Enhanced electrocatalytic activity of Au@Cu core@shell nanoparticles towards CO_2 reduction

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Supporting Information

1. Experimental procedure

Synthesis of Au nanoparticles

Briefly, Au seeds were prepared by the reduction of $HAuCl_4 \cdot 3H_2O$ (2.5×10^{-4} M) by ice-cold $NaBH_4$ (6.0×10^{-4} M) in the presence of CTAB (7.5×10^{-2} M). Au seeds were used to induce the formation of nanocubes in a growth solution containing $HAuCl_4$ (2×10^{-4} M) + CTAB (1.6×10^{-2} M) + L-ascorbic acid (6×10^{-2} M) to which Au seeds (1.25×10^{-8} M) were added. After the reaction was completed, the solution was centrifuged at 3000 rpm for 30 minutes to precipitate the solid and remove the excess of reactants.

Cleaning procedure of electrochemical setup

In order to obtain very clean and reproducible conditions, prior to each experimental session, the cell and all of the glassware were immersed overnight in an acidic solution of $KMnO_4$. Next, the solution was removed and the residual MnO_4^- was rinsed with an acidic solution of H_2O_2 and sulfuric acid (3:1), and then thoroughly washed several times by boiling with ultra-pure water (Elga PureUltra, 18.2 MΩ cm, 1 ppb total organic carbon).

2. Mass spectrometry calibration

The MS was calibrated using two methods:

Calibration of the MS using mixture of gases:

The MS was calibrated using mixtures of gases as similar to the method described in [1,2] . The mass ion current recorded by the mass spectrometer I_R is proportional to the flux of the species into the system F_s; and both are related by a calibration constant *K* as:

$$I_R = KF_s$$

The flux of the gases can be expressed as a function of the volume and pressures as follow:

$$I_R = K\left(\frac{V_c}{RT}\right)\left(\frac{dp_c}{dt}\right)$$

Where V_c is the calibration volume, R is the ideal gas constant, T the temperature in the chamber and p_c is the total pressure of the volume of the gas.

In order to obtain the calibration constants, we prepared mixtures of gases in a stainless steel mixture bottle of 1L. The bottle was connected through a set of pressure meters to the gases to be analysed. The mixtures of gases evaluated and the calibration constant K are shown in the table below:

Table SI1.

Mixture	Inlet composition in % of partial pressure	Calibration constant K
Ar/CO_2	80:20	CO_2 = 0.14
Ar/C_2H_4	90:10	C_2H_4 =0.2
Ar/CH_4	90:10	CH_4 =0.17
He/H_2 *	98:2	H_2=0.09

*Commercial sample BOC research grade.

Considering the system available in our lab (figure SI1) and the error of its pressures gauges, the calibration gas mixtures can be prepared with a relative expanded uncertainty of 2% in the volume fraction for the case of the Argon containing mixtures.

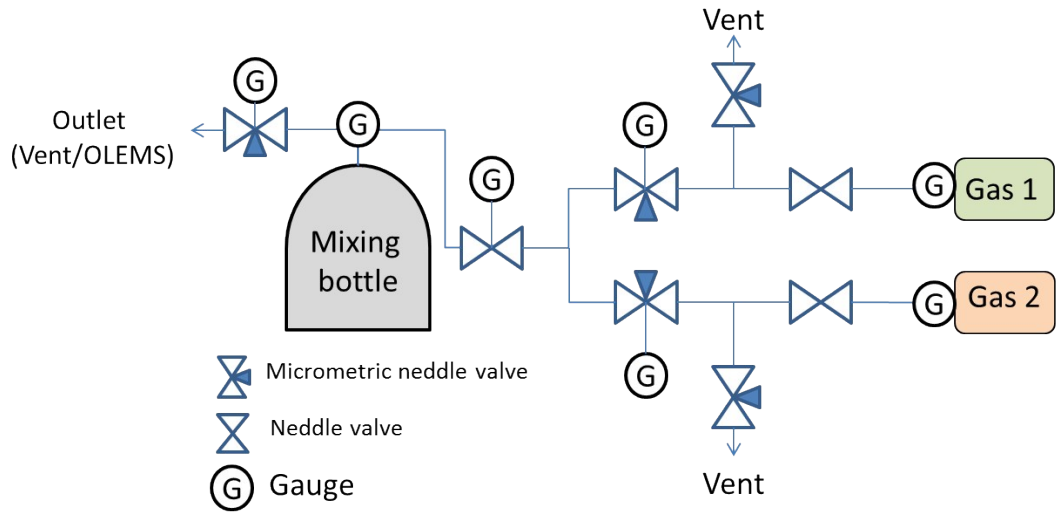

Figure SI1. Experimental setup for the preparation of the gas mixtures.

All the calibrations constants were determined at 20±3 °C (external temperature, measured with a thermocouple). The SEM voltage was 1329 V for the samples of CO_2, C_2H_4 and CH_4 and 2100 for H_2.

Calibration of the electrochemical system:

For the calibration of the OLEMS system, we used a well-known probe, the stripping voltammetry of a monolayer of carbon monoxide oxidation on Pt electrode.

In this case, the flux of the gases is replaced by the amount of CO_2 produced as the CO monoxide monolayer is oxidized from the electrode. Therefore, the charge associated with the Faradaic current of the oxidation reaction and the ion current mass (I_R) can be expressed as follow:

$$I_R = KQ_{CO2}$$

The corresponding stripping voltammetry and the ion mass current of the CO_2 is show in figure SI2. Because the electrochemical surface area of the electrode (0.12 cm^2) is larger than the inlet on the tip (0.04 cm^2), we have use the charge associated to the oxidation of carbon monoxide in an area of 0.04 cm^2.

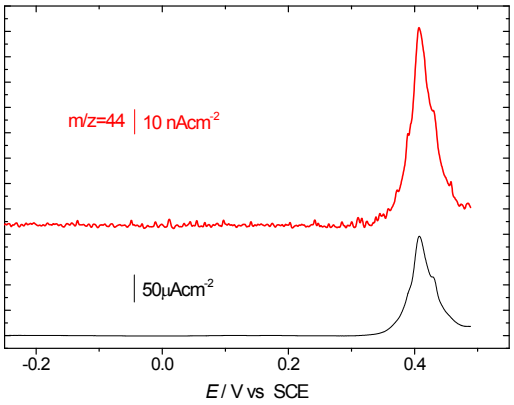

Figure SI2. (Bottom) Voltammetric profile of the oxidation of a CO monolayer adsorbed on Pt polycrystalline electrode in 0.1 M $HClO_4$. (Top) Corresponding ion mass signal of CO_2 (m/z=44). Scan rate υ=5 mV/s. SEM voltage= 1329 V.

Based on these results we have obtained that the calibration constant for the CO_2 is 0.24. The difference between the calibration constants of the CO_2 in the mixtures of gases and the OLEMS system must be associated with the collection coefficient of the gas in the tip and the approximation of the active area exposed in the tip. Since the calibration constants of the CO_2 in the OLEMS is a factor of 1.71 higher than the calibration constant of the CO_2 in the mixture of gases, we used this factor to obtain the calibration constant of the CH_4, C_2H_4 and H_2. The calibration constants depend on the composition of the gas mixture; therefore, we extrapolate that the values for the calibration constants for mixture of two gases is an approximation of our real system where more than two gases and the vapour pressure are present.

3. Calculating the partial pressures

The sum of all the partial pressures will yield the total pressure of the system. Figure SI3 shows the total pressure, the CO_2 partial pressure and water partial pressure during the CO_2 reduction on Au@Cu2 sample as a function of time.

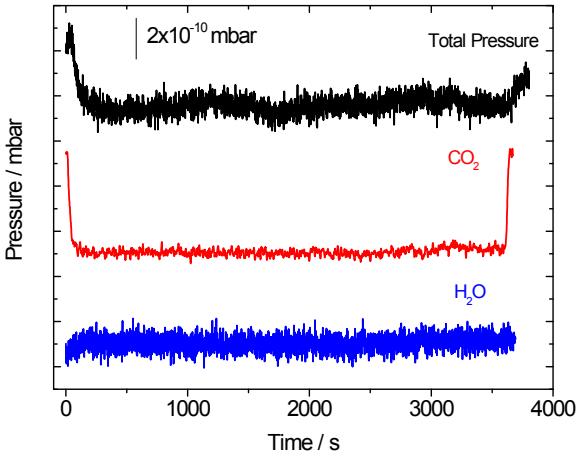

Figure SI3. Total pressure and partial pressures for CO_2 (m/z=44) and water (m/z=18) probed by OLEMS as a function of time for the reduction of CO_2 at 0.6 V vs RHE on the Au@Cu2 and in CO_2 saturated PBS (pH=8) solution. The partial pressure of water and CO_2 have been multiplied by x2 for comparison.

Results

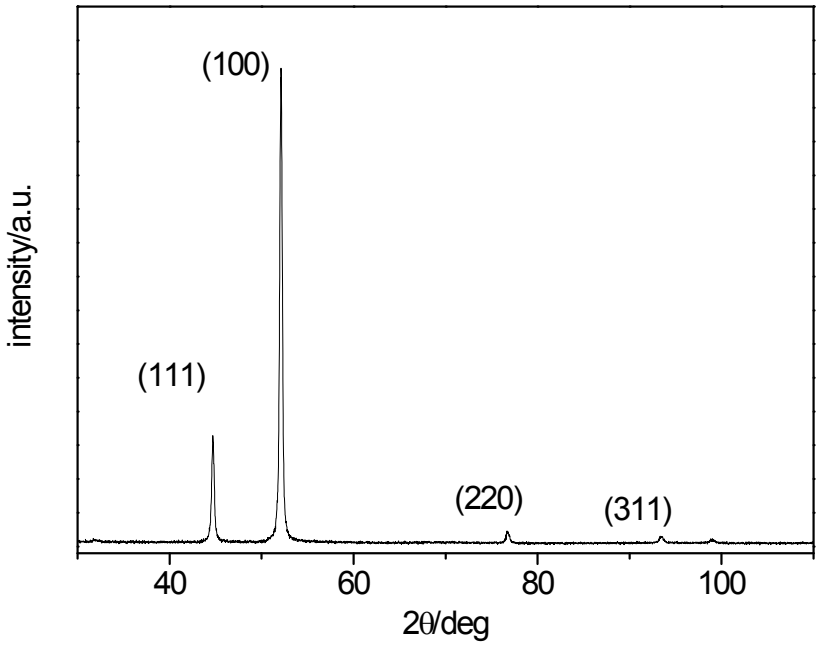

Figure SI4. X-Ray diffraction pattern of Au cubic nanoparticles.

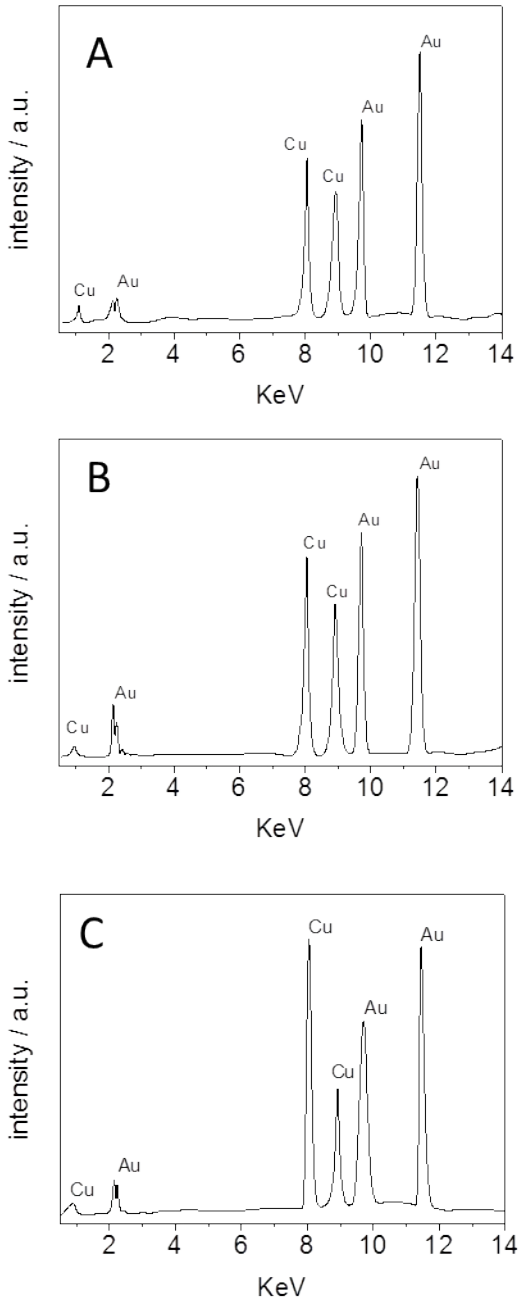

Figure SI5. X-Ray fluorescence spectra of (A) Au@Cu1 nanoparticles, (B) Au@Cu2 nanoparticles and (C) Au@Cu3 nanoparticles. The blue lines correspond to the Au signals and the brown lines correspond to the Cu signals.

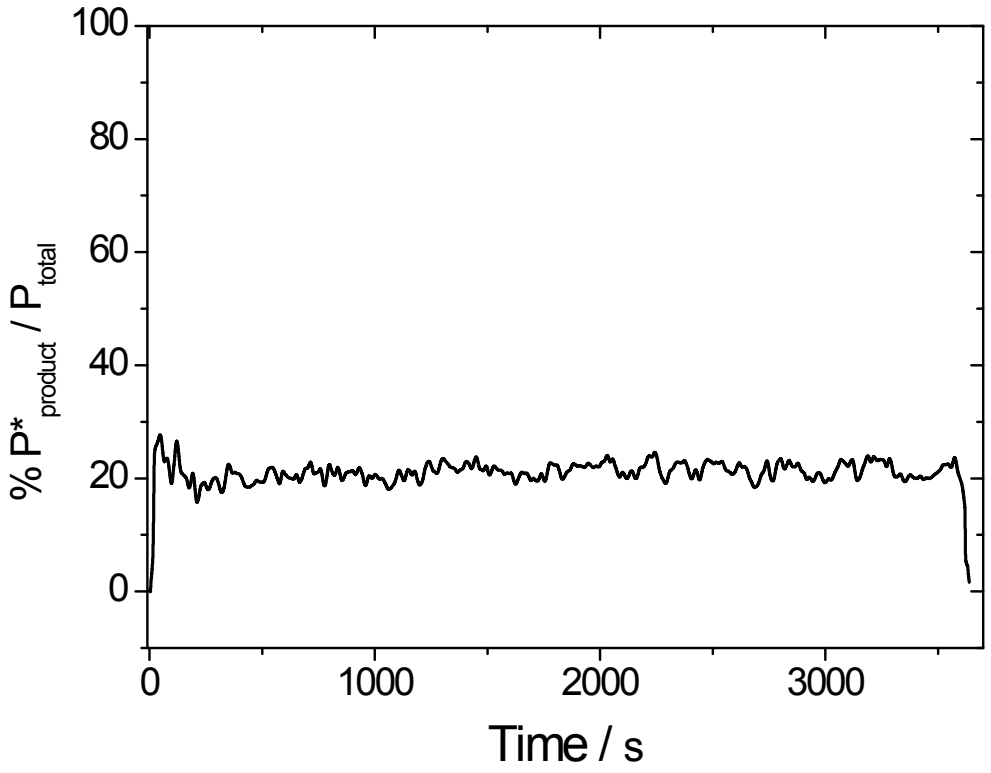

Figure SI6. Normalized partial pressure for hydrogen probed by OLEMS as a function of time for the reduction of CO_2 at -0.6 V vs RHE on Au in a CO_2 saturated PBS (pH=8) solution.

(1) Gervasini, G. http://www.aiv.it/portfolio-items/quantitative-analysis-in-mass-spectrometry-the-identification-of-n2-and-co-with-a-quadrupole/2015;Access Jan 2015

(2) Basford J A, B. M. D., Ellefson R E, Filippelli A R,Holkeboer D H, Lieszkovszky L and Stupak C M *J. Vac. Sci. Technol.A* **1993**, *11*, A22.