Looking for Authentic Electrocatalytic Nanoeffects: A Study of Oxygen Reduction Reaction on Gold Nanoparticle-modified Electrodes in Sulfuric Acid Medium

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The investigation of electrocatalytic nanoeffects is tackled via joint electrochemical measurements and computational simulations. Thus, the response of an electrode modified with nanoparticles is simulated assuming that they “retain” the electron transfer kinetics of the bulk material. This enables us to predict the response expected in absence of nanoelectrocatalysis. Separately, electrochemical experiments are performed with nanoparticle-modified glassy carbon electrodes, the characteristics of the modification being examined by electrochemical and imaging techniques. Finally, the comparison of simulated and experimental voltammograms allows for the detection of differences between the kinetics at the bulk material and at the nanoparticles and, therefore, for revealing authentic nanoeffects.

Using the above strategy, electrocatalytic effects on the oxygen reduction reaction (ORR) by gold nanoparticles are investigated in oxygen saturated 0.5 M sulfuric acid solution at 298 K. Direct electrodeposition of gold nanoparticles of diameter from 17 nm to 40 nm on glassy carbon electrode is employed in order to get “naked” gold nanoparticles and then avoid any capping agent effect.

An overall ECEC mechanism corresponding to a two-electron, two-proton transfer and hydrogen peroxide as final product is proposed for this system [1]. The first electron transfer step of oxygen to superoxide is defined as the rate determining step. For this, the kinetics on gold macroelectrodes is obtained through the fitting of cyclic voltammetry. As shown in Figure 1, no significant change in the ORR kinetics has been found on the electrodeposited gold nanoparticles of diameter from 17 nm to 40 nm: \( k_{\text{ORR, bulk}} = 0.30 \text{ cm s}^{-1} \) on the bulk material and \( k_{\text{ORR, nano}} = 0.21 \text{ cm s}^{-1} \) on nanoparticles; transfer coefficient \( \alpha \) changes from \( \alpha_{\text{bulk}} = 0.45 \) on macro-scale to \( \alpha_{\text{nano}} = 0.37 \) at the nano-scale. For a better comparison of the catalytic activity towards ORR, the corresponding reduction rate constants have been calculated and shown in Figure 2. As can be seen, no significant changes of kinetics for ORR can be inferred.

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k_{\text{red}} = k_{\text{ORR}} e^{-\frac{a_e}{\alpha_e}} \quad \text{(Eq.1)}
\]

\[
\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \xrightarrow{k_{\text{ORR}}} \text{H}_2\text{O}_2
\]

Figure 1. Comparison of the mechanism and kinetics of ORR on gold macroelectrode and gold nanoparticles of diameter from 17 nm to 40 nm in oxygen saturated 0.5M sulphuric acid at 298 K.

Kinetic study of ORR on smaller (5 nm in diameter) citrate capped gold nanoparticles obtained through wet chemistry method is also investigated. A cleaning method proposed by Hernandez [2] et al. is employed aiming to clean the surface of gold nanoparticles. This is based on the cycling of the nanoparticle-modified electrode in lead alkaline solution such that lead dioxide is electrodeposited and stripped from the gold surface several times. A significant enhancement of the kinetics of ORR is observed after this treatment, the value of the transfer coefficient increasing to \( \alpha_{\text{nano}} = 0.57 \). By means of X-ray photoelectron spectroscopy and electrochemical studies, the electrocatalysis is found to be related to the adsorption of lead atoms on the nanoparticle surface. Consequently, the results also point out the occurrence of lead underpotential deposition on such small gold particles.

Reference: