

Voltammetric behavior of carboxyl hydrogel particles on a cavity electrode surface



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ABSTRACT

A platinum electrode with two-dimensional ordered arrays of hemispherical cavities was fabricated via the inverted crystal template technique. Due to the overlap of the diffusion zones, voltammetric response of ferricyanide at the cavity platinum (Cpt) electrode was almost the same as that at a flat platinum (FPt) electrode. Uniformly sized poly(*N*-isopropylacrylamide-co-acrylic acid) (NIPA/AA) hydrogel particles were synthesized and modified into the cavities of the Cpt electrode. Voltammograms of the NIPA/AA-Cpt electrode showed a cathodic peak at -0.38 V in the negative potential range. The peak was attributed to the reduction of H^+ which supplied from the dissociation of carboxyl groups of the absorbed particles. Compared with the peak observed at NIPA/AA-FPt electrode, the peak potential was shifted in the positive direction by 0.19 V. The peak current was increased linearly with the loaded amount of the particles, and was controlled by the participation of diffusion, adsorption and dissociation. The electron-transfer rate constant between dissociated H^+ and the Cpt electrode was estimated to be one order smaller than that between ferricyanide and the FPt electrode.

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1. Introduction

With the fast development of synthetic techniques, various kinds of latex particles have been prepared and used for electrode surface modification to improve the mechanical [1], electronic [2] and catalytic [3] properties. For examples, particle film-coated electrodes have been constructed as a biosensor to study the electrocatalytic redox reaction of nitrite [4,5], phenol [6], and heme proteins [7]. The main advantage of using latex particles is easy generating uniform films with wide area and high porosity by conventional methods, such as casting method, spread method and Langmuir-Blodgett method [8]. The porosity of the films plays a vital role in the development of the electrode properties, which is able to enhance molecules, ions and charges transport through the particle film to the electrode surface [9].

Recently, latex particle film-coated electrodes have been attracted much interests, not only for further development of electrochemical properties of electrodes but also for fundamental studies about the electrochemical behaviors of the particles. Polyaniline particles have allowed researchers to estimate the relationship between adsorption force and the degree of an

electrode reaction [10]. Polyacrylic acid particles have showed reduction wave of the dissociated H^+ , which can be used to evaluate the dissociation constant of carboxyl groups [11]. Furthermore, the electrochemical behaviors of latex particles are strongly depended on their size, shape, structure and composition. Ferrocene-immobilized polystyrene particle has brought about the partial electron transfer depending on the particle size [12]. Ploy(*N*-isopropylacrylamide-co-acrylic acid) (NIPA/AA) hydrogel particles, which has an interconnected porous structure, were totally dissociated and can be worked as a source of the supply of H^+ for the electrochemical reduction of 1,4-naphthoquinone [13]. Electrochemical reacting domains within polystyrene-based particles are restricted to the surface of the particles [11,14] because of the hydrophobicity of the phenylethyl groups. A basic understanding of the electrochemical behaviors of the particles should allow us to elucidate the reaction principle and provide practical application of the electrodes.

To further develop latex particle film-coated electrodes, efforts should be directed not only to synthesize special particles but also to design geometric structures of the substrate. In our previous short report [15], cavity platinum (Cpt) electrode has been shown to provide a significant improvement for surface coating with NIPA/AA particles. Furthermore, the local surface pH of the electrode can be controlled under acid conditions for a concerted proton-transfer reaction by the carboxyl groups in the particles.

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However, to the best of our knowledge, there are no reports in the literature describing electrochemical behavior of latex particles on a hemispherical cavity surface. In this work, the voltammetric behavior of NIPA/AA particles at CPt electrode was systematically investigated. In particular, intensive attentions have been focused on the effect of electrode surface structure on reduction of the dissociated H^+ .

2. Experimental Section

2.1. Chemicals

Styrene (St) was purified successively with 5% aqueous NaOH solution, water, dried with anhydrous $MgSO_4$ for one day, and then distilled under vacuum. Acrylic acid (AA) was purified by distillation under vacuum. *N*-isopropylacrylamide (NIPA) was purified by recrystallization from a mixture of toluene and hexane (1:1, v/v). *N,N*-methylene-bis-acrylamide (MBA; 99%; Sigma-Aldrich) and poly(*N*-vinylpyrrolidone) (PVP; MW 360 $kg\ mol^{-1}$; Sigma-Aldrich) were used as received. The initiators, α -azoisobutyronitrile (AIBN) and potassium persulfate (KPS) were purchased from Aladdin Reagents (Shanghai, China). All the other reagents were of reagent grade and used as received. Aqueous solutions were prepared with ultra-pure water with a resistance of 18.2 $M\Omega\ cm$ (Milli-Q, Millipore).

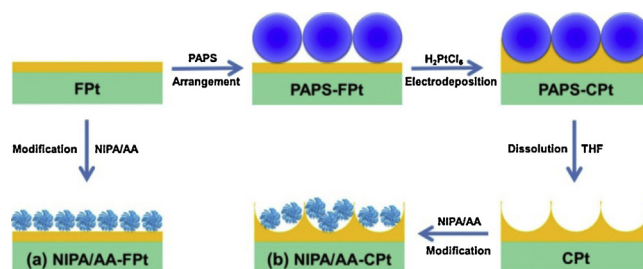
2.2. Synthesis of PAPS and NIPA/AA particles

Negative charged PAPS particles were prepared by a two-step dispersion copolymerization of St with AA in isopropanol/water media. At the first step, the polystyrene (PS) particles were synthesized by a process similar to the documented way [16]. PVP (2.0 g) was dissolved in 100 cm^3 isopropanol/water (80:20, v/v) mixture solution in a 250- cm^3 three-necked round-bottomed flask with a condenser and a gas inlet. After a homogeneous solution formed at room temperature, the solution was deoxygenated by bubbling nitrogen gas at room temperature for 30 min. The flask was then placed in a 70 °C oil bath and stirred mechanically at 200 rpm. A solution of St (10.0 g) containing AIBN (0.10 g) was added dropwise over 30 min to the solution. The polymerization was continued for 24 h, which resulted in a milky-white suspension. The obtained PS particles were used as the seed particles for the next step. AA (0.06 g), St (1.0 g) and AIBN (0.05 g) were added to 100 cm^3 PS suspension (11 wt.%) in a three-necked flask. The mixture was stirred at room temperature under nitrogen purge for 12 h. Then, the mixture was heated to 80 °C and maintained for 8 h. After polymerization, the obtained PAPS suspension was purified thrice by centrifugation to remove non-adsorbed PVP.

NIPA/AA hydrogel particles were synthesized by a one-step surfactant-free emulsion polymerization of NIPA, AA and a cross-linking agent MBA at the loaded molar ratio of 1:0.232:0.072 [11]. NIPA (138 mM), AA (32 mM) and a cross-linking agent MBA (10 mM) were dissolved in 110 cm^3 water in a 250- cm^3 round bottom flask equipped with a condenser, a N_2 gas inlet, a stirrer and a thermometer. The mixture was stirred at 350 rpm under N_2 for 4 h at room temperature. After the mixture was heated up to 70 °C, 30 cm^3 of potassium persulfate (44 mM) was added dropwise into the mixture to initiate the polymerization. The reaction was continued for 6 h at 70 °C under vigorous stirring. The resulting suspension after cooling to room temperature was purified thrice by centrifugation and redispersion with water.

2.3. Preparation and modification of CPt electrode

The fabrication of NIPA/AA particle film-modified CPt and FPt electrodes is schematically illustrated in Scheme 1. The highly



Scheme 1. Schematic illustration of the procedures for fabricating the NIPA/AA particle film-coated FPt (a) and CPt (b) electrodes.

ordered polymer particle template is prepared by casting a given amount of PAPS suspension on FPt electrode surface and being dried. To allow the solution to diffuse all the interstitial spaces of the self-assembled close packed array of the PAPS particles, the templated electrode (PAPS-FPt) was then put into 50 mM H_2PtCl_6 plating bath (at 25 °C) for 10 min prior to reduction. The electrodeposition of platinum was performed by applying a potential at $-0.20\ V$ vs. $Ag|AgCl$ until the required charge has been passed. After rinsing with water in an ultrasonic bath, the obtained PAPS-CPt electrode was transferred into tetrahydrofuran (THF) solution for 6 h to dissolve the PAPS particles. As a result, the desired CPt electrode with a regular cavity structure was obtained.

The NIPA/AA particle film-coated CPt and FPt electrodes were fabricated by dropping a certain amount of the particle suspension ($0.44\ g\ L^{-1}$, pH 7) on the electrode surface, rinsing with water and drying at room temperature.

2.4. Measurements and instrumentation

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a computer-controlled CHI 660D electrochemical workstation (Shanghai CH Instruments, China). Potentials were measured with respect to a commercial $Ag|AgCl$ (3 M KCl) reference electrode and the counter electrode was a platinum coil. Before each experiment, the surface of FPt electrode was polished with 0.5 μm and 0.05 μm alumina paste on a wet cotton cloth and rinsed successively with water, acetone, and 95% ethanol in an ultrasonic bath.

The size and geometry of the particles were determined by a scanning electron microscope (SEM, Hitachi, S-4800). The size distribution and particle dispersion were analyzed by a dynamic light scattering (DLS, Malvern Zetasizer Nano-ZS) at 25 °C. The conductance measurement was carried out on a DDS-307 conductivity gauge (Rex Instruments, Shanghai, China). The pH values were recorded using a PHS-3C pH meter and an E-201-C pH glass electrode (Rex Instruments, Shanghai, China).

3. Results and discussion

3.1. Properties of PAPS and NIPA/AA particles

The morphology of the PAPS particles was spherical (1.10 μm in diameter) as observed from the SEM analysis (Fig. not shown). Due to the electrostatic repulsion between neighboring charged PAPS particles, the highly ordered polymer particle template can be easily fabricated at platinum electrode surface. Therefore, PAPS particles were used to fabricate the particle template for the preparation of CPt electrode.

The NIPA/AA particles were arranged spontaneously on the FPt electrode, as was observed from SEM (Fig. 1A). The SEM image showed that the dried NIPA/AA particles were also spherical and uniform in size with diameter of $0.323 \pm 0.015\ \mu m$, where the error

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