After ultrasonic treatment for 30 min, 10 µL slurry was painted onto the prepared FTO glass and then dried naturally. 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution with 10 vol% triethanolamine (TEOA) were used as the electrolyte. The photoresponse of the prepared photoelectrodes (I-t) was operated by measuring the photocurrent densities under chopped light irradiation at a bias potential of - 0.6 V vs. Ag/AgCl. The transient open-circuit voltage decay (OCVD) measurements were taken for 800 s in all, and the light on and off were controlled at 200 s and 400 s from the start, respectively. The average lifetime of the photogenerated carriers ( $\tau_n$ ) were obtained from the OCVD according to Equation (1):

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

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

#### 4. Photocatalytic reactions

Photocatalytic H<sub>2</sub> production reaction is performed in a 300 mL top irradiation type Pyrex cell connected to a gas-closed-circulation and evacuation system. The amount of evolved H<sub>2</sub> was monitored by an online gas chromatography (Shimadzu 2014C, TCD detector, argon as carrier gas, 5 Å molecular sieve column). Typically, 30 mg photocatalyst powder was dispersed in 100 mL 10 vol% triethanolamine aqueous solution. A 300 W Xe arc lamp (CEL-HXBF300) eliminated ultraviolet light by an optical cut-off filter was used as the visible light source ( $\lambda > 420$  nm). The turbid solutions were put in ultrasonic bath for 10 min before the reaction and stirred during the test procedure in order to eliminate sedimentation. In order to determine the photocatalytic reaction rate, the H<sub>2</sub> product amount was tested every 30 min during 2 h. To test the photocatalytic stability of the obtained Pt<sub>1</sub>Ag<sub>24</sub>/g-C<sub>3</sub>N<sub>4</sub>, the system was irradiated for 12 h and evacuated every 4 h. Before irradiation, no air was present in the gas-closed-circulation system after evacuation thoroughly by vacuum pump.

#### 5. Calculation of the turnover frequency (TOF)

$$TOF(Ag_{25}/g-C_{3}N_{4\ 0.2\ wt\%}) = \frac{n(H_{2})}{n(Ag)\cdot\tau} = \frac{9.1\times10^{-6}mol}{\frac{30\cdot10^{-3}\cdot0.2\%}{108}\cdot\text{h}} = 16.38\ \text{h}^{-1}$$
$$TOF(Ag-NPs-C_{3}N_{4\ 1wt\%}) = \frac{n(H_{2})}{n(Ag)\cdot\tau} = \frac{2.9\times10^{-6}mol}{\frac{30\cdot10^{-3}\cdot1\%}{108}\cdot\text{h}} = 1.04\ \text{h}^{-1}$$



Fig. S1 Typical TEM images and size distributions of (a)  $Ag_{25}(SR)_{18}$ , (b)  $Pt_1Ag_{24}(SR)_{18}$ , (c)  $Ag_{25}(SR)_{18}/g$ -C<sub>3</sub>N<sub>4</sub> and (d)  $Pt_1Ag_{24}(SR)_{18}/g$ -C<sub>3</sub>N<sub>4</sub>.



Fig. S2 S 2p XPS spectra of  $Pt_1Ag_{24}/C_3N_4$  before (gray) and after (black) calcination.



Fig. S3 (a) XRD patterns and (b) FT-IR spectra of g-C<sub>3</sub>N<sub>4</sub>, Ag<sub>25</sub>/g-C<sub>3</sub>N<sub>4</sub> and Pt<sub>1</sub>Ag<sub>24</sub>/g-C<sub>3</sub>N<sub>4</sub>.



Fig. S4 UV-vis absorption spectra of  $g-C_3N_4$ ,  $Ag_{25}/g-C_3N_4$  and  $Pt_1Ag_{24}/g-C_3N_4$ .



Fig. S5 (a) C 1s, (b) N 1s, (c) Ag 3d and (d) Pt 4f XPS spectra of  $Pt_1Ag_{24}/g$ -C<sub>3</sub>N<sub>4</sub>. (e) The normalized X-ray absorption near-edge structure spectra at the Pt L<sub>3</sub>-edge of the Pt foil, PtO<sub>2</sub> and Pt\_1Ag\_{24}/g-C<sub>3</sub>N<sub>4</sub> photocatalyst. (f) The k<sup>3</sup>-weighted Fourier transform spectra from EXAFS.



Fig. S6 Ag 3d XPS spectrum of  $Ag_{25}/g$ - $C_3N_4$ .



Fig. S7 Photocatalytic activity of  $Ag/g-C_3N_4$  with different loading amounts of Ag via impregnation.



Fig. S8 Typical TEM images of Ag/g-C<sub>3</sub>N<sub>4</sub>.



**Fig. S9** Photocatalytic activity of as-prepared catalysts before  $(Ag_{25}(SR)_{18}/g-C_3N_4 \& Pt_1Ag_{24}(SR)_{18}/g-C_3N_4)$  and after annealing  $(Ag_{25}/g-C_3N_4 \text{ and } Pt_1Ag_{24}/g-C_3N_4)$ .



**Fig. S10** Comparison of the photocatalytic activity of 0.016 wt% Pt/g-C<sub>3</sub>N<sub>4</sub>, 0.2 wt% Pt/g-C<sub>3</sub>N<sub>4</sub> and Pt<sub>1</sub>Ag<sub>24</sub>/g-C<sub>3</sub>N<sub>4</sub> for the H<sub>2</sub> production.

|            |                                 | $Pt_1Ag_{24}(SR)_{18}$ | $Pt_1Ag_{24}/g-C_3N_4$ | Theoretical ratio |
|------------|---------------------------------|------------------------|------------------------|-------------------|
|            |                                 | NCs                    |                        |                   |
| ICP ratio  | Ag                              | 95.64                  | 95.78                  | 96                |
| (atomic %) | Pt                              | 4.36                   | 4.22                   | 4                 |
| Catalyst   | g-C <sub>3</sub> N <sub>4</sub> | /                      | 99.7796                | /                 |
| Weight     | Ag                              | /                      | 0.204                  | /                 |
| (mg)       | Pt                              | /                      | 0.0164                 | /                 |

Table S1 Normalized atom ratio of Pt/Ag in ICP-AES of pure  $Pt_1Ag_{24}(SR)_{18}$  NCs and  $Pt_1Ag_{24}/g-C_3N_4$ .

For  $Pt_1Ag_{24}(SR)_{18}$ , NCs was dispersed in DCM.  $100\mu L Pt_1Ag_{24}(SR)_{18}$ /DCM was dissolved in nitric acid and made constant volume to 10 mL by adding deionized water. Raw data: 10mg/L (Ag), 0.83mg/L (Pt).

For  $Pt_1Ag_{24}/g$ -C<sub>3</sub>N<sub>4</sub>, 10 mg catalyst was dissolved in nitric acid and made constant volume to 10 mL by adding deionized water. Raw data: 2 mg/L (Ag), 0.16mg/L (Pt).

#### References

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