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Ultrasmall Au nanocatalysts supported on nitrated carbon for electrocatalytic CO₂ reduction: the role of the carbon support in high selectivity†

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Au is one of the most promising electrocatalysts to convert CO₂ into CO in an aqueous-phase electrochemical reduction. However, ultrasmall Au nanocatalysts (AuNCs, <2 nm) have proven to be favorable for water reduction over CO₂, although they possess a large surface-to-volume ratio and potentially are ideal for CO₂ reduction. We herein report that ultrasmall AuNCs (1.9 ± 0.3 nm) supported on nitrated carbon are remarkably active and selective for CO₂ reduction. The mass activity for CO of AuNCs reaches 967 A g⁻¹ with a faradaic efficiency for CO of ~83% at -0.73 V (vs. reversible hydrogen electrode) that is an order of magnitude more active than the state-of-the-art results. The high activity is endowed by the large surface area per unit weight and the high selectivity of ultrasmall AuNCs for CO₂ reduction originates from the cooperative effect of Au and the nitrated carbon support where the surface N sites act as Lewis bases to increase the surface charge density of AuNCs and enhance the localized concentration of CO₂ nearby catalytically active Au sites. We show that our results can be applied to other pre-synthesized Au catalysts to largely improve their selectivity for CO₂ reduction by 50%. Our method is expected to illustrate a general guideline to effectively lower the cost of Au catalysts per unit weight of the product while maintaining its high selectivity for CO₂ reduction.

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Introduction

Efficient and selective conversion of CO₂ into useful chemicals and fuels has received considerable attention as a means to reduce CO₂ emission, known as an increasing environmental threat.^{1–8} The key for various CO₂ conversions is to develop new catalysts.⁹ Au nanocatalysts (AuNCs), among various metal catalysts developed so far,^{10–15} show high activity to convert CO₂ into CO in aqueous-phase electrochemical reduction.^{16–28}

Despite many advances and successful examples of electrocatalytic CO₂ reduction, there are two unmet challenges that have largely limited the industrial use of Au catalysts for CO₂ electroreduction. On the one hand, poor selectivity (or low faradaic efficiency, FE) of CO₂/CO is often achieved, arising from the competitive reduction of H₂O/H₂. The standard potential of CO₂/CO is -0.106 V (vs. reversible hydrogen electrode (RHE)), all potentials reported here are with respect to RHE), which is more difficult to be reduced thermodynamically compared to H₂O/H₂.^{5,29} The groups of Cuenya³⁰ and Jin²⁴ showed that AuNCs having sub-2 nm diameter catalyzed electrocatalytic CO₂ reduction to CO even at very low overpotentials (η , e.g., <100 mV for Au₂₅ nanoclusters) but the FE for CO₂ reduction was <20% at η = 550 mV. Although the reduction operating at high η achieves higher FE to CO,²⁴ it needs much greater energy input.

On the other hand, the high cost of the catalyst per unit weight of the product (i.e. CO) has largely limited the commercialization of Au catalysts for CO₂ electroreduction. The groups of Sun²² and Bao²⁶ demonstrated that AuNCs in the size range of 2–10 nm exhibited a mass activity of <20 A per g_{Au} toward the formation of CO at η = 550 mV.^{19,22,26} In order to lower the cost of the catalyst per unit weight of the product, an impor-

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tant factor is to reduce the size of Au that increases the proportion of surface atoms and maximizes the usage of all Au atoms. However, AuNCs having smaller sizes have proven to be more favorable for water reduction.^{22,24,30,31}

To solve these challenges in CO₂ reduction, enhancing the favorable interaction of CO₂ with catalysts over H₂O is essential. One way to improve the binding of electrophilic CO₂ to AuNCs is to vary the surface charge density of Au catalysts.^{26,27}

For example, the use of carbene as surface ligands to modify Au nanoparticles (NPs) was demonstrated to enrich the surface charge of Au by the groups of Yang and Chang,²⁷ because of the σ donation from carbene ligands. Carbene-modified Au facilitated CO₂ binding with significantly enhanced CO FE over hydrogen production. Our group recently reported the in situ growth of ligand-free, sub-2 nm AuNCs onto virtually any carbon support using a facile and environmentally friendly "soft nitriding" technique.^{32–34} These AuNCs are ultrasmall in size with a large proportion of surface atoms (>60%, edge/corner atoms predominantly). Nitrogen-rich carbon supports showed strong electronic interaction with Au where N sites enriched the surface charge density of Au.³² Such electron-rich AuNCs with a high surface area are therefore hypothesized to enhance the efficiency for CO₂ binding and reduction, in spite of the ultrasmall size of AuNCs, as confirmed by density functional theory (DFT) calculation. Moreover, we envision that N sites on the surface of carbon supports act as basic sites to potentially increase the localized concentration of CO₂ nearby catalytically active Au.^{35–37} This in turn shifts the binding equilibrium of CO₂ to Au according to Le Chatelier's principle.^{38,39}

AuNCs supported on nitrated carbon (AuNCs@CN) thus favor the electroreduction of CO₂. At $\eta = \sim 544$ mV, AuNCs@CN show a mass activity of 714 A g⁻¹ with CO FE of 89% (Fig. 1), that is an order of magnitude more active (with high selectivity as well) than the state-of-the-art results.^{19,22,26} One of the attractive features is the possibility to use nitrated carbon to support other pre-synthesized AuNCs which are ca. 50% more active for CO₂ reduction, compared to the same AuNCs on pristine carbon.

Experimental

Materials

HAuCl₄, urea, NaBH₄, hydrochloric acid (HCl), sodium hydroxide, Nafion (5 wt% solution in alcohol), chloroform, 1-chloroethanol, potassium iodide, oleylamine, 4-mercaptobenzoic acid (MBA), ascorbic acid (AA), ethanol, and hexane were all purchased from Sigma-Aldrich and used without further purification. Printex U activated carbon was kindly provided by Orion. Deionized water (High-Q, Inc. 103S Stills) with a resistivity of >10.0 M Ω was used in the experiments.

Synthesis of Au-2@CN, Au-5@CN, and Au-8@CN

Au-2@CN was synthesized by following our previous report.^{32–34} Briefly, activated carbon (2 g) was mixed with urea (3 g). This mixture was sealed in a crucible using aluminum

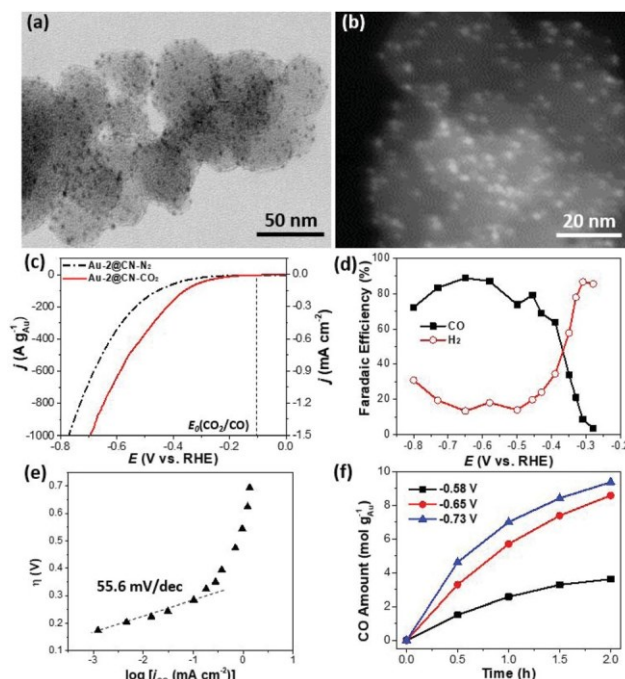


Fig. 1 Electron microscopy of Au-2@CN and its CO₂ electrochemical reduction results. Bright-field (a) and dark-field (b) STEM images of Au-2@CN. (c) LSV scans of Au-2@CN at 10 mV s⁻¹ in N₂ (black, dash) and CO₂ (red, solid) saturated NaHCO₃ solution (0.5 M). (d) Faradaic efficiencies for CO and H₂ at different potentials. (e) Tafel plot of Au-2@CN. (f) CO production amount using Au-2@CN at different potentials.

foil, followed by annealing at 150 °C for 2 h and 300 °C for 2 h. The nitrated carbon (CN) was obtained after washing with water and ethanol three times and dried at 60 °C under vacuum. To prepare Au-2@CN, 100 mg of CN was first dispersed in 200 mL of water by sonicating for 1 h at r.t. 5 mg of HAuCl₄ was added to the above mixture, followed by stirring for 2 h. Then, 6 mL of freshly prepared NaBH₄ solution (ice-cooled, 1 mg mL⁻¹) was added. After stirring for 1 h, Au-2@CN was obtained by washing with water and ethanol, followed by drying at 60 °C. Au-5@CN was prepared by growing Au on CN in the reaction solution with pH = 3, adjusted by adding HCl solution. The Au-8@CN was prepared by growing Au on CN in the reaction solution with pH = 12, adjusted by adding NaOH solution.

Synthesis of AuNCs using Au-2@CN as seeds

Au with different sizes on CN was also synthesized via a seed-growth method using Au-2@CN.⁴⁰ The size of Au can be adjusted via the feeding amount of HAuCl₄. Taking 2.9 nm Au as an example, 20 mg of Au-2@CN was first dispersed in 16.4 mL of ethanol/water solution (ethanol: water = 3 : 1 by volume). Then, 1.95 mL of MBA (0.436 mg mL⁻¹ in ethanol) and 75 μ L of HAuCl₄ (10 mg mL⁻¹ in water) were added into the above solution, followed by adding 976 μ L of AA (7.37 mg mL⁻¹ in ethanol/water). After stirring for 1 min, the solution was aged overnight. The sample was washed with ethanol

twice before drying in an oven at 60 °C. The resulting powder was further annealed at 250 °C in the air for 1 h to remove surface ligands.

Synthesis of physically adsorbed Au on CN and C

Oleylamine-modified AuNPs were synthesized by following the previous report.^{41,42} Firstly, HAuCl₄·3H₂O (0.5 mmol) was dissolved in a mixture of oleylamine (2 mL) and hexane (20 mL) in a round bottom flask at room temperature. 1 mmol of tert-butylamine borane complex was dissolved in 2 mL of oleylamine and 2 mL of hexane simultaneously. The tert-butylamine borane solution was injected into the precursor solution in the round bottom flask. After stirring for one hour at room temperature, ethanol was added to the solution to precipitate the Au NPs, followed by centrifugation to obtain the Au NPs. The Au NPs were re-dispersed in hexane to form 1 mg mL⁻¹ solution for further usage.

The physically adsorbed Au on CN and C was prepared by following the previous report.²² Typically, 50 mg of CN (or C) was dispersed in 20 mL hexane by sonication. Then 1.25 mL Au solution (1 mg mL⁻¹) was added into the CN suspension, followed by stirring in the fume hood overnight to evaporate the solvent. The resulted powder was further annealed at 180 °C in the air overnight to remove the surface ligand.

Synthesis of chloroform quenched Au-2@CN (Au-2@QCN1) and chloroethanol quenched Au-2@CN (Au-2@QCN2)

We used two different methods to quench surface N sites. Au-2@QCN1 was prepared using chloroform as the quenching agent. Briefly, 10 mg of Au-2@CN was dispersed in 5 mL of 0.5 M NaOH solution and 5 mL of ethanol by sonication. Then 2 mg of chloroform was added into the solution, followed by maintaining the reaction at 60 °C overnight. The sample was washed with H₂O and ethanol, followed by drying in an oven at 60 °C. Au-2@QCN2 was prepared using chloroethanol as the quenching agent. Briefly, 10 mg of Au-2@CN was dispersed in 5 mL of 0.5 M NaOH solution and 5 mL of ethanol by sonication. Then 5 mg of chloroethanol and 1 mg of KI were added into the solution, followed by maintaining the reaction at 60 °C overnight. The sample was washed with H₂O and ethanol, followed by drying in an oven at 60 °C. Similar quenching experiments were carried out for CN to obtain QCN1 and QCN2 for XAS measurements.

Electrochemical measurements

A CH Instruments 627E workstation was used for all CO₂ reduction. Pt wire and SCE were used as the counter electrode and the reference electrode, respectively. The working electrode was a pyrolytic graphite (PG) electrode coated with the ink of catalysts. Typically, Au catalysts (2 mg) were dispersed in 380 µL of water, 95 µL of ethanol, and 25 µL of Nafion solution to obtain a uniform ink. 10 µL of the Au catalyst ink was dropped on the PG electrode and dried at room temperature before use. Linear sweep voltammetry (LSV) scans were carried out in 0.5 M NaHCO₃ solution in the potential window of -0.5 V to -1.7 V (vs. SCE) at a scan rate of 10 mV s⁻¹. The elec-

trolyte solution was saturated with N₂ or CO₂ before any test and the potential was converted to RHE using the below equation:

$$E(\text{RHE}) = E(\text{SCE}) + 0.244 \text{ V} + 0.0591 \times \text{pH}$$

The pH was 7.2 and 8.4 when the electrolyte was saturated with CO₂ and N₂, respectively. The mass activity of the catalysts was calculated based on the following equation:

$$j_{\text{CO}} = \frac{i \times \text{FE}}{m} \quad (1)$$

where *i*, FE, and *m* are the current, faradaic efficiency at a specific potential, and loading mass of Au on the electrode, respectively.

The electrochemical surface area was estimated from the reduction peak of Au catalysts in the electrolyte of 0.1 M HClO₄.²³ The electrode was first scanned from 0.26 V to 1.66 V at a scan rate of 50 mV s⁻¹ to oxidize the Au surface. Then, the oxidized Au was reduced with the scan from 1.66 V back to 0.26 V. The reduction peak of Au was used to calculate the electrochemical surface area as described previously. 390 µC cm⁻² was used as the reference charge value for Au.⁴³ The equation to calculate the ECSA is shown below:

$$\text{Charge} = \frac{\text{Area of Au reduction peak}}{\text{Scan rate}} \quad (2)$$

$$\text{ECSA} = \frac{\text{Charge}}{390 \mu\text{C cm}^{-2}} \quad (3)$$

Product analysis

The electrochemical CO₂ reduction experiments were carried out in a customized H-cell with the cathode and anode separated by a frit bridge (Fig. S1†). The working electrode and the reference electrode are sealed in one cylinder and the counter electrode was in the other cylinder. SCE and Pt wire were used as the reference electrode and counter electrode in all experiments, respectively, and the potentials were all converted to RHE. 0.5 M NaHCO₃ was used as the electrolyte in all experiments. 20 mL of electrolyte was added into both cells, leaving 13 mL of head space. The electrolyte was bubbled with CO₂ for at least 20 min before the tests. The I-t curve was measured at different potentials and the products at different potentials were analyzed using gas chromatography. The amount of products (H₂ and CO) was calculated from the peak area using the standard calibration curves.

Characterization

TEM and HR-TEM were carried out on a JEOL 2010 transmission electron microscope with an accelerating voltage of 200 kV. STEM and STEM mapping were performed using a Talos F200X Atomic Resolution Analytical Microscope. TEM and STEM samples were prepared by casting a suspension of the materials on a carbon coated copper grid (300 mesh). XPS was carried out on a PHI Quantum 2000 spectrometer with a multiprobe (Physical Electronics Industries Inc.) using Al Kα

($\lambda = 1486.6$ eV) as the radiation source. The spectra of C 1s, N 1s, and Au 4f were recorded and analyzed/fitted using the Casa XPS software. Thermogravimetric analysis with mass spectroscopy (TGA-mass) was performed on a DuPont 951 thermogravimetric analyzer. During the test, the catalyst was first pretreated under an Ar flow for 2 h at 200 °C. Then, 5% CO₂ in Ar was flowed over the sample for 30 min at room temperature. The Ar flow was carried out for 30 min to remove the physically adsorbed CO₂ before the TGA test from 27 °C to 600 °C with a ramp-up of 15 °C per min under an Ar flow. The flow rates were all 50 mL min⁻¹. The mass spectrometry for CO₂ was performed during the TGA test. The gas products from CO₂ reduction were measured on a Shimadzu GC-2014 GC system. The quantitative calculation of the products was performed using the calibration curves built by the standard gas of CO and H₂. The liquid products were analyzed using ¹H NMR with DMSO as the internal standard on a Bruker Avance 400 MHz spectrometer. The water suppression method was used in each test. The soft X-ray absorption spectra at the N K-edge were recorded at the REIXS beamline of the Canadian Light Source in partial fluorescence yield (PFY) mode. These measurements, sensitive to the unoccupied partial density of states of a particular element, are performed by exciting a core electron to the conduction band while monitoring the subsequent fluorescence decay. In a PFY measurement, the emitted photons are collected using an energy dispersive silicon drift detector, allowing the fluorescence associated with a particular core-hole transition of interest to be monitored. REIXS is an undulator beamline with a spot size of 60 × 10 μm² and the instrumental resolving power ($E/\Delta E$) was approximately 4000. The spectra were normalized to the incoming photon flux using a gold mesh placed in the X-ray beam upstream of the sample and the energy axis was calibrated using an h-BN reference sample and an initial peak position of 402.10 eV. The N peaks were deconvoluted and the peak area was used to calculate the ratio of N sites.

Results and discussion

Sub-2 nm AuNCs supported on nitrided carbon (Au-2@CN) were prepared by the chemical reduction of HAuCl₄ on nitrided carbon as reported previously.^{32–34} In brief, the soft nitriding of carbon (Printex U, Orion Co.) was carried out by annealing Printex U carbon with urea at 300 °C. After thoroughly washing to remove residual urea, nitrided carbon was dispersed in water together with HAuCl₄, followed by chemical reduction with NaBH₄ (see Experimental procedures for synthetic details). Scanning transmission electron microscopy (STEM) shows the growth of ultrasmall AuNCs on nitrided carbon (Fig. 1a and b). Printex U carbon nanospheres have an average diameter of ca. 50 nm and the size of AuNCs is 1.9 ± 0.3 nm. AuNCs are highly dispersed on carbon (see more STEM images in Fig. S2†). The distribution of N sites and Au on carbon was confirmed by STEM energy-dispersive X-ray spectroscopy (Fig. S2†). The loading amount of AuNCs

was estimated to be 2.5 wt% relative to carbon from thermogravimetric analysis (Fig. S3†), consistent with the result from the STEM energy dispersive X-ray spectroscopy (Fig. S2†).

Electrochemical reduction of CO₂ was evaluated in 0.5 M NaHCO₃ aqueous solution (pH = 7.2) using Au-2@CN in an “H” cell. The typical linear sweep voltammetry (LSV) is given in Fig. 1c. Under N₂, only proton reduction occurred; when replaced with CO₂, a much higher current density was seen which is indicative of high selectivity towards CO₂ reduction. The gas products were quantitatively analyzed in the potential window of -0.8 V to -0.28 V using gas chromatography (Fig. 1d and S4–S10†). H₂ and CO were confirmed as the two main gas products. A trace amount of formic acid can be detected from ¹H NMR as well (Fig. S4–S10†), but the FE for formic acid is <1%. Au-2@CN shows an onset potential of -0.28 V where CO can be detected as a gas product, corresponding to an overpotential of 174 mV, given $E(\text{CO}_2/\text{CO}) = -0.106$ V. Au-2@CN gives a high FE for CO and a low FE for H₂ when the potential is lower than -0.45 V. At $\eta = 544$ mV, a mass activity (j_{CO}) of 721 A g⁻¹ and a FE for CO of 89% are achieved (Fig. 1d). A mass activity larger than 1000 A g⁻¹ was achieved at -0.8 V, far better than those of the state-of-the-art Au-based nanocatalysts (Table S1†) for CO₂ reduction.^{19,20,22–27,44,45} We also confirmed that the activity of CO₂ reduction originated from AuNCs other than the carbon support, since both activated carbon and nitrided carbon solely favored proton reduction in the potential range of -0.7 to -1.2 V (see Fig. S11 and S12†). Note that there are reports showing nitrided carbon as active catalysts for CO₂ reduction,^{46–49} however, the nitrided carbon through soft nitriding is inactive for CO₂ reduction under conditions used in our studies. Using an electrolyte with a lower concentration of NaHCO₃ (0.1 M) or higher loading of catalysts would lower the mass activity in CO₂ reduction (Table S2†) since both the conductivity of the electrolyte and the difficulty of CO₂ diffusion through catalysts play key roles in determining the electroreduction.^{50,51}

The kinetics of CO₂ reduction catalyzed by Au-2@CN was examined using a Tafel plot. The specific current density toward CO formation (j_{CO}) normalized to the electrochemical active surface area (ECSA) of Au was obtained from the total current density and CO FE. The plot of η vs. $\log(j_{\text{CO}})$ is displayed in Fig. 1e. A Tafel slope of 55.6 mV dec⁻¹ in the low overpotential region was seen and it is one of the lowest values compared to other reported values for CO₂ reduction using Au catalysts.^{25,27} The smaller Tafel slope is indicative of a fast electron transfer step prior to a rate-determining chemical step,^{25,52} which proves the formation of stable CO₂ intermediates on the surface of AuNCs.^{27,53,54} Electron-rich AuNCs likely facilitate the electron transfer to CO₂ that thus enhances the activity of CO₂ reduction. The stability test of Au-2@CN was carried out at a constant potential for 2 h (Fig. 1f). The rate of CO production is 2–7 mol h⁻¹ per g_{Au} depending on the potential. The depression of CO production was seen after 1.5 h of electrolysis which is likely caused by the increase in the size of AuNCs. After 2 h of electrolysis, the average size of AuNCs

increased to 3.8 ± 0.6 nm as examined by TEM (see Fig. S13†). This agrees with the drop in the ECSA of Au by 77% (Fig. S13†). The low stability of AuNCs is due to the large surface energy similar to other nanocatalysts reported in the literature.^{31,55} The durability of AuNCs in CO₂ reduction is still an obstacle for the practical use of our catalysts.

DFT calculation was applied to estimate the free energy of each step in the catalytic process using electron-rich and neutral Au₂₈ clusters in order to understand the influence of Au surface charge density on CO₂ reduction. This model has been used in our previous simulation for selective oxidation.³² The CO₂ reduction on Au is simply assumed to include the following steps for the two-electron CO₂ reduction:²²

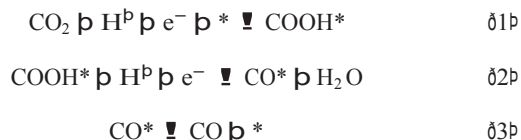


Fig. S14† displays the calculated free energy diagram for CO₂ reduction on Au₂₈ clusters based on the computational hydrogen electrode (CHE) model.⁵⁶ One CO₂ and a proton-electron pair adsorbed on a Au₂₈ cluster to first form a carboxyl intermediate (COOH*); then, the COOH* intermediate can dissociate into CO* and H₂O as products by adding the second proton-electron pair. On the neutral cluster, the CO₂ activation through COOH* formation was associated with a free energy of 0.68 eV, while on the electron-rich cluster, the formation of the COOH* intermediate has a significantly lower free energy barrier of 0.42 eV. As such, electron-rich AuNCs likely favor the reduction of CO₂.

However, electron-rich Au₂₈ clusters also showed much lower activation energy for proton reduction. The CHE model indicated that the free energy change (ΔG) to form the H* intermediate on electron-rich clusters is 0.26 eV, lower than that on the neutral cluster, 0.53 eV (Fig. S14†). The DFT results agreed that AuNCs with smaller sizes favor proton reduction as reported previously.^{22,30} Since electron-rich Au catalysts and nitrated carbon do not solely promote CO₂ reduction, we further investigate the cooperative effect of AuNCs and N sites on the nitrated carbon support.

To gain further insight into the role of N sites on the electrochemical reduction of CO₂, two reactions were used to selectively quench N sites. Carbylamine reaction is known to terminate primary amines with CHCl₃ in the presence of bases,⁵⁷ and alkylation with chloroethanol is known to react all amines to form a quaternary ammonium salt.⁵⁸ Both reactions were carried out under mild conditions which had slight impacts on the size and ECSA of AuNCs (Fig. S15 and S16†). Au-2@QCN1 and Au-2@QCN2 denote the samples quenched by CHCl₃ and chloroethanol, respectively. CO₂ reduction using these two catalysts was examined under identical reaction conditions as described for Au-2@CN. Fig. 2a shows the plot of j_{CO} of Au catalysts before and after quenching N sites. The activity for CO₂ reduction shows a ~10% and ~75% decrease for Au-2@QCN1 and Au-2@QCN2, respectively, compared to

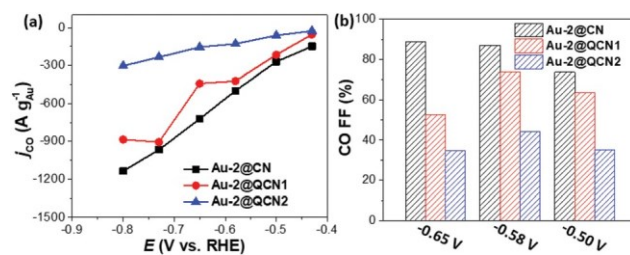


Fig. 2 The effect of nitrogen sites on the electrochemical reduction of CO₂. Mass activity (a) and CO FE (b) of Au-2@CN, Au-2@QCN1 and Au-2@QCN2 at different potentials.

that of Au-2@CN. The CO FE of Au-2@QCN2 is only 30–40% in the potential window of -0.4 V to -0.8 V (Fig. 2b and S15–S16†), close to the reported values from Cuenya³⁰ and Jin.²⁴

X-ray photoelectron spectroscopy (XPS) was used to investigate the change in the electronic states of Au and N along quenching nitrogen sites. Au-2@CN shows two asymmetric peaks at 83.9 eV and 87.6 eV, assigned to the binding energy of Au 4f (Fig. 3c). The quenching of surface nitrogen sites on carbon resulted in a gradual shift of Au 4f peaks. After the alkylation of amines, the binding energy of Au 4f_{7/2} shifted to 84.2 eV. The increase in the binding energy of the Au 4f peaks suggests that the surface of AuNCs became electron-deficient after quenching the nitrogen sites. On the other hand, the binding energy of N 1s had a 0.4 eV decrease from 400 eV for Au-2@CN to 399.6 eV for both Au-2@QCN1 and Au-2@QCN2. Surface nitrogen sites on nitrated carbon contain three main N species, including amine and amide groups (~400 eV), quaternary nitrogen (or graphitic, ~401.1 eV) and pyridinic nitrogen (~398.6 eV).³⁴ The fitting curves show that the graphitic nitrogen gradually dropped from 14.9% for Au-2@CN to 7.0% for Au-2@QCN1 and 3.5% for Au-2@QCN2. The removal of surface graphitic nitrogen sites obviously changed the electronic interaction of AuNCs and the nitrated carbon support in the course of quenching reactions,⁵⁹ although the exact reaction mechanism is unclear currently. In addition, we utilized N K-edge X-ray absorption spectroscopy (XAS) to confirm the evolution of N sites in the quenching experiments (see Fig. 3c, d and Fig. S17†). The N K-edge consists of three main absorption peaks at 398.9 eV, 400.2 eV and 401.4 eV designated as pyridinic N (N1), ureido (or amide) (N2), and graphitic N (N3), respectively. The decrease in pyridinic and graphitic N sites was observed similar to the XPS results. Interestingly, a clear shoulder peak at ~399.2 eV is seen for Au-2@CN that can be assigned to metal–N binding.^{60,61} The disappearance of this feature after quenching N sites is also an evidential sign to the weakened metal–N interaction. These findings show that the quenching of N sites results in the decrease in the surface charge density of AuNCs (or the Au–carbon electronic effect) and electron-deficient AuNCs are less selective catalysts for CO₂ reduction.

Other than the electronic effect on AuNCs, various nitrogen sites (e.g. amine, pyridine and graphitic N) on carbon supports

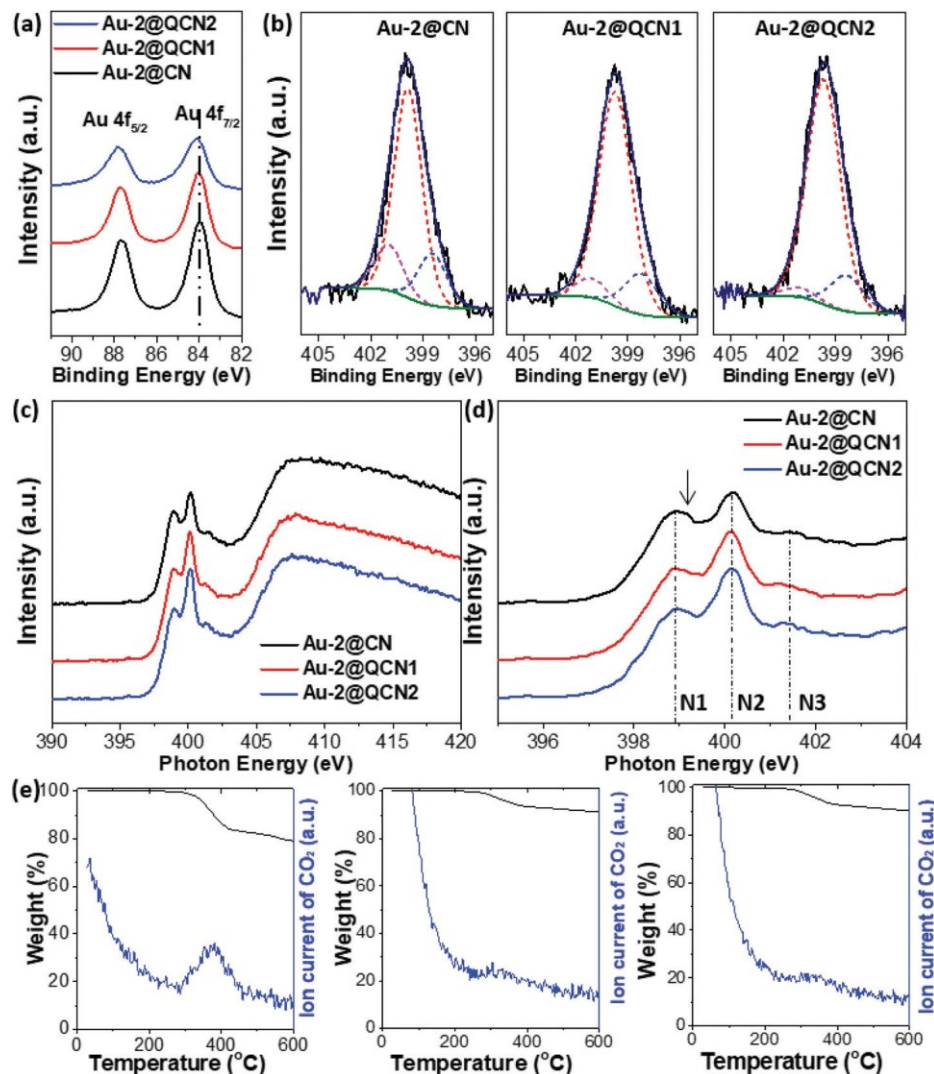


Fig. 3 Surface characterization of catalysts. XPS spectra of Au 4f (a) and N 1s (b), and N K-edge XAS spectra (c, d) of Au-2@CN, Au-2@QCN1 and Au-2@QCN2; (e) TGA-MS results for CO₂ desorption of Au-2@CN (left), Au-2@QCN1 (middle) and Au-2@QCN2 (right).

can interact with CO₂ through acid–base chemisorption. We probed the potential adsorption of CO₂ on Au-2@CN, Au-2@QCN1 and Au-2@QCN2 using thermogravimetric analysis with a mass spectrometer (TGA-MS, see Experimental procedures for the details). Fig. 3e shows that Au-2@CN showed a strong CO₂ desorption peak at ca. 380 °C, while a very weak CO₂ signal could be seen for Au-2@QCN1 and Au-2@QCN2. This suggests that the two catalysts after quenching N sites did not show obvious CO₂ desorption. The adsorption of CO₂ obviously occurred on the surface N sites since the desorption occurred at the decomposition of nitrated carbon. The two catalysts after quenching N sites showed less mass loss, which is caused by the loss of some N species during the reactions (Fig. S18†). We also did not see CO₂ adsorption on pristine Printex U carbon (see Fig. S19†). The adsorbed CO₂ on nitrated carbon can kinetically promote CO₂ reduction through the

increase of localized CO₂ concentration. The primary amines, however, are less likely involved in the cooperative effect because Au-2@QCN1 shows an activity close to that of Au-2@CN. We emphasize that the catalytic enhancement for CO₂ reduction arises from the cooperative effect, i.e., the electronic states of Au and the basicity of the surface nitrogen sites. However, the surface nitrogen sites solely are inactive for CO₂ reduction as shown in our control experiments when using nitrated carbon as catalysts.

The Au–support electronic interaction is known to be size-dependent.³² Larger AuNCs grown on nitrated carbon have proven to be less electron-rich, compared to Au-2@CN. To assess the size effect of Au, we designed two experiments to grow AuNCs having different sizes in the range 2–8 nm. First, ligand-free AuNCs with similar loading masses but different average diameters of 5.1 nm and 8.4 nm were grown on

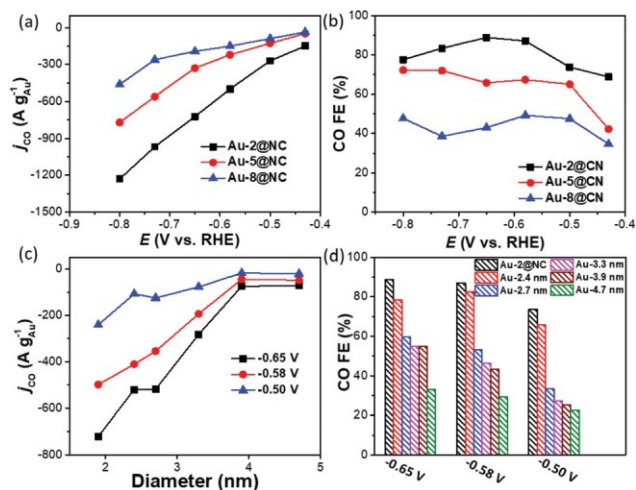


Fig. 4 Size effect of AuNCs on the electrochemical reduction of CO₂. Mass activity (a) and CO FE (b) of Au-2@CN, Au-5@CN and Au-8@CN synthesized using one-step chemical reduction; mass activity (c) and CO FE (d) of AuNCs synthesized via seed-mediated growth using Au-2@CN as seeds.

nitrided carbon by varying the solution pH (denoted as Au-5@CN and Au-8@CN, Fig. S20†).³⁴ The mass activity toward CO₂ reduction and CO FE are summarized in Fig. 4a and b. Au-5@CN and Au-8@CN are less active for CO₂ reduction, though the activity difference in their LSV scans is minimum (Fig. S21†). At -0.8 V, Au-2@CN showed a j_{CO} of $-1200 \text{ A g}_{\text{Au}}^{-1}$, which is 1.5 times and 2.5 times higher than that of Au-5@CN and Au-8@CN, respectively. In the potential window of -0.4 V to -0.8 V, the CO FE of ~70% and ~45% were seen for Au-5@CN and Au-8@CN, respectively. Second, we prepared AuNCs with an average size of 2.4–4.7 nm supported on nitrided carbon using Au-2@CN as seeds via the seed-mediated growth (Fig. S22,† see Experimental procedures for details). The j_{CO} and the selectivity of CO₂ reduction dropped dramatically even after slightly increasing the size of AuNCs (Fig. 4c and d). At -0.65 V (vs. RHE), j_{CO} decreased from $721 \text{ A g}_{\text{Au}}^{-1}$ to $71.8 \text{ A g}_{\text{Au}}^{-1}$ and CO FE decreased from 88.8% to 33.0% when the size of AuNCs increased from 1.9 nm to 4.7 nm. These results therefore confirm that the electronic interaction of Au–carbon played a key role in determining the selectivity of CO₂ reduction over water reduction.

We further investigated whether we can use the cooperative catalytic effect of the nitrided carbon and AuNCs universally. Au NPs with an average size of 6.8 nm were prepared using oleylamine as ligands.^{41,42} These Au NPs were then adsorbed physically on nitrided carbon and pristine carbon (Fig. S23 and S24†). The two Au NPs were studied for CO₂ reduction under identical conditions. Au NPs on nitrided carbon showed a higher mass activity toward CO₂ reduction, compared to that of Au NPs supported on pristine carbon (Fig. 5b). At -0.58 V, 2 times higher mass activity and CO FE were achieved for Au NPs on nitrided carbon, compared to the same AuNPs loaded on activated carbon.

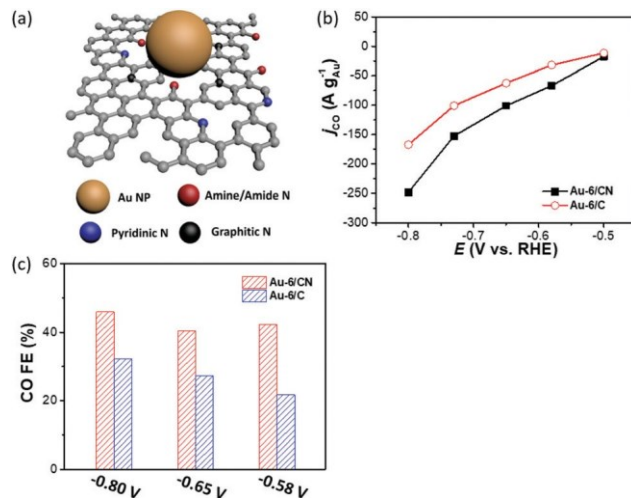


Fig. 5 Electrochemical CO₂ reduction of AuNCs adsorbed on CN and C. (a) Scheme of CO₂ reduction on Au@CN; mass activity (b) and CO FE (c) using Au-6/CN and Au-6/C at different potentials.

Conclusions

In the aqueous-phase electrochemical reduction of CO₂, there are many studies suggesting that ultrasmall Au catalysts with sub-2 nm diameter favor the reduction of water over CO₂.^{24,30,31} Our observation is that the 1.9 nm AuNCs supported on nitrided carbon are highly selective and active in CO₂ reduction. Au-2@CN exhibited a low onset potential of -0.28 V and a high FE (>80%) for CO when the potential is lower than -0.45 V in 0.5 M NaHCO₃ aqueous solution. The mass activity of Au-2@CN reached $>1000 \text{ A g}_{\text{Au}}^{-1}$ at -0.8 V, that is an order of magnitude higher than those of many state-of-the-art Au-based nanocatalysts.^{19,20,22–27,44,45} The N sites on the nitrided carbon have proven to be critical in the control of the selectivity of CO₂ reduction. After quenching the N sites, an obvious drop of CO FE and mass activity was seen (see Fig. 3). The effects of N sites on CO₂ reduction are two-fold. First, the N sites acting as Lewis bases improve the localized concentration of CO₂ nearby catalytically active Au by chemisorption. TGA-MS results confirm that the nitrided carbon has a strong CO₂ chemisorption compared to the ones with quenched N sites. The activity for CO₂ reduction showed a ~75% drop and the CO FE decreased by 50% for Au-2@QCN2 in the absence of N sites, compared to those of Au-2@CN. Second, the N sites enriching the surface charge density of AuNCs likely favor the binding of CO₂, as demonstrated by high-resolution XPS results, DFT and the size effect of Au catalysts on the CO₂ reduction selectivity. When increasing the size of Au catalysts, the CO FE decreased in two independent controls that demonstrated the importance of Au–support electronic interaction. The preferential reduction of CO₂ over water using ultrasmall AuNCs thus originates from the cooperative catalytic effect of the nitrided carbon and AuNCs. We further showed that the Au–carbon interaction can be applied to other pre-synthesized Au NPs to promote the catalytic activity and selectivity for CO₂ reduction.

However, the low stability is still unresolved in our current study which limits the practical use of AuNCs in CO₂ reduction. More efforts are needed to stabilize Au catalysts while maintaining their high mass activity and selectivity.

Conflicts of interest

There are no conflicts to declare.

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