Single Au atoms anchoring on amino-group enriched graphitic carbon nitride for photocatalytic CO₂ reduction

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Abstract: Due to the maximum atom-utilization efficiency and excellent catalytic properties, Au single atom catalysts (SACs) have been extensively studied in various catalytic systems. However, the performance of Au SACs on CO₂ reduction were seldom investigated. Herein, Au single atoms on amino-group modified graphitic carbon nitride (U-ACN) was successfully synthesized through a mild and eco-friendly urea reduction method. U-ACN shows a remarkable performance for CO₂ reduction, with CO and

CH₄ yield to be 1.97 and 4.15 times that of pure graphitic carbon nitride under 2.5 h visible light irradiation. The excellent catalytic activity of U-ACN derives from the introduction of Au single atoms, which lower the energy barrier of CH₄ formation, narrow the bandgap, and hinder the recombination of charge carriers. In addition, the U-ACN has improved CO₂ affinity due to the urea-introduced amino-groups in the catalysts.

Introduction

Since the first demonstration of the Ti single active site on mesoporous silica by Maschmeyer et al.^[1] in 1995, the synthetic methodology and catalytic applications of single-atom catalysts (SACs) have attracted worldwide attention. SACs have been evidenced with high atom-utilization efficiency, remarkable catalytic activity and selectivity.^[2-6] For example, various kinds of SACs have been prepared and investigated in silane oxidation,^[2] hydrogen evolution reaction,^[3] and alkene hydrosilylation.^[4] For instance, Cheng et al.^[5] reported that the H₂ yield of single Pt atoms on N doped graphene is 37 times that of commercial Pt/C catalyst. Pan et al.^[6] synthesized the N₅ supported Co on N-doped graphene, which exhibited nearly 100% CO selectivity for CO₂ reduction.

So far, various Au SACs have been synthesized and extensively studied in acetylene hydrochlorination,^[7] water-gas shift reaction,^[8] oxygen evolution reaction,^[9] and CO oxidation.^[10] However, the performance of Au SACs on CO₂ reduction are seldom reported,^[11] although Au in multi-form have already exhibited a highly selective conversion of CO₂ to CO.^[12] It is well-known that the adsorption of CO₂ on photocatalysts plays a key role in photocatalytic CO₂ reduction.^[12] Especially, the introduction of amino groups into photocatalysts has attracted more and more attention due to the increase of Lewis basic sites in the system and the enhancement of adsorption and activation of CO₂.^[12] In addition, many synthesis methods of Au SACs have been developed, such as atomic layer deposition (ALD),^[13] thermal treatment,^[14] and electrochemical exfoliation,^[13] deposition-precipitation (DP) method.^[15] Among them, DP method was widely used due to its lower cost and that it will not damage the structure of its supports. However, the effective synthesis of Au SACs on photocatalysts with the introduction of amino groups remains a great challenge. Moreover, the mechanism and effectiveness of single Au atom on a substrate, especially anchoring on an organic matrix, have rarely been investigated for photocatalytic CO₂ reduction.

Here, we report the synthesis of Au single atoms on amino-group enriched graphitic carbon nitride through a mild and eco-friendly urea deposition-precipitation reduction method. The distribution, valence state, and chemical environment of Au are systematically analyzed by high-resolution high-angle annular

dark-field scanning transmission electron microscopy (HAADF-STEM) and X-ray absorption fine structure (XAFS). The CO₂ reduction mechanism on the Au single atom photocatalyst was carefully studied by *in situ* DRIFTS. On the other hand, the as-developed urea deposition-precipitation reduction method greatly enriched the amino-groups in the carbon nitride matrix, thus increasing the Lewis basic sites in the catalysts to enhance the adsorption and activation of CO₂.^[12]

Results and Discussion

Figure 1. (a) The synthesis process of Au single atoms on amino-group enriched graphitic carbon nitride by mild urea reduction method. Graphitic carbon nitride is obtained by the pyrolysis of melamine and urea at 550 °C. Urea again was added to act both as pH regulator in oil bath and amino-group precursor under 300 °C calcination. After that, the existed Au nanoparticles are leached by thiourea at 60 °C. (b) HAADF-STEM image of uniformly distributed Au single atoms on amino-group enriched graphitic carbon nitride, the scale bar is 5 nm. (c) STEM-EDS images of C (red), N (green), and Au (yellow) elements in selected area, the scale bar is 20 nm.

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Figure 2. The SIMS spectra of negative secondary ions from U-CAN and CN samples in the region of 0-100 u (a) and 200-300 u (b). ToF-SIMS images of U-ACN's N-contained fragment ion CN^- (c), CN_2^- (d), CHN_2^- (e), C_2N_3^- (f), and $\text{C}_2\text{H}_3\text{NO}^-$ (g) in 0-100 u, and Au-contained fragment ion AuH_3^- (h), $\text{C}_2\text{N}_2\text{Au}^-$ (i), and AuN_2O_4^- (j) in 200-300 u region. The area shares the same number of fragment ions as the right ruler who shares the same color.

Au single-atom on amino-group enriched graphitic carbon nitride (U-ACN) was synthesized through a mild and eco-friendly urea reduction method (Figure 1a, see experiment details in the Supporting Information). The mixture of melamine and urea was calcined at 550 °C in air for 4 h, which led to the formation of graphitic carbon nitride (CN) via polycondensation.^[16] Then, urea acting as the pH regulator, was added in the suspension of CN and HAuCl_4 in 80 °C oil bath to facilitate the formation of Au-containing precipitate $\text{AuCl}_4(\text{OH})_3$ on CN.^[17] Subsequently, $\text{AuCl}_4(\text{OH})_3/\text{CN}$ was calcined at 300 °C in air for 3 h, which concurrently reduced Au^{3+} to Au^0 , improved the polymerization degree of CN, and enriched the amino-group in the CN matrix. Thiourea leaching as the last step was operated to remove Au nanoparticles by forming coordinated bond with Au.^[18,19]

X-ray diffraction (XRD) pattern of U-ACN in Figure S1 only shows the peaks of graphitic carbon nitride,^[20] while the peaks of Au nanoparticles at 38.1° and 44.4° are found in Au/graphitic carbon nitride (P-ACN) prepared by photoreduction of HAuCl_3 in the presence of graphitic carbon nitride.^[21] The HAADF-STEM image (Figure 1b and Figure S2) of U-ACN convinced that the Au with size of under 5 Å (light spots) are stably anchored on the CN substrate, even under the irradiation of high energy electron beam. The EDS-mapping in Figure 1c further confirmed the uniform distribution of Au atoms on CN substrate.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was carried out to reveal the composition of U-ACN. In Figure 2a, the mass-to-charge ratio (m/z) peaks located at 1, 26, and 64 are the characteristic peaks for ionic groups of H^- , CN^- , and C_2N_3^- , respectively. The intensities of H^- , CN^- , and C_2N_3^- in U-ACN are 4.2, 11.7, and 2.8 times of those in CN, respectively. The enhanced intensities of the H^- and CN^- peaks confirmed the introduction of H and C-N into the U-ACN matrix. In addition, compared with CN, the 5% increased N-(C)₃ content of U-ACN indicated from the N 1s XPS spectra (Figure S3), and hardly changed triazine ring bending vibration^[22] and C-N heterocycles stretching vibration^[23] shown from the FTIR spectra (Figure S4)

Figure 3. (a) Normalized XANES of U-ACN with reference Au foil and Au_2O_3 , the inset is the magnification of 11900-12150 eV region. (b) Fourier transforms of k^3 -weighted $\chi(k)$. (c) The EXAFS fitting curve of the corresponding first Au-N/C and second Au-N/C shells of U-ACN. Inset is the proposed structure of U-ACN based on the fitting parameters. (d) Au 4f XPS spectra of samples U-ACN and P-ACN, the peaks of U-ACN have shifted 1 eV higher than that of P-ACN.

together implied that amino-group bonded to C in urea was introduced into graphitic carbon nitride through polycondensation reaction.

In Figure 2b, two peaks corresponding to the Au-contained fragment ions ($\text{C}_2\text{N}_2\text{Au}^-$ and AuN_2O_4^-) can be found. This indicates that Au atoms are existed by forming chemical bond with other atoms in the CN matrix. ToF-SIMS images in Figure 2c-g and 2h-j show the mapping of the fragment ions indicating the presence of amimo-group and Au bonds, respectively. It can be seen that the enriched amino-group and Au are uniformly dispersed in the CN matrix.

Figure 3a exhibits the Au L_{3-2} -edge X-ray near edge structure (XANES) spectra of U-ACN, reference Au foil, and Au_2O_3 . Au foil (Au^0) has very weak white line peak, while the peak of Au_2O_3 (Au^{3+}) is quite strong. The white line peak of U-ACN is stronger than Au foil but weaker than that of Au_2O_3 , indicating that the valence state of Au in U-ACN is around +1.^[24]

Figure 3b shows the Fourier-transform (FT) of k^3 -weighted and phase-uncorrected extended X-ray fine structure (EXAFS) curves of U-ACN, reference Au foil, and Au_2O_3 . The peaks at 1.9-3.2 Å ascribe to the Au-Au bond in Au foil (Figure S5 and Table S1). U-ACN's peak which appears around the Au-O peak of Au_2O_3 at 1.65 Å, is attributed to the scattering of N/C. The peak of U-ACN at 2.46 Å is different from the Au-Au peak of Au foil at 2.64 Å.

The best-fit curve of U-ACN is shown in Figure 3c and Figure S6, with its fitting parameters provided in Table S1. The first shell of Au includes three N atoms with bond length of 2.05 Å, while the second shell has three C atoms with distance of 2.30 Å. In addition, the π -excitation percentage in C1s XPS spectra of U-ACN is decreased (Figure S7 and S8),^[25] suggesting Au might exist in CN heterocycle by forming chemical bond with C or N. Given the above analysis, Au atoms are atomically dispersed in the framework of graphitic carbon nitride by forming chemical bonds with three N atoms,^[2] as proposed in the Figure 3c inset. Figure 3d shows that the Au 4f_{7/2} (85.2 eV) and Au 4f_{5/2} (88.8 eV) binding energies of U-ACN have shifted by 1 eV higher than

Figure 4. (a) The generated CO and CH₄ amounts over U-ACN, CN, and P-ACN after 2.5 hours of visible-light irradiation in an airtight reactor full of CO₂ gas. Inset shows the O₂ to N₂ ratio inside the reactor is 1.2 times that in air. (b) The CO (left in yellow) and CH₄ (right in blue) yield curve of U-ACN, CN, and P-ACN versus visible-light illumination time. (c) *in situ* DRIFTS spectra of U-ACN under 60 min CO₂ adsorption in dark, and then under 365 nm light irradiation (20 min, 40 min, and 60 min). (d) CO₂ temperature programmed desorption (TPD) of CN, U-ACN, and P-ACN under heating rate of 10 °C/min.

that of P-ACN, further indicating that Au exists in the form of Au⁺.^[26]

The photocatalytic CO₂ reduction activities of U-ACN, P-ACN and CN were tested under visible-light irradiation without the addition of cocatalyst and sacrificial agent. As shown in Figure 4a, after 2.5 hours of visible-light illumination, the CO and CH₄ yield of U-ACN are 21.7 and 2.4 μmol/g, which are 1.97 and 4.15 times that of CN, confirming the improved effective-utilization of photo-generated electrons. In addition, the generated CH₄ to CO ratio over U-ACN is about 2 times that over CN, which was higher than that of some g-C₃N₄ based catalysts,^[27] indicating that the eight-electron CO₂-reduction path is more available with the existence of Au atoms. The O₂ to N₂ content ratio of U-ACN was higher than that of residual air, proving that the oxidation product was O₂.

Figure 4b shows the yield curve of reduced CO₂-products over time. CO content increased steadily with time during the 2.5 hours reaction; whereas, CH₄ content increased rapidly during the first 1.5 h, then slowly during the later 1 h, which was due to the evaporation of H₂O under prolonged exposure to 300 W xenon lamp. The reaction mechanism for the U-ACN was further revealed via *in situ* DRIFTS by testing the intermediates^[28] during CO₂ reduction on U-ACN under 360 nm monochromatic light irradiation (*means adsorbed on U-ACN). The absorption peaks of carbon species at 1265,^[29] 1313,^[30] 1437,^[29,30a] 1504,^[30a] 1544,^[30b] and 1621^[30a] cm⁻¹ increased with irradiation time, indicating that the high CO₂ affinity of U-ACN has provide it with sufficient CO₂ reactants. Peaks located at 1198,^[31] 1233,^[30b,31] and 1422^[30b,32] cm⁻¹ are contribute to the formation of HCO₃⁻, which was captured by the OH group. The HCOO⁻ absorption peaks at 1338,^[30a] 1453,^[30a] and 1562^[29,30a] cm⁻¹ first become strong then weak, manifesting that the formation of COOH* can easily dissociate to CO.^[33] Then, COOH* further reduces to HCHO*, whose peak is detected at 1607^[29] cm⁻¹. Moreover, the signal of CH₂* is detected at 1375^[32] cm⁻¹, confirming CH₂* is the hydrogenation products of HCHO*. However, it is difficult to

directly break the C=O bond in the aldehyde group, suggesting the presence of another intermediate reaction. In the process of CO₂ reduction on Pt₁/graphitic carbon nitride, the dissociation of CH₂OH* to

Figure 5. The proposed illustration of electrons distribution and the CO₂ reduction process of U-ACN under visible-light irradiation. CO₂ and H₂O adsorb tightly on the amino-group enriched graphitic carbon nitride. CO and CH₄ are formed after a sequence of intermediate reaction.

CH₂* is the intermediate reaction of CH₄ production,^[34] and CH₂OH* is the intermediate of CO₂ reduction to CH₄ on carbon-based catalyst,^[35] suggesting that the next reduction product of HCHO* is CH₂OH*. The subsequent hydrogenation of CH₂* to CH₄ can easily happen.^[34,36] In a nutshell, the CO₂ reduction process are proposed as follows:

Given the proposed CO₂ reduction process, the remarkably improved CH₄ production of U-ACN can be ascribed to the strong adsorption of intermediates after introducing Au single atoms, which lower the energy barrier of subsequent chemical reaction.^[34,37] In addition, CO₂-TPD in Figure 4d shows higher CO₂ adsorption ability of U-ACN, consistent with the fact that less carbon-species peaks are detected in CN (Figure S9), which highlights the importance of amino-group in CO production.

As shown in Figure S10, the introduction of Au atoms into the framework of graphitic carbon nitride has narrowed the bandgap of U-ACN by 0.05 eV, which favors the generation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Furthermore, the local electric field between positively charged Au⁺ and coordinated N with high electron cloud density enable the photo-generated electrons to transfer to Au⁺, thus inhibiting the recombination-rate of carriers (Figure S11 and S12)^[38] and increasing the lifetime of carriers (Figure S13). As the CO₂ are adsorbed on Lewis basic N^[35] and urea-introduced amino-group, therefore the CO₂ reduction process takes place in two paths: i).

CO₂ adsorbs on Lewis basic N site (around Au⁺), is reduced by the electrons on Au⁺. Moreover, the lower energy barrier of adsorbed intermediates around single Au atom favors the eight-electron path, thus increases the CH₄ production; *ii*). CO₂ adsorbs on amino groups or Lewis basic N (not around Au⁺), is directly reduced by the electrons on graphitic carbon nitride. The holes are consumed by water to produce O₂.

In summary, we have successfully prepared the Au single atoms on amino-group enriched graphitic carbon nitride by mild urea reduction method. The atomically dispersed metal atoms exist in the form of Au⁺ and supported by three N atoms, with bond length of 2.05 Å. U-ACN exhibits a high performance for photocatalytic CO₂ reduction. The yield of CO and CH₄ are 1.97 and 4.15 times that of pure graphitic carbon nitride, while CH₄ to CO ratio is 2 times that of graphitic carbon nitride. The outstanding ability of U-ACN ascribes to its improved intermediate-adsorption ability, narrowed bandgap, decreased carrier-recombination rate by introducing Au. In addition, the introduced amino-group improved its CO₂ affinity.

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Au single atoms on amino-group modified g-C₃N₄ is synthesized through a mild urea reduction method to achieve a high CO₂ reduction activity.

HAADF-STEM image of Au₁/g-C₃N₄

Au₁/g-C₃N₄

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