SUPPORTING INFORMATION

Electrochemistry of Robust Gold Nanoparticle-Glassy Carbon Hybrids Generated Using a Patternable Photochemical Approach

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Pierga Cell

This particular electrochemical cell is designed to carry out electrochemical experiments on different sizes of conductive surfaces with the possibility of controlling both atmosphere and temperature during the measurements. Basically the sample, the working electrode, is employed to close the bottom of the cell, while reference and counter electrodes are introduced from the top.

The surface, in our case a glassy carbon slide, is placed on a 1mm Teflon layer on an aluminum base having 4 vertical screws (see Fig. SI 1). The Teflon layer is used to isolate the sample from the metal base. The electrical contact is created by compressing the sample between the insulated aluminum base and the Teflon mask, whose bottom is equipped with a copper disk (see Fig. SI 1). During this operation, in order to avoid exercising too much pressure on the sample with the danger of rupturing it, thin metal rings are used to build a thickness on the four screws of the aluminum base similar to that one of the sample. The Teflon mask is then tight to the sample using four hexagonal nuts. The softness of the Teflon ensures a contact between the copper disk and the surface of the sample, despite the presence of the 3 mm o-ring employed to seal the electrolyte solution inside the electrochemical cell. In order to avoid the exit of the electrolyte solution, the Pyrex jacket must be tightly compressed to the bigger o-ring on the upper side of the Teflon mask by screwing the upper connector to the hexagonal nuts. At this point a sample protection mask, a little stir bar, and the electrolyte solution can be introduced. Finally the Teflon cap (the electrode holder) can be screwed on the upper part of the Pyrex jacket. The electrode holder has four holes, the larger one is used for the reference electrode, two of the three smaller holes are used for the inlet and outlet of Ar gas used to keep an inert atmosphere inside the cell, while the third small hole is used for the counter electrode, a Pt wire. This apparatus has already been successfully employed to analyze gold surfaces constituted by a gold layer deposited on a glass slide.
Fig. SI 1: Details of Pierga Cell.
Fig. SI 2: Comparison of cyclic voltammograms recorded in 0.1 M KCl at 0.05 V s$^{-1}$ for the AuNP desorption (solid line), the control sample (dotted line), and the Dz-C$_{12}$ modified electrode (dashed line).
Fig. SI 3: Graphs representing current versus square root of scan rate (top), and current versus scan rate (bottom) for clean GC (blue dots), AuNP modified GC electrode (blue dots) and desorbed AuNP modified GC electrode (green dots). The corresponding voltammetric curves were recorded in KCl 0.1 M and Fe[CN]$_6^{3-}$ 1 mM, at 25°C.
**Fig. SI 4:** Cyclic voltammetries of unmodified GC (solid line), GC-C$_{12}$ (dashed line). Voltammetric curves recorded in KCl 0.1 M and Fe[CN]$_6$$^{3-}$ 1 mM, at 25°C and at 0.5 V/s$^{-1}$. 
**Fig. SI 5:** SEM images of the patterned GC plate. The upper image is a zoom in the brighter stripes, showing the homogeneous coverage of the substrate with 4nm AuNP. The bottom image is a zoom in the darker stripes, showing the bare GC and few AuNP probably physisorbed.
**Fig. SI3:** EDX spectra of unmodified GC (black line), control sample (blue line) and modified sample (red line). Spectra recorded with electron beam source at 15 KeV. The inset represents the zoom in the zone of signals related to sulfur and gold.
Fig. SI4: Electrochemical impedance spectra of AuNP modified GC electrode (triangles) and of desorbed AuNP modified GC electrode (circles). Ferricyanate was used as redox probe in concentration 1 mM in 0.1M KCl electrolyte solution and the impedance spectra were recorded at the probe’s standard potential with frequencies ranging between 12000 Hz and 0.05 Hz and with an amplitude of 10 mV.