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COMMUNICATION

Oxygen-assisted stabilization of single-atom Au during photocatalytic hydrogen evolution

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Pre-treatment of graphitic carbon nitride (GCN) with H₂O₂ introduces active C-OH groups that can react with HAuCl₄ to immobilize single atom Au(I) in the GCN matrix through creating robust Au(I)-O coordination bonds. This strong bonding can effectively restrict diffusion of intermediate Au(0) towards formation of Au particles during photocatalytic hydrogen evolution process. As such, the single atom Au(I) incorporated GCN maintained superior activities with excellent stabilities for photocatalytic hydrogen generation.

Introduction

Noble metals have attracted great attentions as cocatalysts for many photocatalytic reactions, in which they play important roles as electron acceptors, active sites for hydrogen evolution reaction (HER), and surface plasma resonance initiators. In particular, for photocatalytic HER, graphitic carbon nitride (GCN) has been widely used as a visible-light-active host material due to its excellent electronic properties¹⁻⁵. Decoration of noble metal nanoparticles has been proved as the easiest way to promote the photocatalytic activities of GCN. However, the relatively low atom utilization efficiency remains the major concern on the use of noble metals.

As such, downsizing the metal particles to small clusters or single atoms has been a sought-after way to maximize the atomic efficiency. Previous studies showed that the characteristic N-coordinating six-fold cavities in GCN could entrap active metal ions in a form of isolated single site due to the lone pair electrons of the nitrogen atom in the tri-s-triazine ring. Consequently, these immobilized metal ions can serve as catalytically active sites.⁶⁻⁹ Specifically, the single metal atom decorated GCN can exhibit excellent catalytic performance in hydrogen evolution,¹⁰⁻¹⁵ CO₂ reduction,¹⁶⁻¹⁸ oxygen evolution,^{19,20} silane oxidation²¹ and so on²²⁻²⁸. Nevertheless, using single metal atom on GCN for photocatalysis is rarely

reported because the individual coordinated metal ions are likely reduced by the photogenerated electrons to create active metal atoms that could not be stably trapped by the nitrogen-coordination effect and readily diffuse in GCN to form large clusters or nanoparticles.

In particular, for gold, researchers have found that Au ions can be readily immobilized in GCN matrix through Au-N interactions. However, under photocatalytic processes, the photogenerated electrons in GCN can readily reduce these individual Au ions into free Au atoms that can easily agglomerate into large gold nanoparticles on GCN surfaces. Therefore, stabilization of single metal atoms sites during photocatalytic reactions is a challenging issue in order to maintain the high reaction activity and atomic utilization efficiency. Herein, in this work, we demonstrate that pretreatment of GCN with H₂O₂ can introduce active C-OH groups that can react with HAuCl₄ to immobilize single atom Au(I) in the GCN matrix through creating robust Au(I)-O coordination bonds. This strong bonding can effectively restrict diffusion of intermediate Au(0) towards formation of Au particles during photocatalytic hydrogen evolution process. As such, the single atom Au(I) incorporated GCN maintained superior activities with excellent stabilities for photocatalytic hydrogen generation.

Experimental section

Synthesis of materials

In detail, CNU was prepared by pyrolysis of 10 g urea at 550 °C for 4 hours, 2.5 °C/min. Then, 50mg CNU, 0.25 mL HAuCl₄(1mg/mL) and 29.75 mL water were added in Teflon-autoclave and sonicated for 30 min. Then, the hydrothermal reaction was operated at 120 °C for 12 hours. The obtained sample was denoted as CNUAu. For H₂O₂ treatment, 300mg CNU was added into 150 mL H₂O₂(30%) solution and reflux at 110 °C for 6 hours, then wash with water and ethanol for several times. Finally, the powder was dried at 60 °C overnight, denoted as CNUH. CNUHAu was also prepared by hydrothermal reaction. 50mg as-prepared CNUH, 0.5 mL HAuCl₄(1mg/mL) and 29.5 mL water were mixed and transferred to Teflon-autoclave. After 30

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min sonication, the solution was reacted at 120 °C for 12 hours. The yellow powder was collected after centrifuge, wash with water and ethanol and dry at 60 °C overnight. In control experiment, 50 mg CNUH, 0.5 mL HAuCl_4 (1 mg/mL) and 29.5 mL water were mixed and sonicated for 30 min, then stirring at room temperature for 24 hours. The obtained sample after wash and dry denoted as CNUHAu-RT.

Characterizations

Powder X-ray diffraction (XRD) characterizations were recorded with a Panalytical XRD, using $\text{Cu K}\alpha$ radiation ($\lambda=1.540598 \text{ \AA}$) operated at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos AXIS Supra system. The C 1s peak at 284.8 eV was used as the reference to calibrate the XPS spectra. The aberration-corrected high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of Au single atoms were obtained by a JEOL Grand ARM300F operated at 300 kV with cold field emission gun and double hexapole Cs correctors. The low magnification bright field TEM image was obtained by a JEOL 2010UHR operated at 200 kV with LaB_6 filament. The metal loading contents were measured using ICP-MS on a Perkin-Elmer Elan DRC-e instrument.

Photocatalytic hydrogen evolution test

The photocatalytic hydrogen evolution tests were performed in a 20 mL quartz reactor. Typically, 10 mg photocatalyst was dispersed in 10 mL mixed solution made of DI water and formic acid (9:1, Volume ratio). This suspended solution was sealed in the quartz reactor by a rubber plug and then bubbled with nitrogen gas for half an hour to remove the dissolved air. Subsequently, the reactor was irradiated under a 300 W Xe lamp (Max-302, Asahi Spectra Co. Ltd.). The gas product composition from the upper space above the liquid in the quartz reactor was analyzed by an Agilent 7890A gas chromatograph equipped with a thermal conductivity detector.

Figure 1. Representative HAADF-STEM image of CNUHAu.

The standard GCN samples (denoted as CNU) were prepared by calcination of urea at 550 °C. The CNU sample was refluxing in H_2O_2 solution (30%) for 6 hours, and the product is denoted as CNUH. Incorporation of Au(I) into GCN was achieved through hydrothermal reaction by using CNUH and HAuCl_4 at 120 °C, and the product is denoted as CNUHAu.

Bright field TEM images (Figure S1) reveal that the CNUHAu sample appears only sheet-like structure without any clear nanoparticles. Further examination by the aberration-corrected HAADF-STEM (Figure 1) indicates that individual Au atoms are dispersed on the surface of CNUHAu, suggesting successful incorporation of single Au atom into the polymeric carbon nitride matrix. XPS analyses (Figure 2, Au 4f) reveal that the Au has valence of +1 in CNUHAu, suggesting that Au^{3+} can react with the GCN structure in hydrothermal condition, and the produced Au(I) species are dispersed in the carbon nitride matrix as individual ions. We note that the O1s XPS result (Figure 2) shows a signature peak at 530.9 eV, corresponding to Au-O bond (Figure S2, Au_2O_3 XPS), indicating the formation of strong Au(I)-O bonding during the hydrothermal process.

Figure 2. XPS spectra of (A) Au 4f of CNUHAu; (B) Au 4f for CNUAu; (C) O1s and (D) N1s for CNUHAu and CNUAu

The photocatalytic H_2 generation test was carried out in the presence of formic acid under visible light irradiation. For comparison, the control sample, CNUAu, was prepared by loading CNU with Au under the same hydrothermal conditions. After 5-hour irradiation, CNUHAu exhibits a H_2 generation rate of 789.1 nmol/h (Figure 3) without colour change for the sample. In contrast, the CNUAu sample changed colour to red within one-hour irradiation and showed much lower H_2 evolution rate of 198.9 nmol/h. XPS analyses after photocatalytic test showed clearly formation of Au(0) species for CNUAu, while CNUHAu still held only Au(I) with no Au(0) indication. Notably, ICP analyses reveal that the actual gold content in CNUHAu (0.18 wt%) is only half of that in CNUAu (0.37 wt%), but the H_2 evolution rate is about 4 times higher, which highlights the significant contribution of the single atom Au(I) in CNUHAu as the catalytically active sites for HER. The stability of CNUHAu was proved by cycling test over 20 hours with maintained activities and no colour change was observed for the sample.

The photocatalytic results suggest that pre-treatment of GCN by H_2O_2 significantly enhances the stabilities of Au(I) on GCN during H_2 evolution reaction, which can be attributed to three consecutive consequences. First, H_2O_2 pre-treatment can increase surface O content from 0.53% to 3.27%, as indicated

by the quantitative analyses of O content based on O1s XPS results of CNU and CNUH (Table S1).

Second, the increased oxygen content is ascribed to the conversion of N2C-NH_2 into N2C-OH , as evidenced by the dramatically increased peak at 532 eV (as C-OH) in the O1s XPS spectra (Figure S3) and the increased vibration intensity at around 3400 cm^{-1} in FTIR spectrum (Figure S4). Consistently, the N1s peak at 401.5 eV shift to 401.1 eV with clearly decreased intensity (Figure S3), suggesting that some terminal amine groups (C2-NH & C-NH_2) were converted to C-OH.

Figure 3. (A) Photocatalytic activity of hydrogen evolution over CNUAu and CNUHAu under visible light irradiation; (B) Cycling test of photocatalytic hydrogen evolution over CNUHAu

Third, under hydrothermal condition, the N2C-OH moieties on the melem ring can reduce Au(III) to Au(I) . Subsequently, the H atom is replaced by Au(I) , creating new CO-Au(I) coordination bond, as evidenced by the signature peak at 530.9 eV in the O1s XPS spectrum. This Au(I)-O bond is very strong and robust, presumably through configuration of bidentate chelating.²⁹⁻³² Importantly, the Au(I)-O coordination interaction can be remained stable even if Au(I) is reduced to Au(0) , and thus is capable of immobilization of single Au atom with retained catalytic activity during photocatalytic reactions. The O1s XPS spectrum (Figure S5) indicates that the Au(I)-O bond was well retained after the reaction. In contrast, for CNU without H_2O_2 pre-treatment, after hydrothermal treatment to obtain CNUAu, some gold atoms existed as Au(III) adsorbed on CNUAu surface *via* electrostatic interaction, while some gold appeared as Au(I) , as indicated by the Au 4f XPS result. It means that the conversion of Au(III) to Au(I) is still achievable through reduction by $-\text{NH}_x$ ($\text{H}_2\text{N-C}$ or HN-C2), which leads to formation of Au(I)-N bonding in CNUAu under hydrothermal condition, as evidenced by the dramatic rise of the peak at 399.8 eV in the N1s XPS spectrum.

Therefore, we believe that in CNUHAu, the amine groups ($-\text{NH}_x$) nearby O-Au(I) may also establish N-Au(I) bonding to create N-Au(I)-O unit (Figure 4A). This allows for facile transfer of photogenerated electrons from excited GCN to Au(I) *via* N-Au(I) linkage to create intermediate Au(0) with retained strong Au(0)-O bonding, which prevents diffusion and aggregation of Au(0) atoms. As such, the Au(0) atoms can serve as active sites for proton reduction towards H_2 evolution.

In comparison, in CNUAu, though Au(I) can be incorporated in CNUAu, the stability of Au(I)-N bond is weak during photocatalytic H_2 evolution reaction. The photogenerated electrons can be transferred to Au(I) *via* the Au(I)-N bonds, creating free Au^0 atom as the N-Au(0) interactions are not strong enough to prevent its diffusion. Consequently, Au

clusters or particles would be formed through diffusion of these free Au atoms on the GCN surface (Figure 4B). As such, the CNUAu sample quickly turned red after the photocatalytic test started, indicating fast formation of Au particles that contribute to the followed HER activities. We note a tracing signature of Au(I)-O bonds at 530.9 eV in O1s XPS of CNUAu because a small portion of amines may be replaced by $-\text{OH}$ during hydrothermal reaction, followed by reacting with Au(III) to generate Au(I)-O bonding. Nevertheless, the quantity of Au(I)-O bonds is much less than Au(I)-N bonds by comparing the relative intensity of the peaks at 530.9 eV (O1s) and 399.8 eV (N1s). Thus, it hardly stabilizes all Au(I)-N bonds during photocatalytic reactions.

Hydrothermal condition is also important because it can provide GCN more surface hydroxyl groups,³³ and appropriate environment to form robust Au-O bond. Previous studies indicate that simple soaking allows for adsorbing of Au ions on GCN surfaces. While our XPS results reveal that in the sample (CNUHAu-RT) made by soaking at room temperature for 24 hours, a large portion of Au ions are present as Au(III) , corresponding to the Au 4f peak at 89.9 and 86.2 eV (Figure S6), and may be adsorbed *via* electrostatic interaction. Some portion of surface Au(I) still can form through formation of weak Au(I)-N bonds, but no Au(I)-O bonding signature was observed in the O1s XPS spectrum. As a result, the sample turns red immediately after starting the photocatalytic test. The XPS studies reveal that the binding energy of Au 4f clearly shift towards Au(0) in the sample after 3-hour reaction (Figure S6). Hence, the pre-treatment with H_2O_2 and hydrothermal treatment are two indispensable factors for the formation of robust Au-O bond.

Conclusions

In summary, we demonstrate that H_2O_2 pre-treatment can significantly improve the stability of Au single atom anchored on GCN surface. The newly formed robust Au(I)-O bond is the key to stabilize the individual gold atom on GCN during photocatalytic HER. We believe that this work will expand our vision for future development of efficient photocatalysts incorporated with highly stable single atom HER catalyst.

Conflicts of interest

There are no conflicts to declare.

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Figure 4. (A) schematic structure evolution of CNUHAu; (B) schematic structure evolution of CNUAu during photocatalytic reaction.

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