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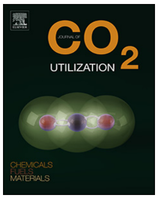

Ligand-free gold nanoparticles supported on mesoporous carbon as electrocatalysts for CO_2 reduction

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ABSTRACT

Gold nanoparticles (AuNPs) have shown good catalytic activity for electrochemical CO_2 reduction. However, they are typically stabilized by poorly conductive organic ligands which partially block their activity for electrocatalysis. In this work, we report a one-pot organic ligand-free synthesis of AuNPs on mesoporous carbon (MC). The size of the AuNPs is controlled by the micro- and mesoporosity of the carbon support and the mass ratio employed of the gold precursor/MC. The produced AuNPs-MC hybrid material, with the largest amount of small AuNPs (1–3 nm), shows good catalytic activity for the electrochemical reduction of CO_2 to CO in aqueous electrolyte. The optimized selectivity is recorded to be, on average, 80% with a mass activity of 12.8 A g^{-1} at an overpotential of 550 mV. The catalyst stability of the material is investigated to give insight into the irreversible deactivation mechanism occurring at the surface of AuNPs. Using 6-mercapto-1-hexanol as the ligand on AuNPs shows a dual effect in terms of an improved stability but a lowered activity.

1. Introduction

The increasing release of carbon dioxide (CO_2) into the atmosphere affects severely the global climate [1]. Nevertheless, from a chemical point of view, CO_2 can be considered as a non-toxic, abundant, and easily available C1 feedstock. Among many ways to utilize CO_2, the electrochemical carbon dioxide reduction reaction (CO_2RR) represents a sustainable and scalable process, when powered by renewable energy sources, such as solar energy and wind power. It offers the production of a plethora of chemicals, i.e. CO, HCOOH, CH_3OH, CH_4, and longer-chain hydrocarbons [2–7]. The use of water as solvent in this process holds great potential, since it is cheap, highly available, and environmentally friendly. The price to pay comes from the low solubility of CO_2 in water and the competing hydrogen evolution reaction (HER). Therefore, electrocatalytic strategies, as have been utilized for HER [8], oxygen reduction [9], and water splitting [10], are still being pursued to enhance the effectiveness of CO_2RR in aqueous medium.

Nanostructured gold has been extensively studied for CO_2RR with respect to different morphology (particles, rods, film) [11,12], size [13–15], and composition (single metal, alloy) [7,16,17]. Zhao and coworkers gave an important contribution by demonstrating that the atomic-level morphology and electronic properties can greatly influence the catalytic performance. In fact, going from rod to spherical shape the faradaic efficiency for CO production (FE_{CO}) increases from 40% to 69% at −0.57 V vs the reversible hydrogen electrode (RHE) [12]. Size is another important factor that determines the performance of a gold catalyst. Zhu et al. found that AuNPs with diameter of 8 nm (among a series of 4, 6, 8, and 10 nm particles) show the maximum FE_{CO} (up to 90% at −0.67 V vs RHE) [13]. In a later study, Mistry et al. demonstrated the size-dependent catalytic activity of AuNPs and found that decreasing NPs size increases the current density but lowers the FE_{CO} in the size range of 1–8 nm [14]. Through judiciously tuning the composition, gold alloys may achieve superior performance compared with gold itself and reduce the cost as well. Sun et al. discovered highly active AuFe core-shell nanoparticles which exhibit exclusive CO selectivity, lowered overpotential, long term stability, and nearly a 100-fold increase in mass activity toward the CO_2RR [16]. Noteworthy, coating Au with a Pd layer changes the CO_2RR selectivity from CO to a

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mixture of C1–C5 hydrocarbons [7].

Typically, the synthesis of the AuNPs is carried out through a wet chemical reduction approach in the presence of a ligand (i.e., oleylamine [13,18], a thiol [12], and diblock copolymers [15]). The ligand helps to suppress the growth and aggregation of AuNPs, but on the other hand, is poorly conductive and partially blocks the active sites by occupying part of the AuNPs surface area. To avoid this and make the AuNPs better applicable for the CO_2RR, an additional step is required to remove the ligand, i.e., high-temperature annealing [13,16,19] or plasma etching [15]. In addition, a support, usually porous carbon, is used to facilitate the attachment of AuNPs and give the required conductivity on an electrode [12,18–20]. The performance of AuNPs is to a great extent affected by the functionality of the carbon support [18–20]. For example, Rogers et al. demonstrated that AuNPs (8 nm) supported on ester-functionalized graphene nanoribbons yielded a 137-fold increase in the total catalytic output over the same nanoparticles supported on a traditional carbon black matrix [18]. Another example is the enhanced activity and selectivity of AuNPs (2 nm) obtained on a nitrogen-doped carbon support, where the nitrogen doping induces a higher local CO_2 concentration along with an enriched surface charge density [20]. In any case, the current way to synthesize active AuNPs for CO_2RR is far from being optimal, considering that it involves the complicated synthesis and post-removal of the ligand and/or the pre-functionalization of the carbon support.

In this work, we have developed an easy, ligand-free one-pot synthesis of AuNPs that are directly anchored on mesoporous carbon (MC), thereby, avoiding any post-modification treatment. The high-area MC supporting material serves as the templating scaffold to confine the growth and prevent agglomeration of AuNPs as well as to ensure a good electrical conductivity of the hybrid material. As a result, the size of the AuNPs can be controlled through the surface morphology of the carbon support and the mass ratio of the Au/MC precursors. The effect of the particle size distribution on the CO_2RR catalytic activity is studied in aqueous electrolyte. The hybrid material, with the largest amount of small AuNPs (1–3 nm), shows the highest CO_2RR activity. A particular effort is devoted to examine the stability of the material, giving insight into the degradation mechanism. Using 6-mercapto-1-hexanol as the stabilizing ligand for AuNPs, the material exhibits improved stability but suffers from decreased activity.

2. Experimental

2.1. Chemicals

All the chemical reagents were commercially available and used as received unless otherwise stated. Tetrachloroauric(III) acid ($HAuCl_4$), sodium borohydride, potassium bicarbonate, lithium oxalate, mesoporous silica (MS, 200 nm particle size, 4 nm pore size), phenanthrene, 6-mercapto-1-hexanol (MCH) and Nafion 117 (5 wt %) solution were purchased from Sigma-Aldrich.

2.2. Synthesis of mesoporous carbon (MC)

The MC material was synthetized as reported in literature [21]. Silica (1 g) and phenanthrene (1 g) were suspended in 15 mL absolute ethanol (EtOH). To this solution 300 μL H_2SO_4 was added to facilitate the impregnation process. The suspension was dried in an oven at 100 °C for 1 h. The dry mixture was pyrolysed at a temperature of 750 °C under an Ar flow for 2 h using a ramping speed of 5 °C min^{-1}. After cooling down to room temperature, the silica template was etched using a solution of 1 M NaOH in EtOH/Milli-Q H_2O (50% v/v) for 72 h. Finally, the MC was obtained after filtration.

2.3. Synthesis of hybrid materials consisting of AuNPs and MC (AuMC)

To prepare a stock solution, 100 mg $HAuCl_4{\cdot}3H_2O$ was dissolved in 12.5 mL 1:1 (v/v) EtOH/Milli-Q water. After 10 min sonication, 1.25, 2.5, 3.75, and 5 mL of the stock solution was transferred to four 25 mL round bottom flasks, respectively. In each of four test tubes, 5 mg of MC was suspended in 2 mL Milli-Q water, followed by adding these MC suspensions to the respective flasks. In each flask an adequate amount of the EtOH/Milli-Q water solution was added to reach the total volume of 7 mL. The resulting suspensions were stirred vigorously for 150 min. To each of the four $HAuCl_4$–MC suspensions, a fresh solution of 14.3 equivalents of $NaBH_4$ (13.7, 27.4, 41.1, 55.0 mg, respectively) dissolved in 5 mL Milli-Q water was added dropwise with a Pasteur pipette. The reaction was then allowed to progress for 17 h. The resulting hybrid materials (denoted AuMC–X, X = 1, 2, 3, and 4, respectively, where the number corresponds to the mass ratio of Au(III)/MC) were washed with Milli-Q water and recovered by centrifugation (centrifuge: Hettich EBA 20) at 6000 rpm for 10 min. This procedure was repeated three times before the materials were dried in an oven at 70 °C. The specific hybrid material consisting of AuNPs and Vulcan carbon (i.e. AuVC–3) was synthesised using the same procedure as that of AuMC–3.

2.4. MCH functionalization of AuNPs (i.e. AuMC–3)

An adapted procedure from literature was used to prepare MCH-stabilized AuNPs [22]. First, a 10 mM MCH solution was obtained by mixing 20.4 μL MCH in 10 mL EtOH. Subsequently, the AuMC − 3 coated electrode was submerged for 17 h. Finally, the electrode was gently rinsed four times using EtOH before being dried. A control experiment was carried out following the same procedure, but in the absence of MCH.

2.5. X-Ray photoelectron spectroscopy (XPS)

XPS analysis was performed with a Kratos Axis Ultra-DLD instrument equipped with Al Kα X-Ray source at 150 W. The pressure in the chamber was kept below 5×10^{-9} mbar during measurements. The full spectra survey was obtained with a pass energy of 120 eV and the high resolution spectra for Au 4f with 20 eV. The deconvolution of the spectra was carried out using the software CasaXPS, where C 1s = 284.5 eV was set as calibration for the binding energy; a 90% Lorentzian and 10% Gaussian peak shape were used for the deconvolution of the gold peaks.

2.6. Transmission electron microscopy (TEM)

The material was suspended in HPLC methanol by ultrasonication. Two drops of the suspension were deposited on a 200-mesh copper grid with a lacey carbon support structure. Prior to analysis, the samples were dried at 100 °C in vacuum ($< 10^{-5}$ mbar) overnight. The images were obtained on a FEI Talos F200X analytical scanning transmission electron microscope with a XFEG at 200 kV. The image analysis was performed with the ImageJ software using background subtraction, band pass filters, and manual colour adjustment to increase the AuNPs brightness with respect to the carbon support. The obtained shape maps were used to count the number of the NPs in the entire area of the images. The radii of AuNPs were measured assuming a spherical shape, giving histograms to compare the AuNPs size distribution in each material. The counts of NPs were normalized to the effective analyzed area of the picture containing the AuMC material.

2.7. Inductively coupled plasma optical emission spectroscopy (ICP–OES)

All materials were treated in concentrated aqua regia made from 67–69 wt % plasma-pure nitric acid and 34–37 wt % hydrochloric acid (volume ratio 1:3). The samples were left on a heating block at 60 °C for 24 h and subsequently diluted to 1% aqua regia concentration with Milli-Q water. Centrifugation was applied to remove the solid carbon support material. The measurements were carried out on a Spectro