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Electrochemical preparation and structural characterization of platinum thin film on a polypyrrole film modified ITO electrode

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ABSTRACT

Platinum nanostructures have been fabricated by electrochemical deposition of platinum onto indium tin oxide (ITO) glass substrate modified with thin polypyrrole film. The crystal size and the number density of the platinum nanoparticles have been examined by varying several deposition parameters, including the thickness of the PPy film and the current densities for platinum deposition. Optimal conditions for uniform growth of nanoparticles well-dispersed on the ITO have been determined, along with insight into the mechanism of crystal growth. The PPy film thickness principally affect the size and number density of the nanoparticles, while the platinum deposition current densities could be used to regulate the shape of the nanoparticles. In addition, the flower-like platinum nanoparticles showed high catalytic activity on electrochemical oxidation of methanol, and its activity was measured to be approximately 1.9 times that of bare platinum.

1. Introduction

Metallic nanocrystals have been extensively studied because their chemical and physical properties are quite different from the bulk material. These properties strongly depend on the size and distribution of the nanocrystals, which are two important factors for evaluating the fabrication of nanomaterials [1–5]. Because their unique optical, electrochemical electronic and photoelectrochemical properties have significant industrial potential in the areas of chemical sensors, catalysis, and magnetic recording, numerous research groups have studied the fabrication and growth of nanocrystals by different approaches [6–9]. Recently, metal nanostructures with a wide variety of morphologies, such as spheres, cubes, rods, wires, prisms, and multipods, have been synthesized by different methods [10–14]. Electrochemical deposition is a promising technique for preparing nanoparticles due to its easy-to-use procedure and low cost of implementation. By reducing metal ions onto selected electrodes from an electrolyte solution, growth of a variety of different sizes and shapes of nanostructured particles has been obtained on metal [15,16], semiconductor [17,18], and polymer surfaces [19].

In the past few years, many studies have investigated the control of platinum nanoparticle size, their composition, and their self-assembly or self-organization into two-dimensional (2D) and three-dimensional (3D) structures. A number of one-step techniques including physical vapor deposition, electrochemical plating, a modified silver reaction, and galvanic replacement have been developed for fabricating 2D nanostructures. Platinum nanoparticles deposited on solid supports exhibit useful catalytic and electrocatalytic properties. Moreover, the catalytic activity of platinum nanoparticles exhibits significant size dependence [20].

On the other hand, as one of the most studied conducting polymers, polypyrrole (PPy) is an excellent material to be used as a substrate or matrix for deposition of metal nanoparticles (including copper, palladium, gold and hybrid materials) [21,22].

In this paper, we examined the growth mechanism of platinum nanostructured particles on a thin polypyrrole film electrochemically deposited on ITO electrode surface. It was found that platinum nanoparticles with spherical and flower-like structures were generated by varying several deposition parameters, including the thickness of the PPy film thickness and the current density of platinum deposition. Furthermore, it was testified that the flower-like platinum nanoparticles are catalytically active in room temperature electrooxidation reactions of interest to methanol.

2. Materials and methods

K_2PtCl_6, H_2SO_4, pyrrole (Py) and KCl were purchased from Shanghai Chemical Company. Pyrrole (Py) was triply distilled until a colorless liquid was obtained and was then stored under nitrogen before use. The ITO glass plates were purchased from Asahi Beer Optical, Ltd. (Japan) and they were used after being washed in acetone, ethanol, and pure water by sonication and drying with a nitrogen stream. All the solutions were prepared using deion-

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ized 1 MΩ cm water. All the electrochemical experiments were performed in a three-compartment cell at room temperature (20–22 °C), and were controlled by CHI660A. A sheet of ITO glass sheet with bare surface area of 0.5 cm^2 and a 2 × 2 cm platinum sheet were employed as the working and the counter electrodes, respectively. Silver–silver chloride (Ag/AgCl) was employed as the reference electrodes for the polymerization of polypyrrole (PPy) and the electrodeposition of Pt. All the solutions were deaerated by dry nitrogen bubbling for 15 min. The surface structures of freshly prepared electrodes were also investigated by LEO l530 scanning electron microscope (SEM) that operated at 20 kV.

2.1. Electrochemical deposition of PPy film

The electrochemical polymerization of polypyrrole (PPy) on the ITO glass sheet was carried out at a constant anodic potential of 0.80 V versus Ag/AgCl in a deoxygenated aqueous solution containing 0.1 M pyrrole and 0.1 M KCl. The thickness of PPy films was controlled by varying the electrodeposition time.

2.2. Electrochemical growth of Pt nanostructures

The working electrode was an ITO sheet covered with a thin PPy film, the counter electrode was a platinum sheet, and the reference electrode was Ag/AgCl. Pt nanostructures were electrodeposited by electrolyzing the aqueous solution of 1.5 mM K_2PtCl_6 and 0.1 M H_2SO_4 at a constant current density.

2.3. Electrocatalytic oxidation of CH_3OH

The working electrode was an ITO sheet coated with a PPy film and Pt nanostructures (Pt/PPy/ITO) and the counter electrode was a platinum sheet. All potentials were referred to Ag/AgCl. The electrolyte was an aqueous solution of 0.1 M CH_3OH and 0.1 M H_2SO_4.

3. Results and discussion

3.1. The effects of PPy film

The polypyrrole (PPy) film is grown by electropolymerization of pyrrole under controlled position in an aqueous of 0.1 M pyrrole and 0.1 M KCl. Fig. 1 shows the SEM images of platinum nanostructures deposited at bare ITO(a) and ITO modified 40 nm-PPy film (b). As can be seen from this figure, the nanoparticles grown on the bare ITO electrode are roundish and located sparsely on the electrode surface. It can be caused that the particles adhered weakly to the substrate and part of them fell off the substrate during the processes of electrodeposition and washing. But on the PPy modified ITO electrode, the platinum nanoparticles tend to aggregate into 3-dimensional nanoarchitectures with morphology like flower and homogeneously dispersed. It was demonstrated that PPy film can improve the adheretion of platinum.

3.2. Effects of the thickness of the PPy film

The thickness of PPy film is controlled by different deposition time at +0.8 V (vs. Ag/AgCl) and measured by EQCM. Fig. 2 shows the SEM micrographs of platinum nanoparticles deposited on PPy film thickness set to 15, 28 and 40 nm. As the PPy film thickness is increased from 15 to 40 nm, the average size of the platinum nanoparticles is found to increase from 70 to 250 nm with a concomitant decrease in the number density. The observed trends with increasing PPy film thickness are consistent with similar results obtained in K.T. Leung group's work, micrographs of copper nanocrystals deposited on PPy [23]. This is possibly due to a thicker PPy film providing fewer pinholes for nucleation and growth of the particles. Because equal charge density produces a nearly equal amount of platinum in unit area, thus larger particles should be generated on a thicker PPy film. In the case of a thinner film, the presence of pinhole defects in the PPy film could also lead to inhomogeneities in the platinum growth morphology [24].

For electrodeposition with instantaneous nucleation, a lower surface potential is found to lead to fewer nucleation centers (i.e., a lower number density) and a larger particle size. In addition, the thicker the PPy film, the rougher is its surface morphology and therefore the less uniform its surface potential becomes. The latter greater nonuniformity in the surface electrical field changes the platinum deposition from an instantaneous, diffusion-limited, controlled growth mechanism to a partially diffusion controlled mechanism, which could account for the larger size distribution in the platinum nanocrystal growth [21].

3.3. The effects of current densities

As above, the nanoparticles grown on a 40 nm PPy film modified ITO at a current density of 5×10^{-4} A cm^{-2} for 200 s have flower-like morphology. The SEM micrographs shown in Fig. 3 illustrate the effects of different current density on the morphology and distribution of the nanoparticles during deposition of platinum nanoparticles on a 40-nm-thick PPy film modified ITO, with all the other deposition parameters kept at their standard values. If the platinum nanoparticles were grown at a relatively low current densities of 1×10^{-5} A, as shown in Fig. 3a, the morphology of the nanoparticles was different from that shown in Figs. 3b–3d. In the stage of low current density, the formation of platinum nanocrystals on the PPy film begins with instantaneous nucleation followed

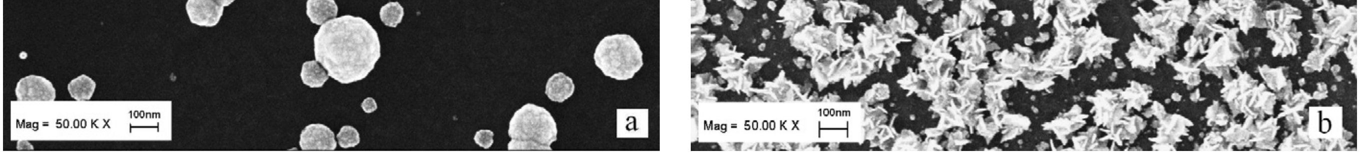

Fig. 1. SEM images of the platinum nanostructures deposited at 5×10^{-4} A cm^{-2} for 200 s each on a bare ITO (a) and the ITO modified with 40 nm-PPy film (b).