Protocol

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Publisher’s note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.
Protocol on irradiation-dark photochemical deposition and characterization of metal nanoclusters on semiconductor support

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https://doi.org/10.1016/j.xpro.2022.101459

SUMMARY

Controlling the size and uniform dispersion of noble metal nanoclusters on the metal oxide based semiconductor are difficult due to the natural tendency for metal atoms to agglomerate. Here, we present the protocol for an “irradiation-dark” photochemical deposition to obtain uniform metal nanoclusters on semiconductor support, and the protocol for measuring the size and size distribution of metal nanoclusters. For complete details on the use and execution of this protocol, please refer to Wu et al. (2022).

BEFORE YOU BEGIN

The photodeposition method has demonstrated to be an effective strategy for the deposition of noble metals on semiconductor supports. However, traditional photodeposition easily forms Schottky junctions between metals and semiconductors, causing rapid electron transfer and resulting in uncontrollable growth rates and the preferred formation of large nanoparticles. In this work, an “irradiation-dark” (i.d.) process was developed to control the particle size. Different from the traditional “irradiation” (i.) method, firstly, Ti$^{3+}$ is obtained as a charge storage form on the surface of TiO$_2$, and then the stored photogenerated electrons are used to reduce noble metal precursors in the dark, thereby controlling the nucleation and growth process of noble metal nanoparticles to gain uniform nanoclusters.

Preparation of metal precursor solutions

© Timing: 30 min

1. Prepare a 0.01 g/mL HAuCl$_4$·4H$_2$O aqueous solution. Measure 1.0 g of HAuCl$_4$·4H$_2$O (Figure 1A), dilute with deionized water to 100 mL (Figure 1B).
2. Prepare a 0.01 g/mL Pt(NH$_3$)$_4$(OH)$_2$·xH$_2$O aqueous solution. Measure 1.0 g of Pt(NH$_3$)$_4$(OH)$_2$·xH$_2$O, dilute with deionized water to 100 mL.
3. Prepare a 0.01 g/mL PdCl$_2$ aqueous solution. Measure 1.0 g of PdCl$_2$ and add 200 $\mu$L concentrated HCl (37%) and deionized water to dissolve, dilute it to 100 mL.
4. Prepare a 0.02 g/mL AgNO$_3$ aqueous solution. Measure 0.2 g of AgNO$_3$, dilute with deionized water to 10 mL. The corresponding devices are shown in Figure 1.
5. Store the prepared solutions at 4°C and must keep them in dark.

△ CRITICAL: Except the AgNO$_3$ aqueous solution which can only be used in 1 h, the other solutions can be stored for a week. AgNO$_3$ is easily photodegraded into Ag NPs in an
aqueous environment (Mahlman and Willmarth, 1964). In order to avoid the influence of photodegradation, all AgNO₃ aqueous solutions in this experiment must be prepared fresh before the experiments.

**Preparation of equipment**

**Timing**: 1.5 h

Preheat the photochemical reaction equipment.

6. Set the cooling water temperature to 13.5°C. Turn on the circulating cooling water pump (Figure 2D), and adjust the power of the lamp to 1000 W (Figure 2E).

7. Add 300 mL of deionized water and magnets to the 500 mL quartz photoreactor (Figure 2F). Turn on the Hg lamp (Figure 2H) and magnetic stirring (Figure 2C). Adjust the power to 1000 W (10 A × 100 V), start timing.

8. After the lamp stabilizes for 1 h, turn off the light source.

9. Prepare the N₂ generator (Figure 2A). Adjust the outlet pressure to 0.4 MPa. To ensure the purity of N₂ gas and control the O₂ concentration within 3 ppm, after turning on the gas generator, open the vent valve, and use it after venting for 30 min. N₂ gas cylinder (99.9 %) is also an option if the N₂ generator is unavailable.

10. Purge the deionized water in the quartz photoreactor with N₂. Adjust the N₂ flow rate to 40 mL/min through a flow meter.

△**CRITICAL**: To ensure the purity of the gas produced by the gas generator, it is necessary to regularly check and replace the adsorbent in the filter device.

**KEY RESOURCES TABLE**

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | Macklin | CAS: 1314-23-4 |
| Zirconium dioxide (≥ 99.7% A.R.) | Macklin | CAS: 1314-23-4 |
| Rutile titanium dioxide (≥ 99.5% C.P.) | Sigma-Aldrich | CAS: 1317-80-2 |

(Continued on next page)
## MATERIALS AND EQUIPMENT

### Alternative sources for reagents

| Reagent or resource | Alternate sources                                      |
|---------------------|--------------------------------------------------------|
| Chemicals, peptides, and recombinant proteins |                                           |
| Zirconium dioxide | Aladdin; Sigma-Aldrich                                  |
| Rutile titanium dioxide | Aladdin                                             |
| Anatase titanium dioxide | Aladdin                                           |
| Tetraammineplatinum (II) hydroxide hydrate | Aladdin                                      |
| Chloroplatinic acid hexahydrate | Aladdin; Sigma-Aldrich                                  |
| Chloroauric acid tetrahydrate | Aladdin; Sigma-Aldrich                                   |
| Palladium chloride | Aladdin; Sigma-Aldrich                                   |
| Silver nitrate | Aladdin; Sigma-Aldrich                                   |
| Methanol | Aladdin; Sigma-Aldrich                                   |
| P25 titanium dioxide | Sigma-Aldrich                                       |
| HAuCl₄ 4H₂O aqueous solution |                                           |

### HAuCl₄ 4H₂O aqueous solution

| Reagent | Final concentration | Volume to 100 mL |
|---------|---------------------|------------------|
| HAuCl₄ 4H₂O | 0.01 g/mL | 1.0 g |
| deionized water | 100 mL |          |

Store at 4°C. Use within 1 week.
### Synthesis of M(i.)/TiO₂

**Timing:** 10.6 h

The samples prepared by the conventional photodeposition strategy were selected as the control group. In the presence of methanol (sacrificial reagent), the TiO₂ suspension to which the noble metal precursor salt was added was exposed to the irradiation of a Hg lamp. The photogenerated electrons transition to the surface of TiO₂ to reduce the metal precursor salt to form metal nanoparticles on TiO₂, and the photogenerated holes transition to the surface of TiO₂ to oxidize the sacrificial reagent (Haselmann et al., 2020; Meng et al., 2016; Wenderich and Mul, 2016).

1. Add 0.3 g TiO₂ powder to a beaker filled with 720 mL of deionized water, ultrasonically treat it for 30 min, and the ultrasonic power is 360 W.
2. Add 100 mL of anhydrous methanol and 10 mL diluted noble metal precursor salt aqueous solution such as HAuCl₄·4H₂O (1.57 mg/mL), Pt(NH₃)₄(OH)₂·xH₂O (1.14 mg/mL), AgNO₃ (0.59 mg/mL), and PdCl₂ (1.25 mg/mL). Stir at 2000 r/min for 10 min.
3. Transfer the reaction solution to a quartz photoreactor, purge N₂ gas (40 mL/min), seal the reactor with rubber stoppers and parafilm.
4. Turn on the 1000 W Hg lamp (working wavelength as 365 nm) and adjust the intensity of the irradiation to 74 mW/cm², detected by an optical power meter (THORLABS PM100D).
5. The irradiation reaction was performed for 30 min at around 20°C.

**Critical:** During the photoreaction process, keep the door of the reaction box closed. Do not look directly at the lamp. Wear optical protective glasses to avoid possible damage to the eyes when opening the door of the reaction box.

6. Separate the suspension through suction filtration with a 50 mm alcohol membrane with 0.45 µm aperture size to collect the solid precipitate.
7. Dry for 8 h at 60°C in the dark, and grind and collect the powders.

### Tables

#### Pt(NH₃)₄(OH)₂·xH₂O aqueous solution

| Reagent                  | Final concentration concentrations | Volume to 100 mL |
|--------------------------|----------------------------------|-----------------|
| Pt(NH₃)₄(OH)₂·xH₂O       | 0.01 g/mL                        | 1.0 g           |
| deionized water          |                                  | 100 mL          |

Store at 4°C. Use within 1 week.

#### PdCl₂ aqueous solution

| Reagent | Final concentration concentrations | Volume to 100 mL |
|---------|----------------------------------|-----------------|
| PdCl₂   | 0.01 g/mL                        | 1.0 g           |
| HCl (37%) |                                | 200 µL          |
| deionized water |                            | 99.8 mL         |

Store at 4°C. Use within 1 week.

#### AgNO₃ aqueous solution

| Reagent | Final concentration concentrations | Volume to 10 mL |
|---------|----------------------------------|-----------------|
| AgNO₃  | 0.02 g/mL                        | 0.2 g           |
| deionized water |                        | 10 mL           |

Store at 4°C. Prepare within 1 h.
8. The catalyst obtained by this method is labeled M(i.d.)/TiO$_2$(A/R), where (i.d.) means irradiation deposition, and A or R means that the crystal of TiO$_2$ is anatase or rutile.

9. Here, the loading amount of noble metals is 2.5 wt. %.

△ CRITICAL: After the precursor is added, the solution should be kept in the dark before the irradiation.

**Synthesis of M(i.d.)/TiO$_2$**

**Timing:** 9.5 h

In this work, an “irradiation-dark” (i.d.) process was developed to control the particle size. Different with the i. process, the TiO$_2$ suspension is containing methanol as sacrificial reagent was exposed to Hg lamp irradiation for 1 h. The TiO$_2$ was then reduced by the photoelectrons to get oxygen vacancy and Ti$^{3+}$ species with the white TiO$_2$ suspension changes to blue. Turn off the light, noble metal precursor then is added and reduced by the Ti$^{3+}$ species to form metal nanoclusters. The aqueous salt solution could be HAuCl$_4$$\cdot$4H$_2$O, Pt(NH$_3$)$_4$(OH)$_2$$\cdot$xH$_2$O, AgNO$_3$, and PdCl$_2$.

10. Add 0.3 g of TiO$_2$ powder to 720 mL deionized water, ultrasonicate for 30 min with an ultrasonic power of 360 W, then add 100 mL of anhydrous methanol.

11. Irradiation reaction stage: transfer the TiO$_2$ suspension to the photoreactor.
12. Purge N₂ (40 mL/min) into the photoreactor and stir at 2000 r/min. Seal the reactor with rubber stoppers and parafilm. See Figure 3A.

13. Turn on the Hg lamp (74 mW/cm²), and react in the irradiation for 30 min in the presence of circulating cooling water. See Figure 3B.

14. Dark reaction stage: turn off the light, take out the quartz jacket, keep stirring and maintain the N₂ flow.

15. Add 10 mL diluted noble metal precursor salt solution such as HAuCl₄•4H₂O (1.57 mg/mL), Pt(NH₃)₄(OH)₂·xH₂O (1.14 mg/mL), AgNO₃ (0.59 mg/mL), and PdCl₂ (1.25 mg/mL) to the reactor within 3 s with a 10 mL disposable dropper.

16. React for 30 min in the dark. See Figures 3C and 3D.

17. Separate the suspension through suction filtration. Collect the solid precipitate.

18. Dry for 8 h at 60°C in the dark, grind and collect the powders.

19. The catalyst obtained by this method is labeled M(i.d.)/TiO₂(A/R), where (i.d.) means irradiation-dark deposition, and A or R means that the crystal phase of TiO₂ is anatase or rutile.
CRITICAL: Be careful when moving out the quartz jacket since the Hg lamp is very hot. When the dropwise addition of the precursor solution is completed, the gap between the reactor and the light source liner is sealed again with a parafilm. The interval time (in 30 min) from the end of the irradiation to the addition of the metal precursor solution has negligible effect on the loading amount, as shown in Figure 4.

CRITICAL: The interval of adding the precursor solution after turning off the light is also used to deposit noble metals on other phases of TiO$_2$ (anatase and P25) and semiconductors (ZrO$_2$), and the experimental process is the same as M(i.d.)/TiO$_2$(R).

**Structural characterization of M(i.d.)/TiO$_2$ and M(i.d.)/TiO$_2$**

In order to characterize the size of noble metal particles deposited on TiO$_2$, high-resolution electron transmission microscope (HRTEM) and scanning transmission electron microscopy (STEM) are applied.

20. Take the sample powder (about 2.0 mg) into a 5.0 mL disposable sample tube.
21. Add 4 mL of absolute ethanol and sonicate for 20 min in a 360 W ultrasonic instrument.

△ CRITICAL: During the ultrasonic process, shake it vigorously to ensure that the powder is evenly dispersed in the alcohol solution. It is better that the final solution has weak optical rotation. The best ultrasound time is about 15–20 min. If the time is too short, the dispersion will not be good, which will affect the shooting process.

22. Copper mesh (Hengxin, HCF300-Cu) coated with ultra-thin carbon film is put on filter paper. Changing the specification from 300 item that we used to 200 item is also an alternative option. Cu should be changed to other metals such as Ni or Mo if the particles of copper itself are tested.
23. Use a disposable dropper to suck 7–8 drops of the suspension and add them to the copper mesh.
24. Put the copper mesh with the sample in the infrared rapid drying oven for 10 min, and then the HRTEM or the STEM test can be carried out.

Note: The samples can also be dried naturally.

25. Fix the prepared sample on the sample rod and insert it into the HRTEM (JEOL, JEM-2010F and 2100F) microscope for testing. All tests are carried out at a high voltage of 200 kV.
26. Analyze the size of metals and supports according to the HRTEM images. We can distinguish noble metals and the support by contrast, the ones with large contrast are noble metals, and those with small contrast are titanium oxides.

27. Analyze the $\text{M(i.)/TiO}_2(\text{R})$.
   a. The average particle size of Au, Ag, Pt, Pd supported on TiO$_2$(R) are 12.8 nm, 11.1 nm, 3.4 nm and 3.2 nm, respectively (Wu et al., 2022). The particles are large and the agglomeration is apparent (Figures 5A–5D).
   b. According to the HRTEM images of $\text{M(i.d.)/TiO}_2(\text{R})$: The average particle size of Au, Ag, Pt, Pd supported on TiO$_2$(R) are 0.6 nm, 0.5 nm, 0.5 nm and 0.7 nm, respectively (Wu et al., 2022). The particles are smaller, and the size is well controlled (Figures 5E–5H).

28. STEM can also demonstrate the deposition of noble metal particles, showing in Figure 6.

29. XRD is used to analyze the crystal structure of materials (Lupescu et al., 2018). By analyzing the peaks, the size of noble metals supported on TiO$_2$ can be explored.

30. Increase the voltage of the device (D/MAX2200V) to 40 kV and the current to 40 mA. The scanning range is 30°–50° (It can be adjusted depending on different metals), and the scanning speed is 10 °/min.

Figure 5. HRTEM images of different noble metals (Ag, Pt, Au and Pd) on TiO$_2$(R) by i. and i.d. method

(A) Ag(i.)/SiO$_2$(R).
(B) Pt(i.)/SiO$_2$(R).
(C) Au(i.)/SiO$_2$(R).
(D) Pd(i.)/SiO$_2$(R).
(E) Ag(i.d.)/SiO$_2$(R).
(F) Pt(i.d.)/SiO$_2$(R).
(G) Au(i.d.)/SiO$_2$(R).
(H) Pd(i.d.)/SiO$_2$(R).
31. The crystal phase can be identified by three major XRD diffraction peaks. All samples have rutile diffraction peaks at $2\theta$ of 36.1°, 39.2°, 41.2° and 44.05°, which proves that the support is rutile (Holm et al., 2019).

32. Besides TiO$_2$ peaks, look for corresponding noble metal peaks in XRD for both M(i.)/TiO$_2$(R) and M(i.d.)/TiO$_2$(R) (Figure 7). Take Figure 7A for an example, a diffraction peak corresponding to Ag can be seen at 38.1° for Ag(i.)/TiO$_2$(R), but it can hardly be seen for Ag(i.d.)/TiO$_2$(R).

33. Analyze the size of noble metals based on the XRD patterns. The larger the size of the metal particles is, the higher the peaks intensity will be.

△ CRITICAL: High intensity indicates that the size of the particles by the i. method is larger than the i.d. method, and those deposited by the i.d. method are well controlled.

UV-vis DRS is a classical method to characterize the optical properties of materials. Especially for noble metals with localized surface plasmon resonance (LSPR) effect, such as Au and Ag, it is a conventional method to reveal the change of particle size (Forcherio and Roper, 2016).

34. Set the slit of the instrument as 1 nm. The BaSO$_4$ integrating sphere is used for background correction. The test scanning wavelength range is 200–800 nm, and the scanning speed is 480 nm/min.

35. Take 0.25 g of the prepared powder into the sample cell and slowly tighten the back cover to make the powder evenly and tightly spread under the quartz glass for testing.

△ CRITICAL: The sample must be evenly spread over the entire quartz glass. Otherwise, it will affect the accuracy.
36. The characteristic absorption peaks of Au and Ag are 550 nm (Dulnee et al., 2014) and 470 nm (Wu et al., 2020) in Au(i.)/TiO₂(R) and Ag(i.)/TiO₂(R). By identifying the high peaks of characteristic absorption, it indicates that the noble metal particles deposited by the method i. are larger in size. See Figure 8.

37. The absorption peak intensity of M(i.d.)/TiO₂(R) is weak. The characteristic absorption peaks of Au and Ag located at 550 nm and 470 nm in Au(i.)/TiO₂(R) and Ag(i.)/TiO₂(R) are not detected, indicating that the size of the noble metal particles deposited by the i.d. method is small.

In order to explore the loading amount at different dark reaction intervals and the final content of noble metals deposited by the i.d. method, an inductive coupled plasma emission spectrometer (ICP) was used for testing.

38. Before testing, dilute the noble metal standard solution (Beijing Nonferrous Metals Research Institute, the original standard solution of Au, Pt, Pd: 10 mg/mL; Ag: 1 mg/mL) with 2% dilute nitric acid solution to 0.1, 0.3, 0.5, 0.7, 1.0 mg/mL, test by ICP and draw the standard curve.

39. For detecting the loading amount of metals on TiO₂, the reaction suspension at different dark reaction intervals is filtered using a syringe membrane filter with a pore size of 0.22 μm to obtain a clear filtrate.

40. Take 1 mL of filtrate, add 8.8 mL of deionized water and 200 μL of concentrated nitric acid (GR) to obtain a 2% dilute nitric acid test solution for ICP test.

41. All samples are tested 3 times and take the average value.
CRITICAL: The powders need to be fully separated from the suspension to avoid blocking the equipment and make the result accurate. The charge of the metal precursors has a significant influence on the loading amount. For the negatively charged AuCl4–, the actual loading is close to the loading amount, while for the positively charged Pt(NH3)42+, Pd2+, Ag+, the actual loading is all lower than the designed loading amount. See Table 1. Therefore, it’s important to choose the charges of TiO2 and the metal precursors.

Experiments under different conditions

42. HRTEM, XRD and UV-vis DRS: Replace the carrier with different metal oxide supports such as anatase TiO2, P25 TiO2 and ZrO2 (Wu et al., 2022).
43. UV-vis DRS experiment with different light intensity: In order to study the difference in metal deposition kinetics caused by light intensity, the light intensity was reduced from 74 mW/cm2 to 12 and 2 mW/cm2 for photodeposition (Wu et al., 2022).

EXPECTED OUTCOMES

In this protocol, the deposition process of metal nanoclusters on semiconductor support through an “irradiation-dark” process was present. Different noble metal nanoclusters, including Au, Ag, Pd, could be successfully loaded on semiconductors. The uniform size could be controlled smaller than 1.0 nm. We also demonstrated the promoted performance in the catalytic oxidation of HCHO over Pt and Au nanocluster on TiO2 (Wu et al., 2022). We believe the combinations of different metal-supports could be used as effective catalysts in other heterogeneous catalysis.

LIMITATIONS

According to the proposed strategies, the photoelectrons are firstly stored as Ti3+, then released to reduce the metal precursors in the dark. It requires the semiconductor support enables to store...
photogenerated charges via a redox process. Besides, the reduced species should be thermodynamically favorable for the reduction of noble metal precursors. Therefore, not all the semiconductor supports are applicable.

**TROUBLESHOOTING**

**Problem 1**

Different metal precursors have different concentrations during the dark reaction. If the deposition rate and concentration do not match, it may lead to the formation of larger nanoparticles. For example, when Au(i.d.)/TiO$_2$(R) is prepared by the above method, a small amount of Au nanoparticles is larger in size, and diffraction peaks can be clearly observed in XRD shown in Figure 7C.

**Potential solution**

Reduce the concentration of the metal precursor solution to avoid the formation of large nanoparticles due to the high local concentration of metal ions, keeping the molar mass of the metal precursor salt unchanged. For example, if the precursor solution of HAuCl$_4$·4H$_2$O is diluted from 1.57 mg/mL (3.8 mM) to 0.157 mg/mL (0.38 mM), the bigger sizes of Au nanoparticles are highly reduced as confirmed by the disappearance of the diffraction peak of Au in XRD shown in Figure 7C. (Synthesis of M(i.d.)/TiO$_2$ step 15).

**Problem 2**

When the charge of the metal precursor salt and the TiO$_2$ surface are contrary, the metal loading may be reduced. For example, when chloroplatinic acid is used to prepare Pt(i.d.)/TiO$_2$(R), the supporting amount of Pt is relatively low. The designed supporting amount is 2.5 wt. %, but only 0.8 wt. % of Pt is successfully loaded.

**Potential solution**

Replace the charging performance of the precursor salt. For example, replacing the negatively charged H$_2$PtCl$_6$·6H$_2$O with the positively charged Pt(NH$_3$)$_4$(OH)$_2$·xH$_2$O can increase the Pt loading from the previous 0.8 wt. % to 2.4 wt. % (Table 1).

**Problem 3**

In the dark reaction stage, the method of directly pouring the noble metal precursor liquid cannot ensure the maximum liquid-liquid mass transfer, resulting in the formation of large nanoparticles.

### Table 1. Comparison of the designed loading capacities of noble metals and the loading amount estimated by ICP

| Sample                  | Metal precursor | Noble metal | Photodeposition condition | Nominal $M^*$ (wt. %) | Measured $M^*$ by ICP-OES (wt. %) |
|-------------------------|-----------------|-------------|---------------------------|-----------------------|-----------------------------------|
| Au(i.d.)/TiO$_2$(R)     | AuCl$_4$        | Au          | 0.5 h dark after Hg lamp (74 mW/cm$^2$), 1.0 h | 2.5                   | 2.43 ± 0.05$^a$                   |
| Pt(i.d.)/TiO$_2$(R)     | PtCl$_6^{2-}$   | Pt          | 0.5 h dark after Hg lamp (74 mW/cm$^2$), 1.0 h | 2.5                   | 2.39 ± 0.04$^b$                   |
| Ag(i.d.)/TiO$_2$(R)     | Ag$^+$          | Ag          | 0.5 h dark after Hg lamp (74 mW/cm$^2$), 1.0 h | 2.5                   | 0.49 ± 0.08$^b$                   |
| Pd(i.d.)/TiO$_2$(R)     | Pd$^{2+}$       | Pd          | 0.5 h dark after Hg lamp (74 mW/cm$^2$), 1.0 h | 2.5                   | 0.18 ± 0.01$^b$                   |
| Pt(i.d.)/TiO$_2$(R)     | [Pt(NH$_3$)$_4$]$_2^{2+}$ | Pt    | 0.5 h dark after Hg lamp (74 mW/cm$^2$), 1.0 h | 2.5                   | 0.80 ± 0.02$^b$                   |
| Pt(i.d.)/TiO$_2$(R)     | PtCl$_6^{2-}$   | Pt          | 0.5 h dark after Hg lamp (74 mW/cm$^2$), 3.0 h | 10.0                  | 6.25 ± 0.06                      |
| Pt(i.d.)/TiO$_2$(R)     | PtCl$_6^{2-}$   | Pt          | 0.5 h dark after Hg lamp (74 mW/cm$^2$), 1.0 h | 10.0                  | 9.96 ± 0.04                      |

$^a$M=Au, Ag, Pt, Pd.  
$^b$indicates that the data is from (Wu et al., 2022).
Potential solution
A 10 mL disposable dropper is used to add the precursor liquid at the center of the liquid vortex to enhance the mass transfer and avoid the formation of large particles. (Synthesis of M(i.d.)/TiO₂ step 2).

Problem 4
Practical industrial production requires high load catalysts (Yoo et al., 2020). Thus promoting the loading amounts of metals is an important problem to solve.

Potential solution
Extend the time of the photoreaction thus increase the amount of Ti³⁺, so as to obtain a higher loading amount of noble metal nanoclusters. For example, by extending the photoreaction time from 1 h to 3 h, the loading amount of Pt can be promoted from 6.25 wt. % to about 10 wt. % at the designed loading of 10 wt. % (Table 1).

Problem 5
The N₂ flow rate in the photoreaction stage should not be too high. If the flow rate is too high, the support will hang on the inner wall of the reactor and affect the reaction process.

Potential solution
Adjust the flow rate before reaction carefully. We set the N₂ flow rate to 40 mL/min through a flow meter to avoid this situation. (Synthesis of M(i.d.)/TiO₂ step 13).

RESOURCE AVAILABILITY
Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Lei Huang (leihuang@shu.edu.cn).

Materials availability
This study did not generate new unique reagents.

Data and code availability
All data reported in this paper will be shared by the lead contact upon request.

This paper does not report original code.

Any additional information required to analyze the data reported in this paper is available from the lead contact upon request.

ACKNOWLEDGMENTS
This work is financially supported by Shanghai Municipal Science and Technology Commission (18520744500, 19DZ2293100, 21DZ2280600).

AUTHOR CONTRIBUTIONS
L.H. directed and conceived this work. H.C.W. and Y.Z. performed the photodeposition experiments and analyzed the data. R.R.J. participated in the discussion of experiments and commented on the draft. L.Y.S. provided funding, supporting, project administration, and supervision of the experiments. L.H., Y.Z., and H.C.W. wrote the manuscript with edits and approval from all authors.

DECLARATION OF INTERESTS
The authors declare no competing interests.
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