Enhanced Electrochemical Reduction of CO₂ by Zeolitic Imidazolate Frameworks-8 Supported Silver Nanoparticles

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Silver (Ag) is a typical catalyst for CO₂ electroreduction. To improve the CO faradaic efficiency, ZIF-8 supported thiol-capped Ag nanoparticles (Ag NPs) of about 3.9 nm were facilely synthesized by reducing Ag⁺ in ZIF-8 suspension in the presence of thiol-containing mercaptopropionic acid (MPA) molecules. MPA can induce the monodisperse Ag NPs formation, cap on the surface of Ag NPs and immobilize on ZIF-8 through coordinating with the unsaturated Zn²⁺ cations. The Ag/ZIF-8 can efficiently reduce CO₂ to CO with a maximum CO faradaic efficiency of 92.3% at the potential of −0.88 V (vs. RHE), higher than that of ZIF-8 and Ag/C. The performance improvement in CO₂ electroreduction over Ag/ZIF-8 is probably attributed to the small-size of Ag NPs and the synergistic effect between Ag NPs and ZIF-8.

Introduction

The growing consumption of fossil resource since the first industrial revolution contributes to a large amount of carbon dioxide (CO₂) emissions to the atmosphere [1], which leads to several environmental problems, especially the global warming [2]. As CO₂ is the main origin of global warming, conversion of CO₂ into a clean energy source is considered to be a promising way to solve the emergent energy and environmental issues. Among various methods of utilizing and converting CO₂, the electrochemical reduction of CO₂ (CO₂RR) seems to be a promising strategy to simultaneously realize carbon cycle utilization and renewable energy storage for its clean, sustainable and effective properties [3].

CO, HCOOH and other hydrocarbon products have been reported as reduction products determined by the nature of the metal electrode that was used [3]. CO is one of the most common and desirable products from CO₂ reduction since it is a key starting material to synthesize other useful chemicals and fuel through, for example, the Fischer-Tropsch process [1]. However, CO₂ is a thermodynamically stable molecule, which needs a suitable catalyst to activate with significantly reduced energy penalty. In the field of metal-catalysts (e.g., Au, Ag, Pd and Zn), [4-8] Ag has attracted much attention because it gives a compromise between the cost and CO₂RR performance. To further improve the catalytic performance of Ag, researchers devote much effort to tuning the size and shape of Ag catalyst [9-10], forming silver alloy [11] or various nanostructures [12-13]. Ag nanoparticles (Ag NPs) show good selectivity and catalytic activity in the past studies [10], but it is not easy to prepare ultrafine Ag NPs, because they possess high surface energy and readily aggregate during the reduction reaction. It is necessary to simplify the nanofabrication of Ag particles and enhance the CO₂RR performance of Ag NPs.

Metal-organic frameworks (MOFs), combining the favorable characteristics of heterogeneous and homogeneous catalysts, have been explored as a novel class of model catalytic materials for understanding CO₂RR. Zeolitic imidazolate framework-8 (ZIF-8) was first used as a catalytic material for CO₂RR as reported by Yulin Wang et al., and delivered moderate catalytic activity with 65% CO yield [14]. Nikolay Kornienko et al. introduced a cobalt−porphyrin MOF, i.e., Al₂(OH)₂TCPP -Co, as an electrocatalyst for CO₂RR, which reveals a selectivity toward CO production more than 76% and stability over 7 h [15]. Xinhe Bao’s group found that ZIF-8 outperforms other structurally similar MOF catalysts (ZIF-8, ZIF-108, ZIF-7 and SIM-1) in CO₂RR, exhibiting a maximum CO Faradaic efficiency of 81% at −1.1V (vs. RHE) [16]. However, there is still a large space for further improvement in the MOF-catalyzed CO₂RR [15].

In this study, ultrafine Ag NPs uniformly decorated ZIF-8 (Ag/ZIF-8) was obtained by reducing Ag⁺ in ZIF-8 suspension in the presence of thiol-containing mercaptopropionic acid (MPA) molecules for electrochemical reduction of CO₂ to CO. The Ag NPs were capped with thiol groups from MPA and immobilize on ZIF-8 with the help of MPA. With the cooperation of ZIF-8 and Ag NPs, Ag/ZIF-8 exhibited apparently increased current density with the CO Faradaic efficiency increasing to 92.3%. Besides, the Ag/ZIF-8 catalyst showed higher CO Faradaic efficiency than Ag/C and ZIF-8. Overall, the strategy developed here demonstrated a novel and
convenient route to synthesize supported small-sized Ag NPs to enhance CO₂RR performance of Ag.

**Experimental section**

**Materials**

Nafion solution (5 wt%) was purchased from Shanghai Hesen Electric Company. 2-methylimidazole (2-MeIM, 99%) was obtained from Aladdin Corporation. Potassium chloride (KCl >99.5%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%), ethylene glycol (EG, 99.8%), absolute ethanol, silver nitrate (AgNO₃, 99.8%) and methanol (>99.8%) were purchased from Sinopharm Chemical Reagent Corporation. 3-mercaptopropionic acid (MPA, 99%) was obtained from Dama Beta Corporation. Sodium borohydride (NaBH₄, 99%) was purchased from Alfa Aesar Corporation. Vulcan XC-72R carbon black was obtained from Cabot Corporation. All electrolytes were prepared using deionized water. The above chemicals were used as received without further purification.

**Catalyst synthesis**

**Synthesis of ZIF-8**

The synthesis of ZIF-8 was modified from a previous report [17]. Typically, zinc nitrate hexahydrate (2.975 g) and 2-methylimidazole (3.284 g) were separately dissolved in methanol (100 mL) and then mixed together under vigorous stirring for 5 min. The solution was stirred at room temperature for 12 h. After that, white powders were collected by centrifugation, washed several times with methanol, and dried overnight at 60°C.

**Synthesis of Ag/ZIF-8 and Ag/C**

30 mL AgNO₃ methanol solution and MPA methanol solution were mixed at a AgNO₃/MPA molar ratio of 1:3. The solution was stirred for 3 hours at room temperature, and white turbidity was collected by centrifugation and purified using ethanol to remove unreacted reagent. The product was finally dispersed in 8.0 mL of methanol by sonicating for 30 min. The prepared carbon black was obtained from Cabot Corporation. All electrolytes were prepared using deionized water. The above chemicals were used as received without further purification.

**Production analysis**

The gas generating components were collected from the closed space above the cathode and analyzed by gas chromatography (GC 9790, FULI). The liquid product was collected and analyzed by ¹H NMR spectroscopy. In our experiments, CO and H₂ were detected as the only products. Faradaic efficiency (FE) is calculated by the following formula:

\[ \text{FE} = \frac{x \times n}{Q} \times 100\% \]

where: \( x = \) number of electrons exchanged (for CO and H₂), \( n = 2 \)

\( n = \) the number of moles for specific product

\( F = \) Faraday’s constant (96485 C/mol)

\( Q = \) the charge passed (C)

The partial current density for a specific product was calculated by multiplying total current density by Faradaic efficiency for this product.

**Characterization techniques**

The crystalline structures were detected by powder X-ray diffraction (XRD, Rigaku MiniFlex), with CuKα radiation (\( \lambda = 1.5418\AA \)) at 40 kV and 100 mA. Transmission electron microscopy (TEM) images was obtained on a FEI Tecnai G2 F20 S-TWIN instrument operated at 200 kV. Scanning transmission electron microscopy (STEM) image, energy-dispersive X-ray (EDX) spectra and STEM-EDX mapping were acquired with a FEI Tecnai G2 F20 S-TWIN instrument operated at 200kV. Scanning electron microscopy (SEM) image was obtained with a Hitachi SU-8010 SEM instrument. XPS (Thermo Scientific K-Alpha+) was utilized to detect the surface elemental chemical composition of catalysts with the adventitious carbon (C 1s) at the binding energy (BE) of 284.8 eV as the reference. The actual Ag loadings of different catalysts were measured by a Perking Elmer inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 720ES).

**Electrochemical performance**

**Preparation of working electrode**

Catalyst-modified glassy carbon was used as working electrode. Firstly, 7 mg catalyst and 3 mg carbon black were dispersed in a mixture containing 200 μL ethanol, 80 μL deionized water and 20 μL 5% Nafion solution by sonicating for 30 min to form a homogeneous ink. Then, 20
μL of the catalyst ink was coated on a 1 × 1 cm² glassy carbon electrode and dried in ambient condition overnight. Finally, we obtain the catalyst-modified glassy carbon.

CO: Electrochemical reduction performance

The electrochemical tests were performed with a CHI660E electrochemical workstation. All the electrochemical experiments were performed in H-type cell with two compartments (Figure S1) and three-electrode electrochemical setup. The cathodic and anodic compartment were separated by a Nafton N117 membrane. The catalyst-modified glassy carbon was used as working electrode. An Ag/AgCl electrode and a Pt net were used as the reference electrode and the counter electrode, respectively. Electrode potentials were iR corrected and converted to the reversible hydrogen electrode (RHE) scale using E (vs. RHE) = E (vs. Ag/AgCl) + 0.197V +0.0592 × pH. The electrolyte used for CO₂ reduction experiment was 0.5M KCl saturated with CO₂. The linear sweep voltammetry (LSV) of catalyst-modified GC electrode was performed in an Ar- or CO₂-saturated 0.5 M KCl aqueous electrolyte at room temperature with the scan rate of 10 mV/s.

Result and discussion

The typical preparation route of Ag/ZIF-8 nanocomposites is shown in Fig. 1a, starting from the pristine ZIF-8. ZIF-8 was synthesized according to previous report with a little modified parameters [17]. In order to decorate the ZIF-8 with the Ag nanoparticles (Ag NPs) uniformly, we introduced 3-mercaptopropionic acid (MPA) as the capping agent during the NaBH₄-assisted reduction of AgNO₃, which contains a thiol group (−SH) and a carboxyl group (−COO⁻) that are located at two ends of the MPA molecule. (Fig. 1b). In principle, the thiol group has stronger interactions with silver [18], meanwhile the carboxylate anions of MPA can coordinate with the unsaturated Zn²⁺ cations on the exterior surface of ZIF-8 (Fig. 1c).

Fig. 2 shows that both ZIF-8 and Ag/ZIF-8 exhibit similar X-ray diffraction (XRD) peaks to the simulated ZIF-8 [14]. Compared with ZIF-8, Ag/ZIF-8 shows no significant loss of crystallinity and no supplementary Bragg peaks, indicating that the structure of ZIF-8 is maintained after decoration with Ag NPs. It is difficult to observe the peaks of Ag in the XRD pattern of Ag/ZIF-8 (Fig. 2), because these peaks are too weak due to the ultrafine sizes of Ag NPs and also overlap with the relatively strong peaks of ZIF-8. However, the Ag XRD peaks for carbon-supported Ag NPs (Ag-C) synthesized with a similar procedure, especially the peak at 38.1° that corresponds to the Ag (111) reflection are much easier to distinguish (Figure S2), due to the less intense XRD peaks of carbon black and/or larger size of Ag NPs. Furthermore, due to the high MPA/Ag⁺ ratio during the preparation of Ag/ZIF-8 and Ag-C, some Ag₃S-like phase may exist [19], but can’t be detected in the XRD pattern of Ag-C, let alone in that of Ag/ZIF-8.

To investigate the structure of the MPA-bridged Ag/ZIF-8, X-ray photoelectron spectroscopy (XPS) was conducted. The comparison between the XPS survey spectra of ZIF-8 and Ag/ZIF-8 (Figure S3) confirms the presence of MPA and silver species in Ag/ZIF-8 due to its additional S 2p, Ag 3d and Ag 3p peaks. The high-resolution XPS spectra give more information (Fig. 3). The Ag 3d₅/₂ and Ag 3d₇/₂ double peaks in the Ag3d XPS spectrum are separated by a spin–orbit splitting of 6 eV (Fig. 3a). Ag/ZIF-8 possesses two main Ag 3d peaks at 374.3 and 368.3 eV (Fig. 3a), which reveals that metallic silver (Ag(0)) is the dominant silver species [20]. The second spin-orbit pair of small intensity at higher BE values (Ag 3d₇/₂ at about 369 eV, Fig. 3a) is attributed to the more oxidized surface Ag atoms bonding to MPA molecule through a Ag-S bond [19]. The possibly presented Ag ion...
(Ag+) in Ag$_2$S can’t be distinguished because a Ag(0)−Ag$_2$S peak separation is too small to be appreciated. There are three distinct chemical states for S shown in the S 2p spectra (Fig. 3b), where the S2p$_{3/2}$ and S2p$_{1/2}$ peaks were separated by a spin-orbit splitting of 1.2 eV. The S 2p$_{3/2}$ peak at the BE of nearly 162 eV (the red line, Fig. 3b) is associated with an Ag-S bond which results from the interaction of organometallic thiols with Ag surface [21]. The S 2p$_{1/2}$ signal close to 163 eV (the blue line, Fig. 3b) is due to sulfur atoms of physically adsorbed MPA molecules [19]. A spin-orbit bimodal with a lower BE value (BE S2p$_{3/2}$ component close to 161 eV, the green line in Figure 3b) can be associated with S in a chemical state like Ag$_2$S [19]. The XPS technique confirms the existence of Ag2S-like phase in Ag/ZIF-8, overcoming the above-mentioned inability of XRD technique to detect this species. Therefore, the NPs on ZIF-8 is probably composed of metallic Ag and small amount of Ag$_2$S-like phase [19]. Despite this, we still label the NPs as Ag NPs.

**Fig. 4.** SEM images of (a)ZIF-8 and (b)Ag/ZIF-8, and TEM images of (c) ZIF-8 and (d) Ag/ZIF-8.

**Fig. 4** displays the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images before and after the decoration of Ag NPs. **Fig. 4a** and **Fig. 4d** show the presence of ZIF-8 rhombohedral dodecahedrons with the size of about 100 nm. After being decorated with Ag nanoparticles, the main structure of ZIF-8 is well maintained (Fig. 4b). The TEM image clearly shows that Ag nanoparticles are uniformly distributed on the Ag/ZIF-8 (Fig. 4d) with an average size of 3.9 nm (Figure S4c). The crystal lattice spacing of the Ag/ZIF-8 is 0.23 nm (Figure S4b), which is consistent with the interplanar spacing of Ag (111) planes [10]. The electron diffraction also confirms the existence of Ag (Figure S4d). It can be seen from the Figure S4d that the electron diffraction pattern is ring-shaped and is accompanied by intermittent bright spots. The diffraction ring corresponds to the characteristic crystal planes of silver nanoparticles (111), (200), (220), (311). STEM-EDS mapping images (Figure S5) of the select area indicate the homogeneous dispersion of Ag and S atom on ZIF-8, but can’t exclude the core-shell structure of Ag NPs. It worth noting that the Ag NPs in the abovementioned Ag-C (without ZIF-8) are also uniform and nanoscale (Figure S6a), but the average particle size is 8.15 nm (Figure S6b), obviously higher than that of Ag NPs in Ag/ZIF-8. This comparison indicates that the capping agent MPA causes the uniform and nanoscale dispersion of Ag particles, [4] and meanwhile ZIF-8, rather than carbon black, can assist in further reducing the size of Ag NPs. For comparison, the Ag/C (with similar size of Ag NPs) was synthesized using a modified protocol according to reference, Figure S9a clearly shows that Ag nanoparticles are uniformly distributed on the Ag/C with an average size of 4.4 nm (Figure S9b), which is close to the Ag NPs in Ag/ZIF-8.

Figure S7 presents the linear sweep voltammetry (LSV) curves of Ag/ZIF-8 modified electrode in Ar- and CO$_2$-saturated KCl (0.5 M) electrolyte. The current density started to increase from approximately −0.7 V versus the reversible hydrogen electrode (RHE) in the Ar-saturated electrolyte, which is contributed by the hydrogen evolution reaction (HER). By contrast, the electrode in the CO$_2$-saturated electrolyte shows significantly higher current density owing to the occurrence of additional CO$_2$RR, which implies that Ag/ZIF-8 is an excellent CO$_2$RR catalyst.

The CO$_2$RR performance of the catalysts was evaluated at different potentials in a two-compartment cell with 0.5 M KCl at room temperature. In the experiment, CO is the major product and H$_2$ is the byproduct derived from the competitive HER. There are no liquid products detected by $^1$H NMR spectroscopy. To better compare the CO$_2$RR performance of Ag/ZIF-8, we evaluated another two catalysts, i.e., ZIF-8, and Ag/C, toward the CO$_2$RR. As shown in **Fig. 5a**, the current densities of Ag/ZIF-8 are slightly higher than those of Ag/C, but both of them are obviously higher than those of ZIF-8. This proves that Ag is the major contributor to the current density derived from CO$_2$RR and HER.

As shown in **Fig. 5b**, the Ag/C shows a maximum CO Faradaic efficiency (CO FE) of 87.6% at −0.88 V (vs. RHE), while the maximum CO FE for Ag/ZIF-8, with a similar Ag loading to Ag/C (Table S1), achieves to 92.3% at the same potential. Actually, Ag/ZIF-8 has higher CO FE than Ag/C at all the applied potentials. Without the Ag NPs, ZIF-8 shows a maximum CO FE of only 65% at −1.2V, which is line with the previous report$^{14}$ but largely inferior to Ag/ZIF-8 and Ag/C. Furthermore, CO partial current density ($j_{CO}$) was calculated by multiplying the CO FE by the total current density and plotted against the test potentials as shown in **Fig. 5c**. The partial current density for CO ($j_{CO}$) production increases with the increase of negative working potential (**Fig. 5c**). Among the three catalysts, Ag/ZIF-8 has the highest $j_{CO}$ in the applied potential range and reaches a maximum CO FE of 18.5 mA/cm$^2$ at −1.36V. For comparison, we have also listed the previous performance of similar catalysts for CO$_2$RR in supporting information Table S2.
Kim et al., synthesize Ag NPs/C with the help of cysteamine as the thiol-containing anchoring agent, but the cysteamine/Ag⁺ is very low, resulting in negligible Ag:S-like phase. For Ag/ZIF-8, the amount of Ag:S-like phase is relatively high, but their stability may be susceptible to the CO₂RR condition. To verify the speculation, XPS was employed to characterize the used Ag/ZIF-8 catalyst after CO₂RR under the maximum applied potential, i.e., −1.36 V (Figure S8). The S2p XPS spectrum (Figure S8b) is more informative than Ag 3d spectrum (Figure S8a). The almost-complete disappearance of S2p½ peak at 161 eV indicates that the Ag:S-like was reduced into Ag by the negative potential (−1.36 V, Figure S8b). However, the MPA still adsorbed on the Ag NPs, as shown by the peak at 163 eV (Figure S8b). It comes as no surprise that the XPS spectra exhibits the presence of sulfate species (above 167 eV, Figure S8b), because they are mainly contributed by the sulfonic acid (SO₃H) groups in Nafion mixed with the catalyst. For potentials less negative than −1.36 V, the Ag:S-like phase can’t be always reduced into Ag. Therefore, we concluded that the species that participate CO₂RR may be Ag:S-like phase or Ag, which depends on the CO₂RR potential. The effect of sulfation [22-23] or Ag-S interaction [4], either positive or negative, on the CO₂RR performance can’t be excluded, but it will not cover the catalytic advantage of Ag/ZIF-8 over Ag/C because Ag NPs in both catalysts were prepared by using MPA and would not exhibit too many differences. The small-sized Ag NPs (3.9 nm) on ZIF-8 and the possible synergistic effect between Ag NPs and ZIF-8 can account for the catalytic advantage of Ag/ZIF-8 over Ag/C.

When the Ag(0) can exposed to ZIF-8, the synergistic effect between Ag NPs and the ZIF-8 can be a possible positive factor for enhanced CO₂RR performance [24]. To obtain insights into the electrokinetic mechanism for CO₂ reduction on these catalysts, Tafel plots (A Tafel plot relates to overpotential versus logarithm of the partial current density of a specific product) for them were displayed in Fig. 5d. The plot of the ZIF-8 is linear over the range of overpotentials from 0.45 to 0.65 V with a slope of 122.5 mV/dec, indicating that the initial electron transfer of CO₂ activation is the rate-determining step. Tafel slopes of Ag/C and Ag/ZIF-8 are 75.5 and 71.8 mV/dec, respectively. This dramatic decrease in Tafel slopes proves that the introduction of thiol-capped Ag NPs largely accelerates the initial electron transfer to a CO₂ molecule. These silver-containing catalysts exhibit similar Tafel slopes, which suggest that Ag is the major contributor to the CO₂RR.

The long-term stabilities of the Ag/ZIF-8 were evaluated at −0.88V vs. RHE for 10 h (Fig. 6). Within 10 h of reaction, the current density declines slightly from 3.5 mA to 3.1 mA. Meanwhile, the Ag/ZIF-8 exhibits slightly loss of FE₉O₂ from 92.3% to 82.2%. The above results indicate that the Ag/ZIF-8 possesses a relatively good stability.

In summary, ultrafine thiol-capped Ag nanoparticles uniformly decorated ZIF-8 (Ag/ZIF-8) was successfully prepared and applied to CO₂RR for the first time. The major product CO on the Ag/ZIF-8 catalyst could achieve a high Faradaic efficiency of 92.3% at a moderated potential of −0.88 V with a current density of 3.8 mA/cm². The Ag/ZIF-8 catalyst showed higher CO faradaic efficiency and current density than ZIF-8 and Ag/C. What’s more, the Ag/ZIF-8 catalyst’s stability is good as it can serve a working lifetime without large deactivation for 10 hours. Overall, the strategy developed here demonstrated a novel and convenient route to synthesize supported small-sized Ag NPs to enhance CO₂RR performance of Ag.

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Conflicts of interest
There are no conflicts to declare.

Supporting information
Supporting information are available online at journal website.
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