Fabrication of a novel covalently bonded cysteine network for immobilization of gold nanoparticles

Mohammad Rezaur Rahman[a,b] and Takeo Ohsaka[a]

[a]Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259-G1-5 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
[b]Faculty of Science (Chemistry), University of Ontario Institute of Technology, 2000 Simcoe St. N., Oshawa, ON L1H 7K4, Canada

Gold-nanoparticles (GNPs) were found to have extraordinary electro-catalytic properties for potential applications in numerous fields. The catalytic activity of the GNPs depends on the size, shape, particle coverage, catalytic support, and methodology used for the immobilization of the particles on the electrode surface. The catalytic activity of the GNPs deposited on the glassy carbon (GC) and other conducting substrates is usually hindered due to the agglomeration (coalescence and Ostwald ripening) of the nanoparticles [1]. Since size and coverage of the nanoparticles have great control over the electro-catalytic activity of the nanoparticles, it would be promising to develop a nanoparticle array or nano-electrode ensemble based electrodes in which agglomeration can be inhibited. Self-assembled monolayers (SAMs) of various thiols, sulfides and disulfides are highly ordered structures which can be formed through a spontaneous organization of molecules on the surface of gold substrate. These SAMs are attractive because they can introduce functionality to the electrode substrate in a convenient, flexible, and chemically well-defined way. Therefore, in order to develop the ensemble of nano-electrodes, it would be quite interesting to fabricate a network having thiol functional groups where GNPs can be conveniently immobilized in a unique fashion.

In the present study, intermolecular covalent bond between cysteine molecules was formed using cross-linking reagents and a covalently bonded cysteine network was achieved over a polycrystalline gold (poly-Au) electrode. Typically, 1-ethyl-3-[3-(dimethylamino) propyl] carbodiimide (EDC) and *N*-hydroxysulfosuccinimide (NHSS) were used which are classified as so-called zero-length cross-linking reagents because they do not become part of the final crosslink between the two linked moieties [2]. EDC activates the terminal -COOH groups of the cysteine SAM, forming a highly reactive *O*-acylisourea intermediate. NHSS reacts with this *O*-acylisourea to give aminoacyl ester (poly-Au/cys-NHSS ester) which is stable and facilitates further reaction to amide bonds. In the next step, a subsequent nucleophilic attack by the amino group of a non-bonded cysteine molecule in the solution brings about the formation of the amide linkage. The whole process can continue further to finally provide a three-dimensional network of intermolecular cysteine network over the poly-Au electrode (poly-Au/*n*-cys). The network of the cysteine molecules is believed to possess a high number of active thiol sites for the immobilization of the GNPs. Finally, GNPs were immobilized from a colloidal GNP solution onto this network though Au-S bond formation. The thus prepared network was characterized by FT-IR, XPS, SEM and TEM.

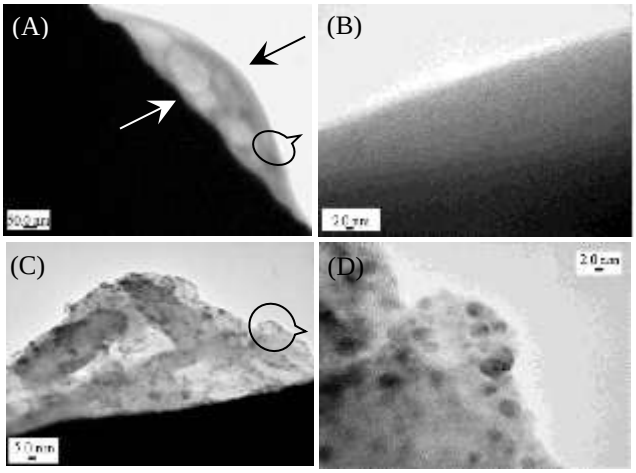

Figure 1. (A) TEM image of the cysteine network (marked between the arrows) over poly-Au electrode. (B) represents the higher magnification of a selected segment of the cysteine network in 'A'. (C) TEM image of the immobilized GNPs over the cysteine network. (D) represents the magnified image of the selected segment of 'C'.

References:

1. C. Li, K. L. Shuford, M. Chen, E. J. Lee, S. O. Cho, *ACS Nano* **2008**, 2, 1760.
2. S. S. Wong, Chemistry of Protein Conjugation and Cross-linking, CRC Press, Boca Raton, **1991**, pp. 195.