

Characteristics of Polypyrrole Deposited on Silver-Containing Nanocomplexes

Yu-Chuan Liu

Department of Chemical Engineering, Van Nung Institute of Technology, 1, Van Nung Road, Shuei-Wei Li, Chung-Li City, Tao-Yuan, Taiwan, R.O.C.

It is generally accepted that the enhancement of the Raman emission of molecules adsorbed on the metal surface has a double origin: the electromagnetic enhancement¹ due to an apparent increase in the Raman cross section and an excitation of surface plasma, mainly confined to Ag, Au and Cu, and the chemical enhancement,² concerning the charge transfer on the adsorbate-metal surface. The chemical mechanism contributing to Raman scattering exaltations is based on an increased polarizability of molecules adsorbed on metal surface under the influence of incident radiation, as a result of which new chemical bonds with the metal surface are formed.³ As shown in the literature,^{4,5} the most suitable roughness microstructure for SERS studies ranges from 10 to 100 nm. Recently, Henry et al.⁶ reported that chlorauric acid can act as an oxidant to oxidize chemically polymerized polypyrrole (PPy) to produce composite PPy colloids. Burke and Hurley⁷ reported that gold surfaces can be superactivated by a combination of thermal and cathodic pretreatment. They display inexplicably high catalytic activity for some reactions in the form of oxide-supported microparticles. Hepel⁸ also reported that PtCl_4^{2-} anions were trapped inside the PPy matrix during the electropolymerization of pyrrole. In the next step followed by solution exchange, PtCl_4^{2-} anions were reduced to Pt(0) particles with an average size of 10 nm. The methanol is electrocatalytically oxidized at these finely dispersed Pt nanoparticles in PPy films. All of these studies reveal that fine metals or metal-containing complexes with nanostructures demonstrate specially electrocatalytic activities. However, the detailed exploration and the mechanism of the catalytic activity for the electrooxidation pathway for the polymerization of conducting polymers were less observed in the literature.

In this study, the silver substrates were cycled in a deoxygenated aqueous solution containing 0.1 N KCl from -0.3 to +0.3 V vs. Ag/AgCl at 5 mV/s with 3 scans. Then a deoxygenated aqueous solution containing 0.5 M pyrrole was instantly dropped onto the as-prepared roughened Ag substrate. Then it was placed in a desiccator with nitrogen and dark atmospheres for 2 h. Finally the sample was rinsed throughout with deionized water and dried in a vacuum-dryer with dark atmosphere at room temperature before test. Figure 1 shows the surface image of the roughened Ag substrate. It is a typical aspect of a rough surface with a good Raman activity, which demonstrates a microstructure smaller than 100 nm. Encouragingly, pyrrole monomers can be autopolymerized on the roughened Ag substrates due to the electrochemical activity of the complexes. During the polymerization of pyrrole and the further oxidation of PPy, the AuCl_4^- complexes act as oxidants and the Cl^- ions act as dopants, respectively.

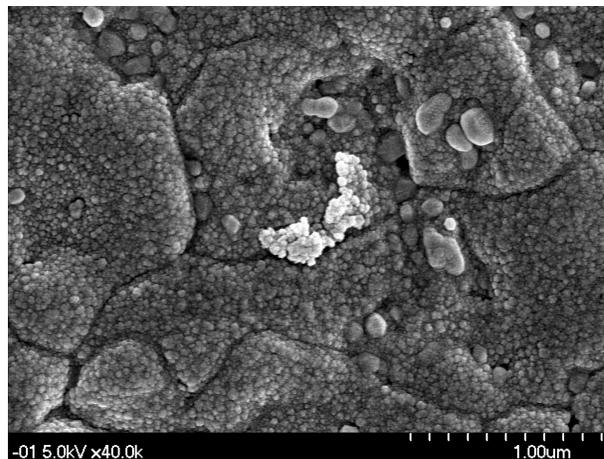


Figure 1. SEM image of silver substrate after ORC treatment.

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