Preferential surface orientation of gold nanoparticles

Javier Hernández-Ferrer, José Solla-Gullón, Enrique Herrero, Juan M. Feliu and Antonio Aldaz
Dpto. Química Física, Univerisidad de Alicante,
Apdo. 99, E-03080 Alicante, Spain

Many important electrocatalytic processes are structure sensitive since they take place at a different rate on electrode surfaces of different orientation. This is particularly evident in the case of oxygen reduction on gold in basic media. The 4 e^- reduction to OH^- only takes place on (100) type sites. Conversely on the other orientations the reaction is limited to the transfer of only 2 electrons, the final product being HO_2^-.

For practical purposes the electrocatalysts should be made of nanoparticles dispersed in a convenient support. In order to increase the performance of the electrode several factors such as nanoparticles size and dispersion should be controlled. Another important factor should be the surface characteristics of the nanoparticles. If it is possible to preferentially induce the appropriate orientation, the final material will be more efficient for the desired reaction.

Au nanoparticles were prepared by means of a micellar method that leads to uniform size around 3 nm. In this process, water-in-oil microemulsions were formed using heptane as organic phase and Brij®30 as a surfactant, aqueous phase contained $AuCl_4^-$ as a gold precursor. The reduction inside the micelle was carried out by hydrazine. As surface modifiers, different strongly adsorbed anions (I^-, S^{2-}) were used. Once produced the nanoparticles were attached to graphite electrodes.

In order to study surface structure effects, the dispersed nanoparticles have to be cleaned in a process that does not alter its surface structure. Moreover, it is necessary to find a method, preferable in situ, capable to point out the existence of different surface sites. It has been found that oxidation/reduction of Pb(II) in 0.1 M NaOH fulfills both requirements. First of all, the oxidation of dissolved Pb(II) is able to clean the surface of the Au nanoparticles from its micellar envelope, i.e. Brij®30 is easily oxidized. Moreover, lead UPD may be used as a structure sensitive reaction, to point out the different surface contributions. As can be seen in figure 1, the different gold basal planes lead to the presence of characteristic peaks corresponding to the deposition of a lead submonolayer, similarly to that observed in acidic media.

The overall process was first tested by using a single crystal gold bead, on which the surfactant was adsorbed. The oxidation of the Pb(II) solution was able to clean the surface, while maintaining the characteristic fingerprint of Pb UPD in this medium. The same procedure was used to clean the nanoparticles in pure 0.1 M NaOH and then transferred to the Pb(II) containing solution. The results indicate (fig. 2) that the nanoparticles cleaned in the presence of Pb(II) in solution have a better defined surface structure, as revealed by the presence of the peak at ~0.47 V, which would correspond to Pb UPD on wide (100) terraces.

The interesting point is that nanoparticles prepared in the presence of I^- show a preferential growth of the lead UPD peak at ~0.47 V thus suggesting an increase of Au (100) domains (fig 3). A small increase of the (111) domains is also observed (peak at 0.42 V). Conversely, the synthesis of the gold nanoparticles in sulfide-containing solutions leads to surfaces in which preferential formation of (110) sites is induced and the (100) domains becoming negligible. This result suggests that it is possible to modify the surface distribution of sites present on gold nanoparticles, a promising step in the development of tailored electrocatalysts.

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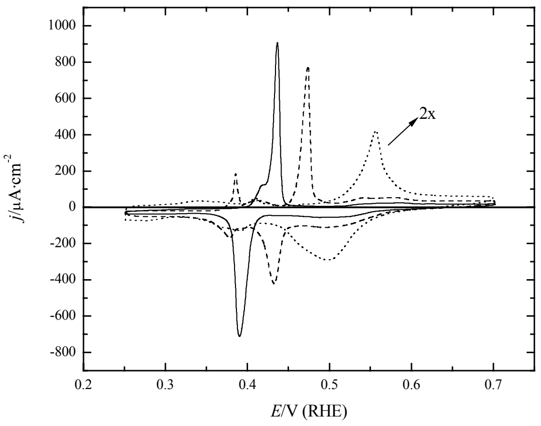

Figure 1. Pb UPD in 0.1 M NaOH + 10^{-3} M Pb(II) for Au(111) (______), Au(100) (- - - -) and Au(110) (…..) electrodes.

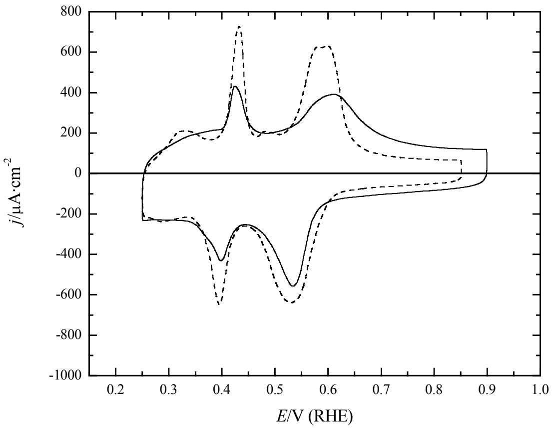

Figure 2. Pb UPD in 0.1 M NaOH + 10^{-3} M Pb(II) after oxidatively cleaning of the nanoparticles in 0.1 M NaOH (____) and in 0.1 M NaOH + 10^{-3} M Pb(II) (- - - -).

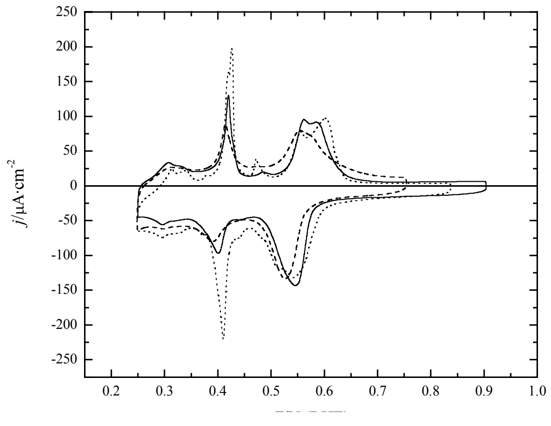

Figure 3. Pb UPD in 0.1 M NaOH + 10^{-3} M Pb(II) for nanoparticles formed in the absence (_____) and in the presence of S^{2-} (- - - -) and I^- (………).