Surface chemistry of Nafion-immobilized Au^{25} Clusters for use in Electrochemical Reduction of CO_2

Andrews, Flake

Recently, metal nanoparticles have become considered as candidate electrocatalysts for CO_2 reduction (1). In particular, Au_{25} nanoparticles have been used because of their unique electron structure, which resembles that of a molecule, rather than a metal (2, 3). Further, the nanoscale cluster provides a net anionic charge.

Au_{25} nanoparticles are typically stabilized by protective thiol ligands which prevents agglomeration and loss of the Au_{25} structure (3). For use in electrocatalysis, these thiolated nanoparticles are often immobilized in a Nafion binder matrix. Nafion is considered an excellent binder for electrochemical purposes, as it is inactive, chemically resistant and also highly conductive.

In this work, GC and NMR techniques were used to analyze the gas and liquid products of CO_2 reduction at electrodes Au_{25} nanoparticles. XPS and XANES were used to observe the effects of Nafion and potential on the Au_{25} nanoparticles.

Synchrotron-source XANES analysis shows that the Au_{25} surface changes after immobilizing the nanoparticles in a Nafion matrix suggesting a change in or desorption of the stabilizing thiol groups. Likewise, XPS also shows changes in the surfaces of nanoparticles after the addition of Nafion. The surface is undergoes further modifications after use as an electrode.

Here, we show carbon monoxide as a primary product and formate as a secondary liquid product. The Au_{25} surface analysis shows surface termination is a function of pretreatment chemistry and use as an electrode.

1. D. R. Kauffman, D. Alfonso, C. Matranga, H. Qian and R. Jin, *Journal of the American Chemical Society*, **134**, 10237 (2012).
2. J. F. Parker, C. A. Fields-Zinna and R. W. Murray, *Accounts of Chemical Research*, **43**, 1289 (2010).
3. R. Jin, *Nanoscale*, **2**, 343 (2010).

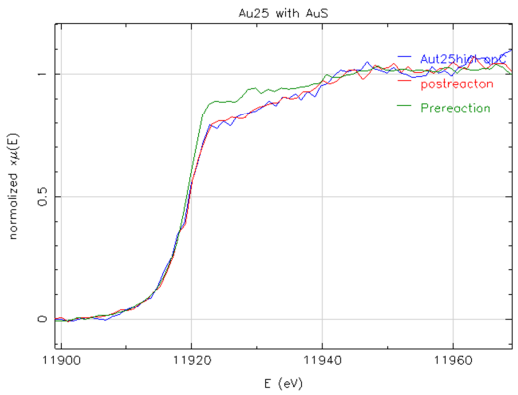

Figure 1: XANES spectra of Au25 nanoparticle samples with and without nafion, before and after applying potential.