

Patterns of conducting polypyrrole with tunable morphologies

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ABSTRACT

An effective and reliable method was established to fabricate ordered arrays of conducting polypyrrole (PPy) with tunable morphologies. A polydimethylsiloxane (PDMS) stamp was used to lift up the top layer of silica spheres with a closed-packed hexagonal arrangement on a silicon wafer. The lattice spacing of the silica sphere array on the PDMS stamp could be tuned by controlling the swelling of the stamp. Afterwards, the silica spheres were transferred onto a poly(vinyl alcohol) (PVA) film which was pre-spin-coated on an ITO glass. The silica spheres were etched away with hydrofluoric (HF) acid, and the resulting porous PVA film maintained an identical ordered array but of holes. Electrochemical polymerization of pyrrole monomer was carried out with the ITO glass as a working electrode, on which was the PVA film with ordered holes. Different charge densities applied led to PPy patterns with different morphologies; a possible mechanism was addressed.

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1. Introduction

Recently, patterned conducting polymer materials have received considerable attention owing to their potential applications in various areas including sensors, microelectronics and microelectrodes [1–3]. Approaches such as electrochemistry, dip-pen lithography, photochemical patterning and nanoimprint lithography are feasible to engineer conducting polymer patterns [4–8]. Among the various techniques, electrochemical method is particularly attractive due to its several advantages including low toxicity, low cost of electrochemical workstation and fast preparation process; furthermore, the morphology of the pattern can be readily controlled to a certain degree, through changing the electrochemical parameters such as current, voltage, charge density and electrodeposition time [9]. Therefore, the electrochemical method is an important approach to the fabrication of conducting polymer patterns.

Among various conducting polymers, polypyrrole (PPy) is an outstanding member with particular importance in sensing applications. In addition to its several virtues such as inert to environment, PPy has exhibited fast response to some toxic gas such as NH₃ and H₂S, due to its high conductivity and good redox property; meanwhile, it can be easily synthesized by different approaches, including electrochemical polymerization and chemical oxidative polymerization [10–14]. Several research groups have investigated

on the fabrication of PPy patterns by electrochemical method [15,16]. Although several attractive structures have been reported, little has been achieved in the preparation of micropatterns with tunable morphologies from identical templates. The merits of the capability of making micropatterns with tunable morphologies from identical templates are significant: (i) different morphologies may satisfy different applications; (ii) usually, one template only leads to one corresponding pattern; it is easy to understand that the usage efficiency of one “mother” template increases, when it leads to several patterns with various morphologies.

In this paper, we report the preparation of two-dimensional (2D) ordered PPy patterns with tunable morphologies from one identical template. On an ITO substrate, a PVA polymer thin film consisting of ordered holes was fabricated via soft-lithography. The morphology of a resulting PPy pattern is highly related to the charge density applied and the swelling of PVA on the ITO glass by the electrolyte.

2. Experimental

2.1. Materials

Pyrrole monomer was purchased from Sigma–Aldrich, and was distilled under reduced pressure and stored at –4 °C prior to use. Polydimethylsiloxane (PDMS) elastomer kits (Sylgard 184) were obtained from Dow Corning (Midland, MI). Poly(vinyl alcohol) (PVA, $\bar{M}_w = 7.7 \times 10^4$), polystyrene (PS, $\bar{M}_w = 2.2 \times 10^6$), lithium perchlorate (LiClO₄·3H₂O), acetonitrile, hydrofluoric (HF) acid and

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tetraethyl orthosilicate (TEOS) were analytical grade and used as-received. In all preparations, absolute ethanol and deionized water were used.

2.2. Preparation of PPy patterns with tunable morphologies

Fig. 1 outlines the procedure of preparing PPy patterns with tunable morphologies, which begins with the assembly of mono-disperse silica spheres on the surface of a silicon wafer by the ethanol evaporation of a silica suspension (a) [17]. The mono-disperse silica spheres with diameter of ca. 560 nm were synthesized according to Stöber method [18]; and they were dispersed in ethanol. With lift up soft-lithography, one monolayer of silica spheres with a closed-packed hexagonal array was transferred to the surface of a PDMS stamp (b). The closed-packed silica array could be easily tuned to a non-closed-packed (ncp) silica array;

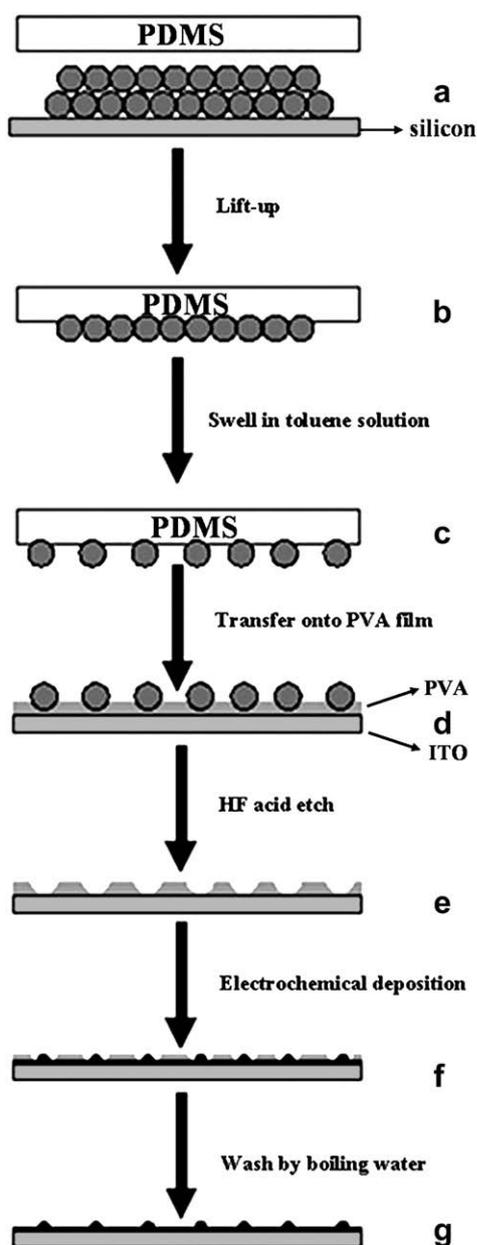


Fig. 1. Schematic drawing of the fabrication process of our PPy patterns with tunable morphologies.

furthermore, the lattice spacing, namely center to center distance of two neighboring spheres, could be flexibly controlled with the toluene concentration of a toluene–acetone mixture, in which the PDMS stamp was dipped. The higher the toluene content used, the larger the lattice spacing obtained (c) [19]. The obtained 2D ncp array on the swelled PDMS stamp was thus transferred to the surface of an ITO glass by using a modified microcontact printing (μ cp) technique [20]; the ITO glass was pre-spin-coated with a thin film of PVA. Afterwards, the PDMS stamp was carefully peeled away (d). Subsequently, the ITO substrate was dipped into 3 wt% HF acid for 10 min to remove the silica spheres; accordingly, a PVA template with ordered holes on the ITO substrate was successfully obtained (e). The resulting ITO glass was used as a working electrode in a three-electrode electrolytic cell, with a platinum wire as a counter electrode and an Ag^+/Ag electrode as a reference electrode. In our electrochemical approach, a typical electrolyte was an acetonitrile solution consisting of 0.2 M pyrrole monomer and 0.1 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. Electrodeposition was carried out at room temperature and with a constant electric potential of 0.7 V vs. Ag^+/Ag reference electrode. Subsequently, PPy patterns with different morphologies were obtained with different charge densities (f). Finally, the PVA film on the surface of ITO glass was easily washed away in hot water (above 85 °C) for 15 min (g).

2.3. Characterization

The electrochemical experiments with constant electric potential were performed on a BAS100W electrochemical workstation. The morphologies of the silica sphere arrays, PVA hole templates and PPy patterns were investigated by a JEOL JEM-6700F field-emission scanning electron microscope (SEM) with primary electron energy of 3 kV. Atomic force microscopy (AFM) images were recorded in a tapping mode with nanoscope IIIa scanning probe microscope from digital instruments under ambient conditions.

3. Results and discussion

3.1. Preparation of PVA templates

Fig. 2a displays a SEM image of 2D hexagonal ncp silica sphere array on a PVA-coated ITO glass. This pattern was created by a PDMS stamp swelled with 100 wt% toluene. The lattice spacing of the obtained ordered structure in Fig. 2a is about 780 nm. The highly ordered hexagonal arrangement was preserved and the ncp structure of the silica array was mechanically stable during the μ cp process because the spheres sank into the PVA film. As we know, the conductive layer (indium tin oxides layer) of ITO glass could be etched by strong acid. To avoid destroying the conductive layer of ITO glass, we have diluted the concentration of HF solution (initial concentration: 40 wt%) to 3 wt%. After dipping the ITO substrate into the HF acid for 10 min, the silica spheres were completely etched away, leaving the PVA film with corresponding ordered holes. A typical SEM image in Fig. 2b shows that the PVA holes are very smooth and the average inner diameter is about 550 nm which almost equals to the diameter of the silica spheres used; such similarity suggests that nearly half of a silica sphere body sinks into the PVA film, with the possible existence of the PVA film between the silica spheres and the ITO substrate. The pre-coated PVA film was ca. 800 nm in thickness. The lattice spacing and the hexagonal arrangement of the holes shown in Fig. 2b are the same as those of the corresponding silica sphere array on the PVA film shown in Fig. 2a. It is important to point out that the bottom of PVA hole is not directly open to the ITO glass below. From the curved porous PVA film (Fig. 3), it can be observed clearly that there is still a PVA film left between the bottom of the PVA hole and the surface of ITO

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