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Electrochemical impedance spectroscopy of poly (1-ethyl 3-(2-methacryloyloxy ethyl) imidazolium chloride) brushes with locally generated Pd

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Abstract

The electrochemical impedance spectroscopy of polyelectrolyte brushes (poly (1-ethyl 3-(2-methacryloyloxy ethyl) imidazolium chloride) (PEMEIm-Cl) incorporated with locally generated palladium nanoparticles was first studied, which exhibits evidently different electrochemical behavior with the PEMEIm-Cl brushes in electrolyte solution. The PEMEIm-Cl brush containing Pd nanoparticles exhibits high electrocatalytic activity for the reduction of oxygen. Furthermore, the electrocatalytic activity of PEMEIm-Cl/Pd brush for oxygen reduction was highly tunable by changing the thickness of the composite film.

Keywords: Palladium nanoparticles; Electrochemical impedance spectroscopy; Polyelectrolyte; Oxygen reduction

1. Introduction

Recently, polyelectrolyte brush has aroused a paramount research interests because of the responsive behavior to a variety of environment triggers, for example, pH, salt concentration and temperature, etc. [1]. The swelling-collapse behavior of the polyelectrolyte is to a large extent governed by electrostatic interactions and the osmotic pressure of the counterions [2]. There are different ways to trace the configuration change and the conformation change of polyelectrolyte brush including AFM, thickness measurement, contact angle measurement, etc. [3,4]. From electrochemical point of view, the swelling-collapse behavior will affect charge-transfer process, specifically the interface resistance. Electrochemical impedance spectroscopy (EIS) represents a highly efficient way to macroscopically reflect the electron-transfer process [5,6], which has been used to study the structure and the behavior of self-assembled monolayer [7–12], polyelectrolyte multilayer [13–15], and the barrier properties of polyhydroxyl ethylmethacrylate brushes and their derivatives [16–19]. As for polyelectrolyte modified substrate, swelling offers fast transport of redox species to the substrate surface, while polymer brushes in collapse state block mass transport.

Construction of nanoparticles is at the focus of materials research because of their unique electronic, catalytic, and optical properties. Noble metal nanoparticles are of fundamental interest and technological importance because of their applications as catalysts. In the most interesting and practically promising field, such as sensors and photo- or bio-electrochemical devices, they are utilized in the form of thin films deposited on suitable substrates [20]. Surface initiated atom-transfer radical polymerization has been intensively applied to the preparation of the polymer and

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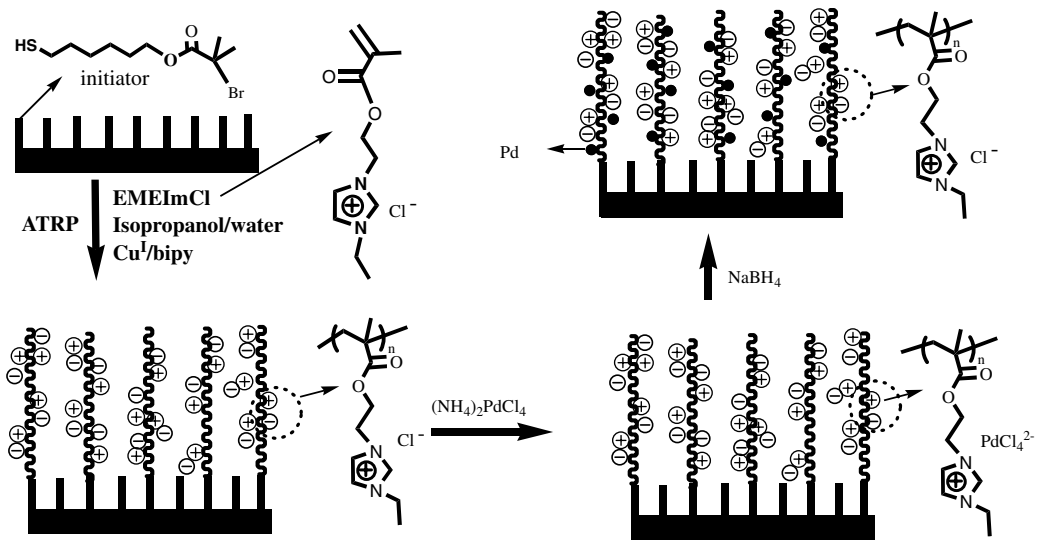

Scheme 1. Schematic preparation of PEMEIm-Cl/Pd brush on Au surface.

polyelectrolyte films on different substrates [21–25]. It allows to control accurately thickness of the films. Inorganic/polymer composites on substrates provide unique materials of electronic and catalysis properties.

Although there are theoretical and experimental studies on charge and mass transport through polyelectrolyte in our previous work [26,27], charge transport through polyelectrolytes/nanoparticles composite film has not been carefully investigated and characterized the interest in these systems yet at its early stage of development [28,29]. It is crucial for many applications, in any case, to ascertain the charge transport mechanisms taking place and to provide quantitative results on the physical properties ruling them as well as the means to control the permeability of polylelectrolyte/nanoparticle composite film.

In this work we describe the study on the electrochemical impedance spectroscopy (EIS) of polyelectrolyte brushes incorporated with locally generated metal nanoparticles. Pd nanoparticles are created via reduction of $PdCl_4^{2-}$ bound as counterions within cationic brushes, i.e., poly 1-ethyl 3-(2-methacryloyloxy ethyl) imidazolium chloride (PEMEIm-Cl). Scheme 1 shows the preparation of Pd incorporated PEMEIm-Cl brush composite surface. Meanwhile, the Pd nanoparticles in PEMEM-Cl brush can effectively catalyze the reduction of O_2.

2. Experimental

2.1. Reagent

Monomer 1-ethyl 3-(2-methacryloyloxy ethyl) imidazolium chloride and initiator $BrC(CH_3)_2COO(CH_2)_6SH$ were synthesized according to the literature [30,24]. Copper (I) bromide was purified by reflux in acetic acid 1 h. $(NH_4)_2PdCl_4$ was obtained from Chemical reagent company of Shanghai (Shanghai, China). Other chemicals were used as received.

2.2. Preparation of PEMEIm-Cl brush containing Pd nanoparticle on Au surface

The preparation of PEMEIm-Cl/Pd brush on Au electrode was described in Scheme 1. First, PEMEIm-Cl brushes were grown from initiator modified gold surface by atom-transfer radical polymerization (ATRP) in an isopropyl alcohol/water (1:1) mixture, as described in our previous work [26]. The thickness of PEMEIm-Cl brush was controlled by changing polymerization time. The prepared of PEMEIm-Cl brushes were immersed in 0.1 M $PdCl_4^{2-}$ solution for 30 min to exchange anion, then the film was immersed fresh 10 mM $NaBH_4$ for 30 min to reduce Pd (II). The obtained PEMEIm-Cl/Pd composite brushes were washed several times with water.

2.3. Characterization

Chemical composition information about the samples were obtained by XPS, the measurement was carried out on a PHI-5702 multi-functional spectrometer using Al Kα radiation. The thicknesses of the samples were determined by Gaertner model L116C ellipsometer with a laser ($\lambda = 632.8$ nm) at angle of incidence of 50° (It should be noted that these brushes are hygroscopic and without special precautions; they will contain some water.) The static water contact angles were measured by the sessile drop method, in a CA-A telescopic goniometer. All electrochemical experiments were performed at room temperature using a CHI 660B Electrochemical Workstation. Electrochemical measurement was performed in a single-compartment cell with a standard three electrode configuration: The brush modified Au as a working electrode (0.196 cm^2), a platinum wire as a counter electrode (0.253 cm^2) and a saturated calomel electrode (SCE) as a reference electrode. The frequency range of EIS was between 10,000 and 0.1 Hz using amplitude of 5 mV at an open circuit potential. Impedance spectra fitting and