



	Experiment title: Structure, chemical state and reactivity correlations during the in situ electro-oxidation of 2-propanol	Experiment number: CH-4227
Beamline: BM25A	Date of experiment: from: 01 October 2014 to: 04 October 2014	Date of report: 27.02.2015
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Report:

Abstract

C- and Ti foil supported gold nanoparticles (NPs) were studied *in operando* during 2-propanol electro-oxidation. Gold was found to have different oxidation state depending on the support used. Gradual growth in particle size was observed after each step of the electrochemical experiment – after 15 cyclic voltammograms (CVs) and after chronoamperic measurements at fixed electrode potentials.

Goals

The proposed research aims to investigate the catalytic properties of well-defined Au NPs on different support materials during the electro-oxidation of 2-propanol using XAFS. Au NPs with different average size distributions (1 – 10 nm) were synthesized using reverse micelle encapsulation and deposited onto C and Ti foil supports, and the evolution of NP structure (size and shape), stability (sintering, loss of material) were monitored using extended X-ray absorption fine structure spectroscopy (EXAFS). In addition, the chemical state of the NPs (metallic versus ionic) was monitored during the reaction using X-ray absorption near-edge structure (XANES). The catalytic activity of the NPs was also monitored during the electrochemical (EC) measurements.

Our electrocatalytic measurements have revealed a clear structure-activity correlation in the 2-propanol electro-oxidation reaction over supported gold nanoparticles. Thus, activity of Au NPs supported on TiO₂/Ti foil is clearly dependent on NPs size (Fig. 1). Moreover, larger particles are more prone to deactivation than smaller ones.

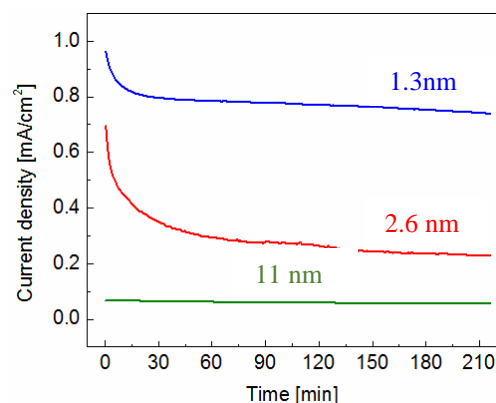


Fig. 1. Working electrode current measured at 1.1 V (2-propanol electrooxidation) for different particle

Experimental results

Inverse micelle encapsulation was used to synthesize Au NPs with narrow size distribution in the size range of 1 – 10 nm [1]. Two solutions of polystyrene-b-poly (2-vinylpyridine) block copolymer micelles in toluene were loaded with Au to form monodisperse NPs. The size of the NPs can be tuned by varying both the Au loading and the weight of the polymer P2VP head. The Au NPs were deposited onto TiO₂/Ti foil as well as C-foil (both Goodfellow) and treated with O₂ plasma etching to remove polymers at room temperature, and X-ray photoelectron spectroscopy (XPS) was used to ensure the complete absence of polymers from the samples. This room temperature plasma treatment (versus an annealing-based ligand removal treatment) minimized undesired NP coarsening phenomena. The samples were measured with atomic force microscopy (AFM) to check NP size distributions, which were 1.3 ± 0.4 nm and 2.6 ± 0.5 nm.

XAFS measurements were performed in a home built electrochemical cell [2]. 1M KOH + 1M 2-propanol was used as electrolyte. The counter electrode was a Pt-wire and the reference electrode Ag/AgCl. This cell allows measurements in both fluorescence and transmission configuration and the simultaneous measurement of the reference data (foil) for calibration purposes.

To reveal structural changes of Au nanoparticles, several states of the catalyst were measured using XAFS in operando using the following protocol. First, the initial state of the catalyst was measured inside the electrochemical cell at room temperature. Then, 15 CV scans in the 0.1 – 1.4 V region were made to clean catalyst surface and stabilize the particles. Chronoamperometry (electrode current measurement at fixed potential) was performed at potential values showing distinctive features on CV scans. Finally, two XAFS measurements were performed with the final catalyst state – inside the cell with electrolyte and once removed from cell and dried.

XANES reveals significant difference in the gold chemical state in as-prepared samples.

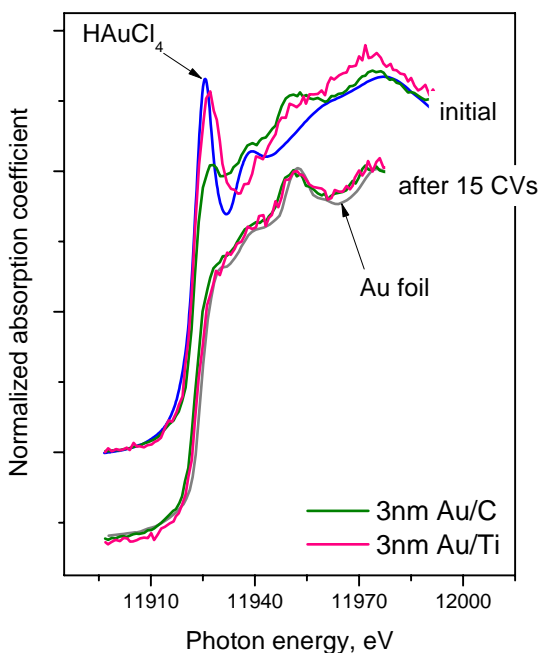


Fig. 2. XANES spectra of 2.6 nm Au NPs supported on carbon and TiO₂/Ti foils as prepared and after 15 CV sweeps.

While the spectrum of the carbon supported sample has only a small peak associated with cationic state (white line), the TiO₂/Ti supported sample shows the white line as intense as a reference Au³⁺ spectrum (see Fig. 2). However, the XANES spectra of both samples become alike after 15 CV sweeps and resemble all the features of metallic gold.

EXAFS spectra of both 1.3 and 2.6 nm samples supported on carbon foil show similar features and behavior after the EC measurements at different potentials (Fig. 3). There is a low-r backscattering event at ca. 1.8 Å indicating O-like atoms present in the Au local environment along with expected metallic Au structure. Since XANES did not reveal a significant amount of cationic gold in carbon supported samples, the light backscatterer may represent either O or C atoms from the support becoming visible due to small particle size. Presence of polymer residuals however cannot be ruled out completely. The light backscatterer peak is less intense on spectra measured after 15 CV

sweeps. At the same time, Au-Au coordination number (CN) increases after each

EC treatment step indicating particle size growth. Thus for the 2.6 nm Au/C sample, the CN_{Au-Au} was found to be 9.6 in the as-prepared state, 11.0 after 15 CVs, and 11.9 after all EC tests. The 1.3 nm Au/C sample shows a similar trend, although the CN_{Au-Au} increase is not so dramatic – from 6.8 in the as-prepared state to 7.1 after EC tests. Particle agglomeration can serve as an obvious explanation for the deactivation process observed during 2-propanol electro-oxidation. Unfortunately, EXAFS spectra recorded for TiO_2/Ti supported samples have significantly lower signal to noise ratio and do not allow us to perform similar analysis.

References

- [1] B. Roldan Cuenya, *Acc. Chem. Res.* 46 (2013) 1682
 [2] J. McBreen, W. E. O'Grady, K. I. Pandya, R. W. Hoffman, D. E. Sayers, *Langmuir* 3 (1987) 428

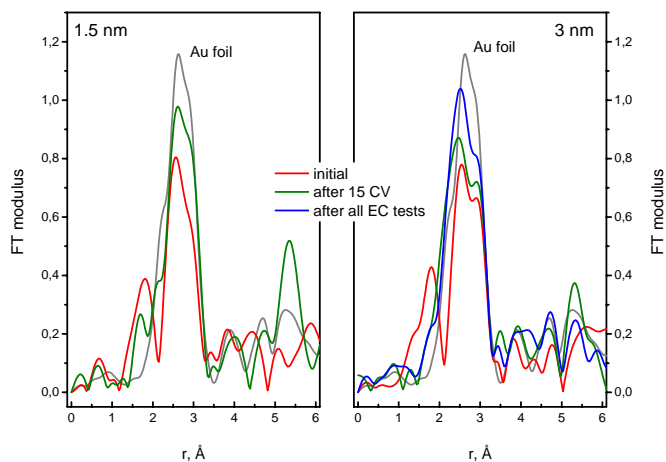


Fig. 3. EXAFS spectra demonstrating growth of the particle size for 1.3 (left) and 2.6 nm (right) Au NPs supported on C foil