Journal of Electroanalytical Chemistry 775 (2016) 105–109

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Electrochemical behaviors of polyaniline confined in highly ordered micro-sized SiO_2 cavities

Yanqing Zhang [a,b], Wenya Chu [a], Qun Zhou [a,*], Shuangshuang Li [a,b], Na Li [a], Junwei Zheng [a,b,*]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China
[b] College of Physics, Optoelectronics and Energy, Soochow University, Suzhou 215006, PR China

ARTICLE INFO

Article history:
Received 12 April 2016
Received in revised form 20 May 2016
Accepted 24 May 2016
Available online 25 May 2016

Keywords:
Polyaniline
Cavity
Ascorbic acid
Electrochemical Sensor
Edge effect

ABSTRACT

An array of microelectrodes is fabricated with highly ordered SiO_2 cavities modified on an indium-doped tin oxide (ITO) electrode, benefiting from the confinement of the insulating SiO_2 cavities. Aniline can be electrochemically polymerized to form polyaniline (PANI) independently inside each SiO_2 cavity. The edge effect of the microelectrodes leads to the radial diffusion of aniline in the SiO_2 cavities; as a result, the PANI grows uniformly along the wall of the cavities and eventually covers the whole surface area of the SiO_2 cavities to form an array of PANI cavities. Thus, the effective area of the PANI modified electrode could be greatly enlarged through such a surface structure modification. Moreover, it is demonstrated that the electrochemical reaction of ascorbic acid can be enhanced due to the radial diffusion of ascorbic acid inside PANI cavities. The specific features of the PANI cavity array enables us to develop a sensing platform of ascorbic acid detection with a detection limit of 0.14 μM (S/N = 3) and a linear range of 0.5–131 μM.

1. Introduction

Diffusion and reaction of molecules occurring inside a confined micro-/nano-sized volume have drawn strong attention for the importance in the application of energy storage, surface-enhanced Raman scattering, and electrochemical analysis [1–4]. In particular, the micro-/nano-sized electrodes with specific structure of highly ordered confined space to form an array system have been fabricated and used in addressable detection and monitoring reactions, due to their rapid response time, fast diffusion, high signal-to-noise ratio, and small *iR* drop [5,6]. The extensive application of the array of the micro-/nano-sized electrodes promotes the development of the array fabrication technology. Those include nanoimprint lithography, focused ion beam milling, and electron beam lithography, which provide a good repeatability and precise control of the patterns [7–10]. However, those techniques rely on expensive equipments. An efficient and economic approach for the fabrication of highly ordered micro-/nano-sized electrodes is still desirable for both fundamental research of the special properties and application in various fields. Recently, template-assisted technique has been attempted to fabricate such array electrodes to form the inverse highly ordered cavity structures on the surface of the electrodes [11, 12]. With self-assembled micro-/nano-sized monodispersed particles on a conductive substrate as a template, materials with various functionalities are infiltrated or deposited into the interstices among the template particles to produce an array of micro- or nano-sized cavities after removal of the template particles. We have demonstrated previously that the highly ordered cavities can act as microcontainers and localize the electrochemical reactions occurring inside the cavities [13, 14]. Benefiting from the confinement effect of the insulating cavities on the electrochemical reactions and high conductivity of the underlying substrate exposed at the bottom of the cavities, the micro-/nano-sized cavities can serve as the microelectrodes arranged in a highly ordered manner, exhibiting fast electrochemical response [15,16].

Herein, we demonstrate a new approach to fabricate highly ordered polyaniline (PANI) cavities on the surface of silica cavity array on an ITO electrode. PANI is a conductive polymer widely used in electrochemical sensors, energy conversion and storage, memory devices, optoelectronic devices, and anticorrosion coatings, because of its chemical stability, ease of preparation, and high electronic conductivity [17–20]. The growth and electrochemical behavior of PANI in a micro-sized volume would be quite interesting particularly for the development of a new type of electrochemical devices. It is revealed that the confinement effect of the silica cavities on electrochemical polymerization of aniline leads to independent growth of PANI inside each cavity and eventually to form PANI cavity array, which fully covers the surface of the entire electrode. The effect of the cavity structure on the diffusion of the species involved in the electrochemical reactions leads to an enhanced oxidation of ascorbic acid (AA). This enables us to develop an electrochemical sensing platform for AA detection with fast response and low detection limit.

---

* Corresponding authors.
E-mail addresses: zhq@suda.edu.cn (Q. Zhou), jwzheng@suda.edu.cn (J. Zheng).

http://dx.doi.org/10.1016/j.jelechem.2016.05.042
1572-6657/© 2016 Elsevier B.V. All rights reserved.

2. Experimental

2.1. Chemicals

Colloidal SiO_2 and ascorbic acid were purchased from Sigma-Aldrich and J&K Co., respectively. Styrene was distilled under reduced pressure to remove the antipolymerizer before use. The other chemicals are reagent grade. All solutions were prepared with Millipore-Q water.

2.2. Fabrication and instruments

The fabrication of highly ordered silica cavities on the surface of an ITO electrode and the formation of PANI inside the cavities are illustrated in Fig. 1. The polystyrene (PS) spheres template and the SiO_2-cavity/ITO electrodes were fabricated according to the protocol reported previously [13,21]. The monodispersed PS colloidal suspension was dispersed onto the surface of water to spontaneously generate a monolayer of the PS particles with diameters of 1.6 μm at the air/water interface. A few drops of 2% sodium dodecylsulfate solution were then added onto the water surface to alter the surface tension and to make the PS particles to be arranged compactly. After that, the monolayer of the close-packed PS particles was transferred onto the surface of an ITO electrode. The substrate was heated at 106 °C for 30 min to make the bottom of the PS spheres to be slightly fused, so that the PS spheres were well fixed on the surface of the ITO electrode. Next, the colloidal SiO_2 was infiltrated into the interstices and solidified at room temperature for 1–2 days. After a complete removal of the PS template in toluene, the SiO_2-cavity/ITO electrode with a structure of highly ordered array was obtained. Then, the electrode was activated in a 0.5 M H_2SO_4 solution with a potential range from −1.0 to 1.0 V by cyclic voltammetry (CV). Finally, the PANI in the cavities was electrochemically polymerized in a 0.5 M H_2SO_4 solution containing 0.02 M aniline in a potential window between −0.2 and 1.3 V for different cycles.

The SEM images were captured on a Hitachi S4700 (Japan) field emission scanning electron microscope. The CVs and chronoamperometry were conducted with an Autolab PGSTAT302N electrochemistry workstation (Netherlands). A conventional three-electrode cell was used, including a modified ITO electrode as the working electrode (5 mm in diameter), a saturated calomel electrode (SCE) as the reference electrode, and a platinum foil as the counter electrode.

3. Results and discussion

Polystyrene particles can be spontaneously assembled into a monolayer with a relatively large area at air/solution interface, due to the lateral capillary force and convective flow from an imbalance of the surface force arising from differences in the curvature of the liquid surface and the evaporation of the liquid [22]. As the monolayer is transferred onto the surface of the ITO electrode, a template based on the close packed structure of uniform polystyrene spheres is generated. Then, SiO_2 nanoparticles are infiltrated inside the interstices of the assembled PS spheres, forming SiO_2-based cavities after solidification by evaporation of solvent and removal of polystyrene spheres. Although the solidified SiO_2-cavity is insulating, the underlying ITO at the bottom of each cavities is conductive and can serve as active site for electrochemical reactions, leading to the polymerization of PANI occurring in a micro-sized volume. In other words, PANI can independently grow in each cavity due to the confinement of the insulating SiO_2 cavities to the electrochemical reactions. Fig. 2 depicts the morphologies of the monolayer of the PS spheres and SiO_2 cavities in the ITO electrodes. As can be seen from the SEM images in Fig. 2a, the PS spheres are arranged hexagonally to form a close-packed 2-dimensional array on the surface of the ITO electrode. The solidification of the infiltrated SiO_2 nanoparticles results in the formation of well-ordered SiO_2 cavities, which exactly reflect in the assembled array structure of the PS particles (Fig. 2b). The depth of the SiO_2 cavities can be finely controlled by the amount of SiO_2 nanoparticles infiltrated inside the interstices of the assembled PS spheres. In this case, nearly semispherical SiO_2 cavities with a radius of the cavities around 0.77 μm were obtained. The depth of the cavity

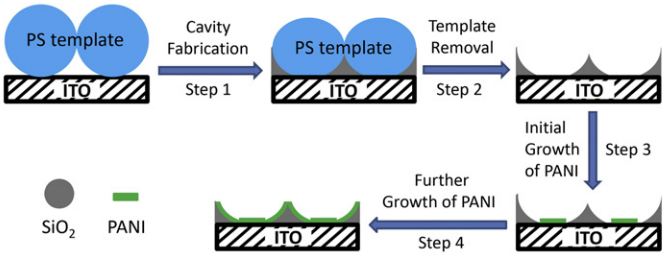

Fig. 1. Schematic illustration of the steps for fabrication of polyaniline inside the highly ordered SiO_2 cavities.

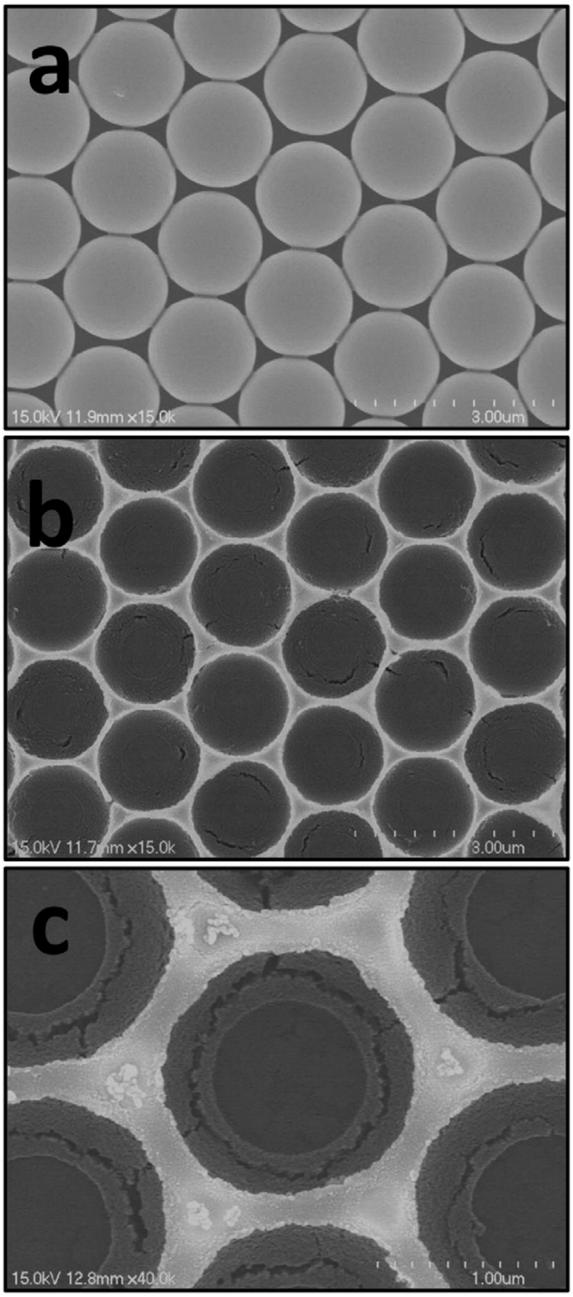

Fig. 2. SEM images of PS template (a) and SiO_2 cavities (b, c).