Gold nanospheres and nanorods attached ITO surface: A biocompatible matrix for myoglobin and hemoglobin immobilization

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Gold nanoparticles are the most intensively studied and applied metal nanoparticles in electrochemistry owing to their stable physical and chemical properties, useful catalytic activities and small dimensional size.¹ These attractive properties allow them providing some important functions for electroanalysis and the construction of electrochemical sensors.² Especially the small size of gold nanoparticles allows the conductive materials to come into a close proximity of the active process and provides bioelectrocatalytic activity that can be utilized in biosensor devices.³ On various electrodes modified by gold nanoparticles, the direct electron transfer of redox proteins such as myoglobin (Mb) and hemoglobin (Hb) has been realized and applied for biosensors based on their electrocatalytic activity.

In the present work, we described a novel ITO surface modified by gold nanoparticles, namely nanospheres and nanorods (Fig.1). The synthesis of gold nanoparticles was based on a surfactant-assisted seeding growth approach that was actually intended to prepare gold nanorods in solution.⁴ This wet-chemical synthesis provided ~ 4% yields of rod-shaped gold nanoparticles and large amount of spherical nanoparticles. We adapted this method for ITO modification, ⁵ which was composed of two steps. Firstly, ca. 4 nm gold seeds consisted of citrate-stabilized gold nanoparticles were deposited on the ITO electrode surface. Secondly, in a growth solution, surfactant capped gold ions were reduced when encountering the gold seeds on the electrode surface, leading to the growth of gold nanoparticles.

The as-prepared gold nanoparticles-modified ITO electrode was then utilized for heme proteins immobilization. In the cast film of Mb on Au/ITO surface, the direct electron transfer between protein and electrode was observed (Fig.2), in contrast to the sensitivity of bare ITO electrode to the impurities of proteins. While Hb was adsorptively immobilized on Au/ITO, an efficient catalytic response to the reduction of H₂O₂ was obtained with good reproducibility and stability (Fig. 3). The catalytic current was found to be linear to the addition of H₂O₂ in a wide concentration range from 1 × 10⁻⁵ to 7 × 10⁻³ M.

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Figure 1. SEM image of an Au/ITO surface.



Figure 2. Cyclic voltammograms of Mb/Au/ITO in acetate buffer solution (pH 4.0) at different scan rates.



Figure 3. Cyclic voltammograms of Hb/Au/ITO before (a) and after (b) adding 2 mM H_2O_2 into PBS (pH 7.0). Scan rate: 0.1 V/s.