

Size- and Crystallographic-Orientation Controls of Electrochemically Prepared Au Nanoparticles

Mohamed S. El-Deab*, Tadashi Sotomura** and Takeo Ohsaka*

* Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

** Advanced Technology Research Laboratories, Matsushita Electric Industrial Co., Ltd., 3-4 Hikaridai, Seika-cho, Kyoto 619-0237, Japan

Introduction— Nanometer-scale materials exhibit superior electrocatalytic behaviour compared to their bulk counterparts [1-3]. The small size of these particles makes them ideal catalysts for many chemical as well as electrochemical applications. Two major parameters control the chemical, physical and electrocatalytic properties of the nanoparticles, which are the particle size and the shape (in other words the crystallographic orientation) of the prepared nanometer-scale material.

Here, we demonstrate the effects of the presence of some additives (like cysteine, iodide and sulfide ions) to the electrochemical deposition bath of Au nanoparticles onto glassy carbon (GC) electrodes aiming at the preparation of Au nanoparticles with a controlled-design in terms of size and crystallographic orientations. This is of prime importance regarding the fabrication of nano-material oriented electrochemical devices [4].

Experimental— Au nanoparticles were electro-deposited from the acidic bath of 0.5 M H₂SO₄ solution containing 1.0 mM Na[AuCl₄] by applying a potential step from 1.1 to 0.0 V vs. Ag/AgCl/KCl(sat) for 60 or 300 s, in the presence of either 10, 100 μM cysteine, 100 μM S²⁻ ions or 100 μM I⁻ ions.

Results and discussion— Fig. 1 shows the CVs for the oxygen reduction reaction (ORR) measured at (a-c) nano Au/GC electrodes and (d) poly-Au electrode in O₂-saturated 0.5 M KOH at a potential scan rate of 100 mV/s. The electrodeposition was made from 0.5 M H₂SO₄ solution containing 1.0 mM Na[AuCl₄] in (a) the absence of cysteine and I⁻ ions and (b) the presence of 100 μM cysteine, (c) 100 μM I⁻ ions. The potential was stepped from 1.1 V to 0 V for 300 s. Inspection of this figure reveals some interesting points:

- 1-The ORR proceeds quasi-reversibly at the nano Au/GC electrodes prepared in the presence of I⁻ ions (see curve c). This behavior is similar to that obtained at an Au(111) electrode [5]. Thus it could be concluded that this nano Au/GC electrode has a higher ratio of Au(111) than the other nano Au/GC electrodes (compare curve c with curves a and b).
- 2-The ORR proceeds irreversibly at the nano Au/GC electrode prepared in the absence of any additive. Thus an almost natural ratio of the different facets of Au was formed and consequently the electrode behaves like the poly-Au electrode (compare curves a and d).
- 3-Also at the nano Au/GC electrode, prepared in the presence of 100 μM cysteine, the ORR proceeds irreversibly with a small positive shift of the cathodic peak potential and small increase in the peak current. This may be attributed to the enrichment of Au(100) facets in the nano Au, which in turn increases the activity of the electrode towards the ORR [4].

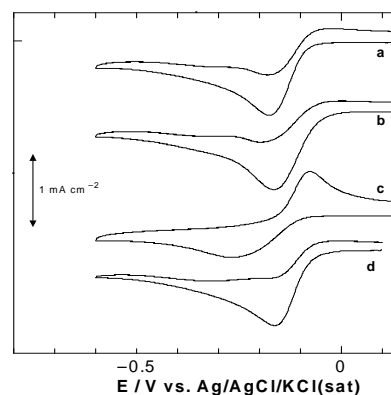


Fig. 3

Moreover, SEM micrographs show that, the Au nanoparticles prepared in the presence of I⁻ ions are of the smallest particle size in addition to the relatively narrow range of particle size distribution (10-40 nm), and the particle density of this nano Au/GC electrode (300 particle/μm²) is highest among the nano Au/GC electrodes examined here. On the contrary, the Au nanoparticles prepared in the presence of cysteine are bigger (aggregates) with a particle size reaching 300 nm, suggesting that the adsorption of cysteine molecules is not effective for preventing the coalescence of the

Fig. 1: CVs for the oxygen reduction reaction at (a-c) nano Au/GC electrodes ($\phi = 3.0$ mm) measured in O₂-saturated 0.5 M KOH. Curve d shows the CV response for the ORR at polycrystalline Au electrode in the same solution. Potential scan rate: 100 mV s⁻¹.

neighboring Au nanoparticles. Also a sharp decrease in the particle density is observed (32 particle/μm²) [4].

REFERENCES

1. M. S. El-Deab, T. Ohsaka, *Electrochem. Commun.*, **4**, 288 (2002); *Electrochim. Acta*, **47**, 4255 (2002).
2. M. Haruta, *Catal. Today*, **36**, 153 (1997).
3. S. Schimpf, M. Lucas, C. Mohr, U. Rodemerck, A. Bruckner, J. Radnik, H. Hofmeister, P. Claus, *Catal. Today*, **72**, 63 (2002).
4. M. S. El-Deab, T. Sotomura, T. Ohsaka, *J. Electrochem. Soc.*, (2004) in press.
5. M. S. El-Deab, K. Arihara and T. Ohsaka, *J. Electrochem. Soc.*, **151**, (6), E213-E218 (2004).