

Electronic Supplementary Information

Synthesis of atomic metal clusters on nanoporous alumina

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Experimental Procedures

Nanoporous alumina

Working electrodes are prepared from aluminium 1145 (99.5%) with a surface of 6 mm². Surface pretreatment was carried out consisting of degreasing the surface in a ultrasonic bath with acetone, then the surface was electropolished with ethanol: HClO₄ 5:1 at 18V for 1 min, and finally, the oxide layer formed was removed with a 0.24 M Na₂CO₃ solution at 80°C for 2min.

The cleaned surface was exposed to an acid electrolyte (15% H₂SO₄) at room temperature and applying to the aluminium a constant potential of 15 V for 1 minute, using a lead plate as counter electrode in front of the working electrode. Once the electrode was anodized, it was left 5 min in the acid environment. This step thinned the oxide barrier of the pores. In this way a reproducible nanoporous structure is obtaining with the following characteristics: 10 nm pore diameter, 1 μm depth and 35nm interpore distance. The system is rinsed with water, dried with nitrogen current and ready for the next step.

Atomic gold cluster synthesis

Gold electrodeposition was carrying out using as electrolyte an electroplating commercial solution of 15 g L⁻¹ KAu(CN)₂ (Vilmet, Argentina). The previous anodize aluminum was used as working electrode and a plate of gold as counter electrode. The gold electrodeposition cycle consists of: a first step at -3 mA cm⁻² in which the metal is deposited (8 ms), a second step at 3 mA cm⁻² enabling to decrease the capacitive oxide layer and interrupt the electric field at the interface where it is being deposited (2 ms) and, a third step in which no current is applied during 500ms, to recover the ion concentration in the pores by diffusion from the solution. 3000 cycles were performed.

Atomic nickel cluster synthesis

Nickel electrodeposition was carrying out using as electrolyte a solution containing 100 g L⁻¹ NiSO₄·6H₂O, 45 g L⁻¹ NiCl₂·6H₂O and 45 g L⁻¹ de H₃BO₃ at pH 4.5. The previous anodize aluminium was used as working electrode. The Ni electrodeposition cycle was carried out in two different conditions, consisting of: a first step at -3 (or 10) mA cm⁻² in which the metal is deposited (8 ms), a second step at 3 (or 10) mA cm⁻² enabling to decrease the capacitive oxide layer and interrupt the electric field at the interface where it is being deposited (2 ms) and, a third step in which no current is applied during 500ms, to recover the ion concentration in the pores by diffusion from the solution. 3000 cycles were performed.

Clusters Characterization

UV-Vis absorption spectra of the gold clusters were recorded in 1M NaOH at room temperature with an Ocean Optics spectrophotometer.

Atomic Force Microscopy was performed on a microscope Agilent 5500 in non-contact mode with a resonance frequency of 157.6 Hz. The gold and nickel clusters were distributed on a clean graphite surface (HOPG, SPI supplies), obtained by exfoliation with adhesive tape. To deposit the clusters on this substrate a small droplet (about 1μl of a diluted solution) is placed on the freshly cleaved HOPG surface.

Electrochemical measurements were carried out in a μAutolab type III potentiostat provided with software for data acquisition. Square wave voltammetry was carried out applying the following parameters: Amplitude 20 mV, frequency 25 Hz, step 5mV.

Reduction catalysis

The reduction of 4-nitrophenol was followed by UV-Vis spectroscopy. To a 2 mL aqueous solution containing 50 μM of 4-nitrophenol and 20 mM NaBH_4 an aluminium shaft containing atomic metal clusters ($\text{Al}/\text{Al}_2\text{O}_3/\text{Au}_n$ or $\text{Al}/\text{Al}_2\text{O}_3/\text{Ni}_n$) was introduced and the change in absorbance for the 4-nitrophenol peak was followed at 2 minute time intervals to establish a pseudo-first order rate constant (k'). Control experiments were carried out at $\text{Al}/\text{Al}_2\text{O}_3$ shafts where the electrodeposition step was not carried out and reduction of 4-nitrophenol was not observed.

For gold an apparent rate constant was calculated taking into account the NaBH_4 concentration, the reaction volume and the mass of catalyst; the last one was calculated from the currents observed in ferrocyanide cyclic voltammetry experiments and considering the number of alumina pores generated per square centimetre (see electrochemical results in the main text).

Table S1.- Pseudo-first order rate constants for the different atomic metal clusters presented in this work

	$k'/10^4 \text{ s}^{-1}$
$\text{Ni} (3\text{mA cm}^{-2})^a$	7.1 ± 0.4
$\text{Ni} (10\text{mA cm}^{-2})$	7.6 ± 0.2
$\text{Au} (3\text{mA cm}^{-2})$	16.8 ± 0.6

a) the terms in parenthesis correspond to the current used in cluster preparation.

Figures

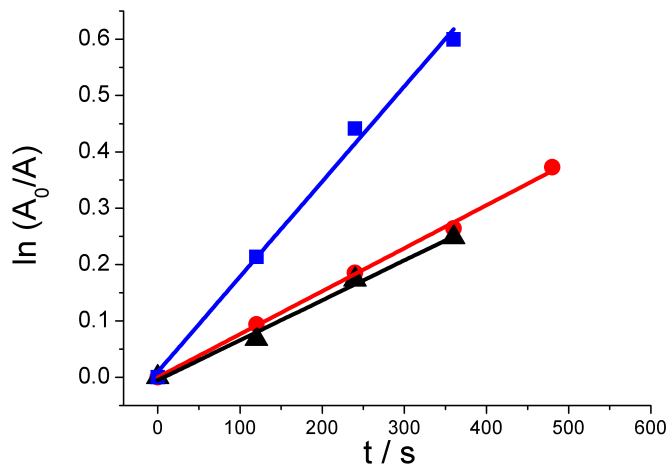


Fig S1: Kinetic pseudo-first order plot of 4-nitrophenol reduction. Absorbance was followed at 405 nm. Au (blue squares); Ni electrodeposited at -10 mA cm^{-2} (red dots); Ni electrodeposited at -3 mA cm^{-2} (black triangles).

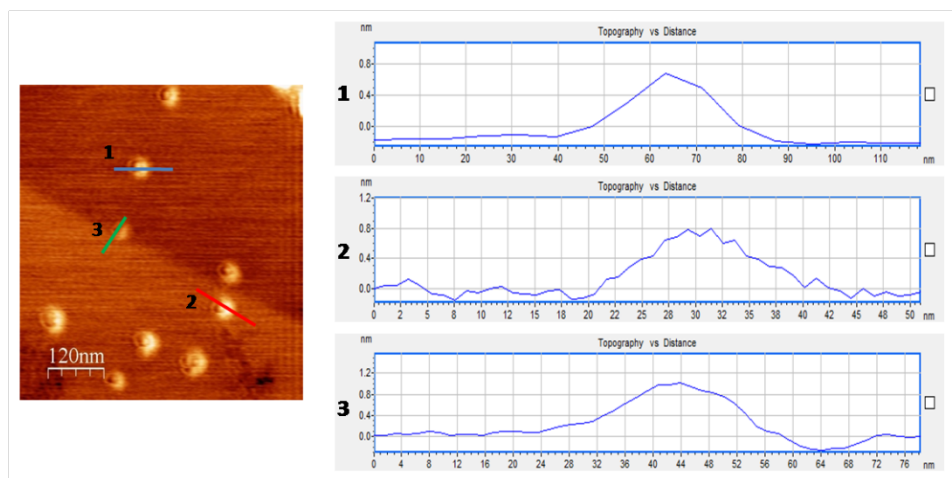


Fig S2: AFM topography image of gold (left) and examples of the performed section analysis is given on the right.

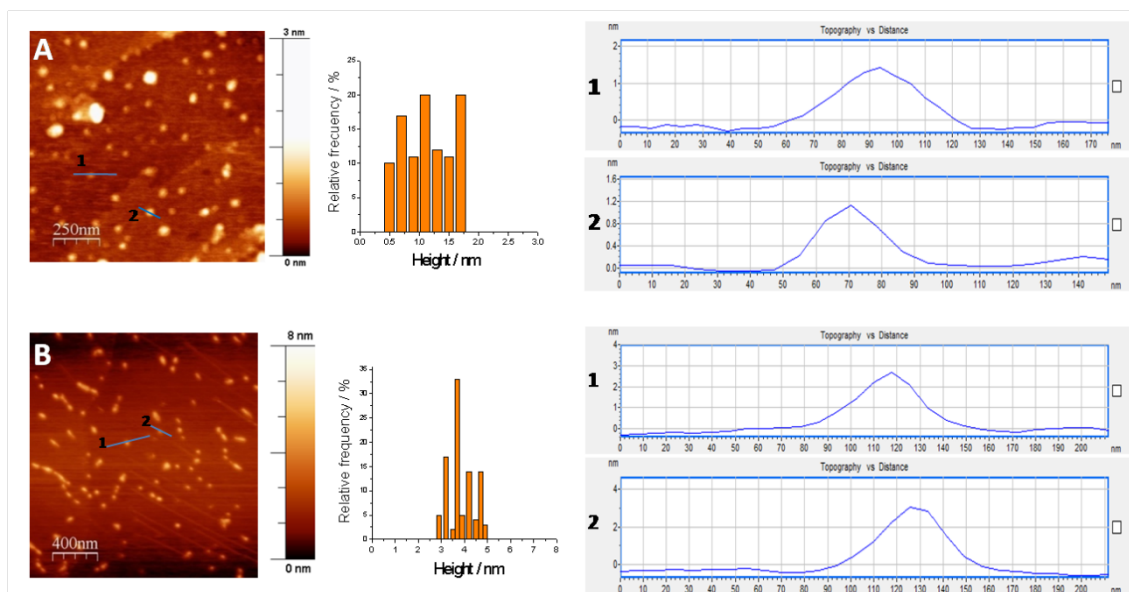


Fig S3: AFM results for Ni pulsed electrodeposition at (A)-3 mA cm⁻² and (B) -10 mA cm⁻². AFM topography image of Ni clusters on HOPG substrate (left), cluster size distribution (center) and examples of the performed section analysis is given on the right.

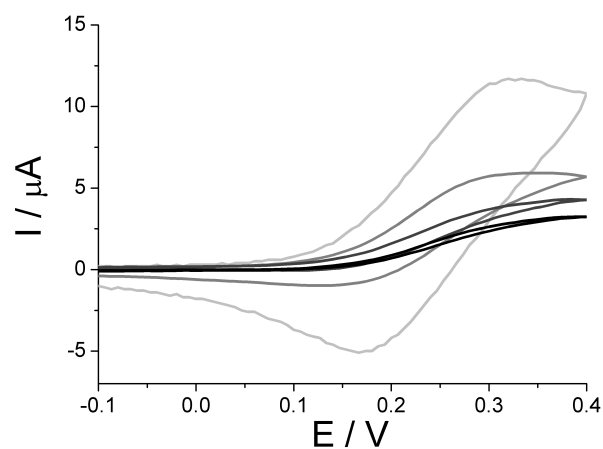


Fig S4: Cyclic voltammograms of 50 mM [Fe(CN)₆]⁴⁻ in buffer HEPES 50mM pH 7.0 at different scan rates: 5V s⁻¹ (light gray line), 500mV s⁻¹ (gray line), 50mV s⁻¹ (dark gray line) and 5mV s⁻¹ (black line).

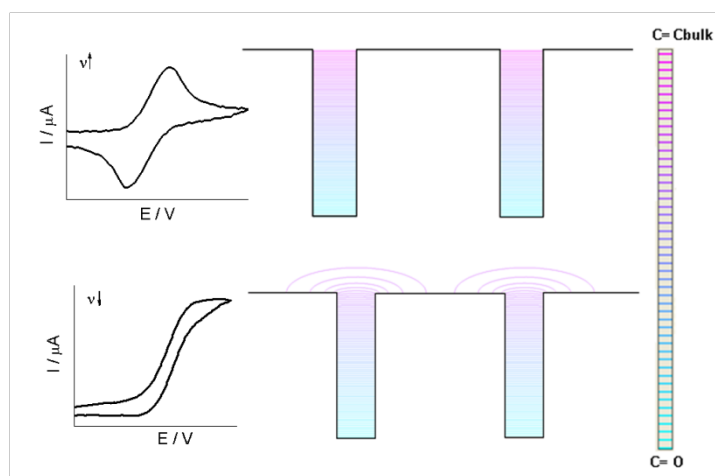


Fig S5: Schematic representation of the cyclic voltammograms (left) and concentration profiles (right) for different diffusion regimes: linear (top) and radial (bottom).

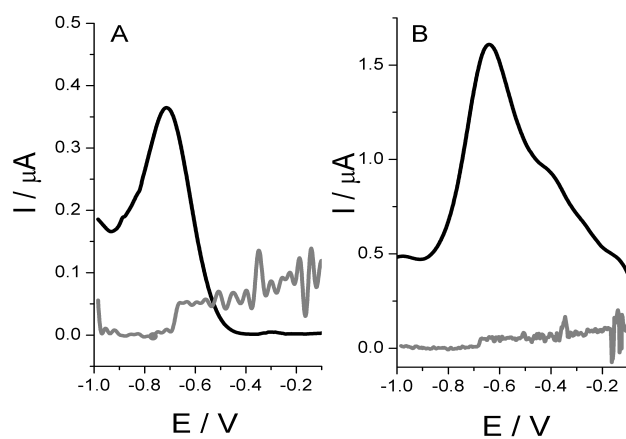


Fig S6: Square wave voltammetry for the reduction of 50 μM 4-nitrophenol on (A) Al/Al₂O₃/Au (black line) and (B) Al/Al₂O₃/Ni (black line). In both figures the gray line corresponds to the signal obtained for the same solution on Al/Al₂O₃.