



An electrochemical study of carbon dioxide electroreduction on gold-based nanoparticle catalysts



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ABSTRACT

We report here on an electrochemical study of carbon dioxide electroreduction (CO₂ER) employing electrochemical impedance spectroscopy (EIS) and a rotating ring-disk electrode (RRDE) on different gold based catalysts, namely bulk polycrystalline gold, gold nanoparticles (Au NPs) and Au@Ag core-shell nanoparticles. RRDE measurements allowed the identification of the reduction potential of CO₂ to CO and the characterisation of NPs based on their selectivity for CO₂ER with respect to hydrogen evolution. Gold–silver combined catalysts were found to be more selective than Au NPs although at higher overpotential. One gold–silver catalyst exhibits a constant selectivity over a wide potential range. For the first time, EIS data showed the existence of two charge transfers during the reduction of CO₂. These are attributed to two surface confined reactions that involve an adsorbed intermediate which is correlated with a proposed mechanism. The potential range of these reactions is specific for each catalyst with gold–silver catalysts exhibiting a slower electron transfer than Au NPs, Au and Ag polycrystalline electrodes.

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1. Introduction

Carbon dioxide is a major environmental pollutant resulting from human activities. Currently, CO₂ feedstock is used for the synthesis of some chemicals like urea, some pharmaceutical ingredients and polycarbonates (plastics). However, if CO₂ could be converted into fuel-type products, of which the worldwide consumption is two orders of magnitude higher than that of chemicals, the use of CO₂ in industry would increase with one order of magnitude. This valorisation of CO₂ emissions would be an important strategy for reducing global warming and pushing energy companies towards a more sustainable use of resources [1]. Among the possible routes of CO₂ conversion, thermal, photocatalytic and photoelectrocatalytic reduction under solar radiation are some of the long term solutions to increase carbon recycling and reduce fossil fuel consumption.

Carbon dioxide electroreduction (CO₂ER) has been studied in the past years employing various metallic electrodes and various electrolytes (aqueous and non-aqueous) leading to the conversion of CO₂ to different components of the fuel pool such as alcohols (methanol and ethanol), aldehydes, hydrocarbons (methane and ethylene) and carboxylic acids (formic and oxalic acids). According to Hori et al. [2], gold and silver in 0.1 M NaHCO₃ are converting CO₂ mainly to carbon monoxide, with a current efficiency of 87%

and 82% respectively (10% and 12% respectively for hydrogen evolution). Despite the large number of papers studying CO₂ER, there has been little research conducted on gold nanoparticles (NPs) with even less on gold based alloys as catalysts for this reaction. Recently, gold–copper alloys [3] and gold–copper NPs (AuCu, Au₂Cu, AuCu₂) [4] have been studied for CO₂ER, proving that the amount of CO produced depends on the gold percentage of the alloys and that Au₂Cu NPs exhibit a lower onset potential than Au and Cu alone. The physical origin of this phenomenon is however not explained as yet.

Linear sweep voltammetry (LSV) has been widely employed for the study of CO₂ER, where the reduction wave obtained in a CO₂ saturated electrolyte is compared to that of a N₂ saturated electrolyte. But, as already stated by other authors [5], due to the dependence of the CO₂ER on the electrolyte and especially due to its contribution to the suppression of the hydrogen evolution reaction (HER), linear polarisation curves alone could not offer enough information about the CO₂ER and should therefore be combined with other techniques in order to gain more insight about this reaction.

In this view, we report here on an electrochemical study employing the use of electrochemical impedance spectroscopy (EIS) and a rotating ring-disk electrode (RRDE) for the characterization of different gold based catalysts for CO₂ER. The activity of pure gold for CO₂ER was compared to that of gold nanoparticles (Au NPs) and gold–silver core-shell nanoparticles (Au@Ag NPs). The choice of testing core-shell nanoparticles is justified by the recent discoveries proving the superior activity of this type of NPs over the classic monometallic or alloy NPs in reactions like (i)

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oxygen reduction [6,7] and formic acid oxidation [7], (ii) hydro- gen oxidation with high CO tolerance [8] and (iii) preferential CO oxidation in hydrogen [9,10]. Therefore, the aim of this study is to (a) identify new electrochemical parameters for CO₂ER via EIS and RRDE techniques and (b) to use them as a comparison tool for different catalysts tested. The first parameter refers to the poten- tial of CO₂ conversion to CO, determined via a synchronization of cyclic voltammetry and chronoamperometry on a RRDE. From these measurements we were also able to define selectivity pro- files comparing the CO₂ER with the HER recorded in two different electrolytes. These profiles show the variation of catalyst selec- tivity towards CO₂ER with applied potential and correlate well with selectivity profiles obtained from LSV measurements. Finally, from EIS data a potential corresponding to a double charge trans- fer occurring during CO₂ER was identified for each tested catalyst. This double charge transfer is discussed in the light of the mecha- nism of CO₂ER and correlates well with the results of LSV and RRDE measurements.

2. Experimental

2.1. Reagents

Chloroauric acid (HAuCl₄ aq) and sodium borohydride (NaBH₄) were obtained from Fluka while cetyltrimethylammonium bro- mide (CTAB) and sodium hydrogen carbonate (NaHCO₃) were obtained from ACE Chemicals. Ascorbic acid, Nafion (5% wt in mix- ture of lower aliphatic alcohols and water), silver nitrate (AgNO₃) and potassium fluoride (KF) were obtained from Sigma-Aldrich. Carbon dioxide in a compressed tank was purchased from Afrox. All the chemicals were used as purchased without further purifi- cation and all the solutions were prepared with deionized Milli-Q water.

2.2. Synthesis of Au and Au@Ag NPs

Synthesis of gold nanoparticles was performed as described elsewhere [11]. The Au NP colloid solution was centrifuged for 20 min at 10,000 rpm and washed twice with Milli-Q water. The final NP solution was obtained by concentrating 50 times the col- loid solution obtained after washing. The concentration of Au NPs was assessed with inductively coupled plasma atomic emission spectroscopy (ICP-AES) employing a Thermo iCAP 6300 ICP spec- trometer and found to be 2.1 mg/mL.

Synthesis of gold–silver core-shell nanoparticles was performed as described elsewhere [11]. Four samples of Au@Ag NPs were obtained by variation of the silver nitrate concentration (3, 5, 7.5 and 10 mM respectively). The Au@Ag NP colloid solution was cen- trifuged for 20 min at 10,000 rpm and washed twice with deionized Milli-Q water. The final solution was obtained by concentrating 50 times the colloid solution obtained after washing.

The NP solutions obtained as described above were charac- terized without further purification with transmission electron microscopy (TEM) employing a FEI Tecnai G2 operated at 200 kV. UV–Vis spectra were acquired employing an Analytik Jena spec- trophotometer Specord S600.

2.3. Electrochemical characterization

Electrochemical measurements were performed in a three- electrode electrochemical cell. The reference electrode was a standard calomel electrode (SCE) and the counter electrode was a Pt spiral wire. The working electrode (\varnothing 5 mm) was, in turn, gold and silver polycrystalline disks and glassy carbon (GC) disks. These were polished with 1 μ m and 0.05 μ m Alumina suspensions and thor- oughly cleaned in deionized Milli-Q water by sonication. The Au

and Au@Ag NPs were immobilized on the GC disks by drop casting $2 \times 15 \mu$ L of the colloid solutions prepared as described above and drying at room temperature. This resulted in a loading of 0.63 mg of Au on each electrode. 10 μ L of a solution of 2 wt% Nafion were drop casted onto the modified GC disk and left for drying at room temperature. For gold NP electrodes a preconditioning treatment was performed by sweeping the potential between 0 and 1.2 V vs. SCE for five cycles in a 0.05 M Na₂HPO₄ (pH 6.8) solution and finally employing a chronoamperometry at an applied potential of -0.4 V vs. SCE for 1 min in the testing solution. For Au@Ag NPs the precon- ditioning treatment consisted of applying a constant potential of -0.4 V vs. SCE for 1 min in the testing solution. The testing solution were (i) 0.1 M NaHCO₃ saturated with CO₂ (pH 6.8 after bubbling CO₂ for 15 min), (ii) 0.1 M NaHCO₃ saturated with N₂ (pH 8.9 after bubbling N₂ for 15 min), and (iii) 0.05 M Na₂HPO₄ saturated with N₂ (pH 6.8 after bubbling N₂ for 15 min).

Electrochemical impedance spectroscopy was recorded in the 50 kHz–30 mHz range, with a sinusoidal ac potential perturbation of 10 mV superimposed on different dc potentials in the range of -0.8 to -1.5 V vs. SCE and readings were taken at 20 discrete frequencies per decade. All electrochemical measurements were performed at 25 °C and atmospheric pressure employing a Bio- Logic VSP double channel potentiostat with a built-in impedance spectrometer.

3. Results and discussion

3.1. Physical characterization of gold-based nanoparticles

Gold nanoparticles were synthesized following the method of Fan et al. [11] and spherical particles with a diameter around 25 nm were obtained (Fig. 1a). The UV–Vis spectrum of these NPs presents the expected surface plasmon absorption band at about 535 nm (Fig. S1).

Gold–silver core-shell nanoparticles were synthesized using a modified two-step seed-mediated growth method [11]. The cen- tration of silver ions was increased progressively from sample Au@Ag 3 to sample Au@Ag 10 (with the numbers representing the concentration of Ag⁺ in mM) with the purpose of obtaining increas- ing thickness of the silver shell (Fig. 1b–e). The total reaction time was identical for all samples. For a low concentration of silver ions a change in the morphology of the NPs from spherical to partially edged was observed. This suggests that the Ag shell does not cover the Au core entirely and explains the blue shift in the Au plasmon adsorption in the UV spectra and the appearance of a small shoulder at about 390 nm (not shown). This shoulder becomes more defined with an increase in the concentration of Ag⁺ ions and it was associ- ated to the surface plasmon absorption of silver nanoparticles [12]. At this same time, the blue shift of the Au plasmon adsorption band becomes more pronounced with an increase in the concentration of Ag⁺ used for the synthesis of these NPs. This phenomenon was observed also during the synthesis of Au@Pt core-shell nanoparti- cles where the increase in the Au surface coverage with Pt atoms causes the same blue shift [13]. The Au core is represented in the TEM images (Fig. 1c–e) as a dark spot while the Ag shell has a gray color. The increase of the thickness of Ag layer correlates well with an increase in the concentration of Ag⁺ ions and with the inten- sity of the surface plasmon absorption of silver nanoparticles in the UV-spectra.

3.2. Electrochemical characterization of gold-based nanoparticles

Electrochemical characterization of modified GC electrodes was performed in 0.05 M Na₂HPO₄ saturated with N₂ for Au NPs and in 0.1 M KF saturated with N₂ for Au@Ag NPs. The purpose of these

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