



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;

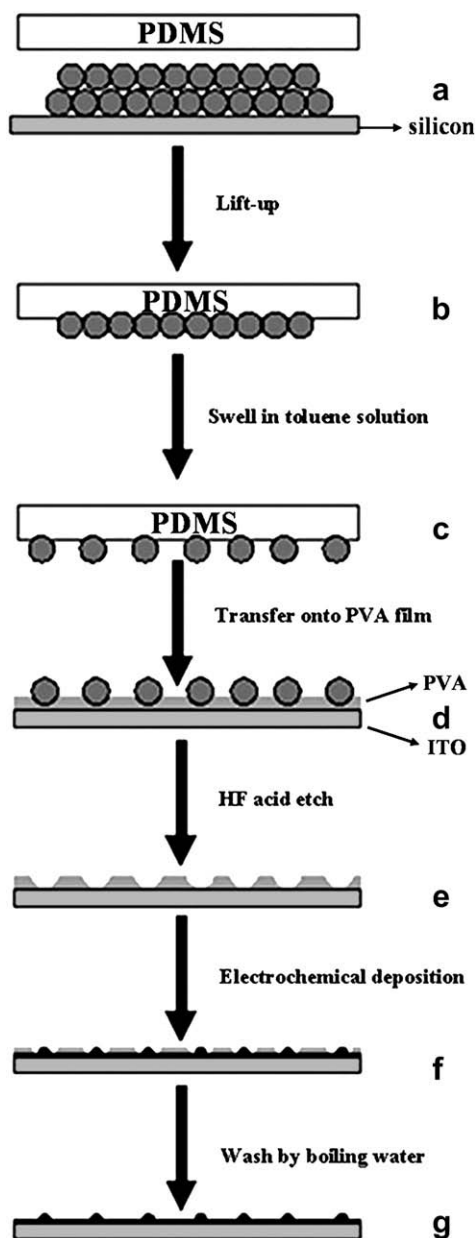


Fig. 1. Schematic drawing of the fabrication process of our PPy patterns with tunable morphologies.

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

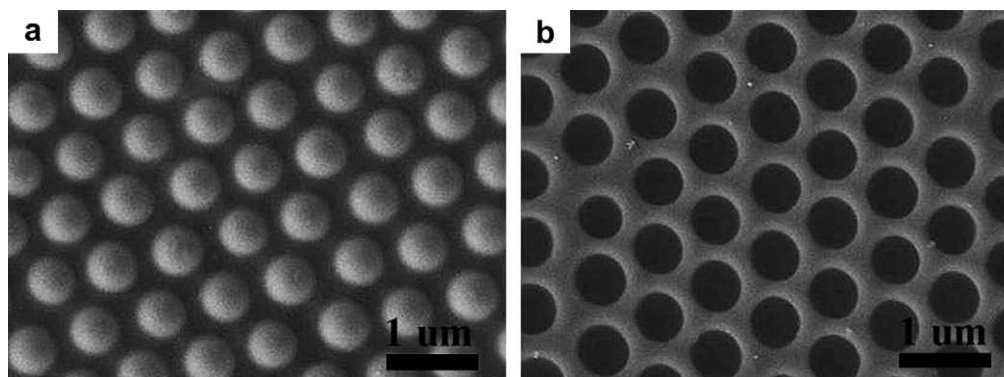


Fig. 2. SEM images of (a) silica spheres with diameter of 560 nm on the surface of a PVA film. The PDMS stamp was dipped in a 100 wt% toluene solution, the lattice spacing of the micropattern array is 780 nm; (b) Dipped into a HF solution, the silica spheres were completely etched away and a porous PVA film with ordered holes is left on the surface of an ITO glass.

glass (indicated by the arrows). This suggested that the thickness of the PVA film was larger than the size of silica spheres sinking into the PVA film.

3.2. Preparation of PPy patterns with multiple morphologies

In this study, the porous PVA patterns with the ncp hexagonal arrangement were used as templates to prepare PPy patterns with tunable morphologies. The whole fabrication process was monitored by AFM. Fig. 4 displays the three-dimensional profiles of the PPy patterns obtained from electrodeposition with different charge densities. Fig. 4a and b shows that the samples were electrodeposited with the charge density of 20 mC/cm² and 25 mC/cm², respectively. The morphologies of the PPy patterns look like hills that stand perpendicularly to the substrate. The thickness of the PVA film at the bottom of a hole is the thinnest; the hill-like PPy micropattern only appears at the place with the hole locates. In order to confirm it, after electrodeposition, the electrode was dipped into boiling water, and was quickly taken out. The PPy micropatterns exist at the place where the pre-existing holes located as shown in Fig. 5. It is evident that in some areas of the electrode, the

PVA film was not washed away completely, but still reminded. With the two charge densities, the size of the hill at the bottom is about 300 nm and 500 nm, while the height is around 90 nm and 140 nm, respectively. It is obvious that the bottom size of the two hill-like patterns is smaller than the inner diameter of the hole; therefore, the hills are separated from each other. When the charge density increases to 30 mC/cm², the bottom size of each micropattern, as shown in Fig. 4c, is about 600 nm with 170 nm in height. Noticeably, rings with the thickness of ca. 100 nm appear around the hills, which change the morphology of the micropattern. The middle part of the hill is much smoother than the surrounding rings. It is easy to appreciate that the top of the hill arises from the polymerization in solution, while the ring from the polymerization in the PVA film. When the charge density reached 60 mC/cm², the morphology of the micropattern becomes volcano-like as shown in Fig. 4d. The bottom size of the volcano-like patterns increases to 760 nm, which nearly equals to the lattice spacing of the PVA hole array (Fig. 2c). The thickness of the ring grows up to about 200 nm, indicating that more pyrrole monomer polymerized in the PVA film with the increase of charge density. The rings formed around the hills, leading to the morphologies of patterns evolving from hill-like to volcano-like. The PPy microstructures almost connect with each other but still with obvious boundaries between them. When the charge density continues to increase, PPy formed a homogeneous film on the surface of ITO glass, leading to the disappearance of the pattern array.

3.3. Possible mechanism: the electrolyte swells the PVA film with an ordered array of holes

Based on the experimental results described in Figs. 1–5, a possible mechanism was proposed. Both the PVA pattern and PVA swelled capability in the acetonitrile electrolyte played a key role in the formation of the patterns with the morphological transition from hill-like to volcano-like, along the increase of the charge density during electrodeposition. When the working electrode was dipped into the acetonitrile solution consisting of pyrrole monomer and LiClO₄·3H₂O, the PVA film was swelled in acetonitrile solution, thus pyrrole monomer and electrolyte anions diffused into the film. The polymerization took place in the PVA film [21–23]. It is necessary to point out that when the surface of an ITO glass was spin-coated with a thin PS film instead of a PVA film, no PPy patterns were observed with similar electrodeposition. The PS film could not be swelled by acetonitrile; hence, the polymerization of pyrrole monomer did not take place.

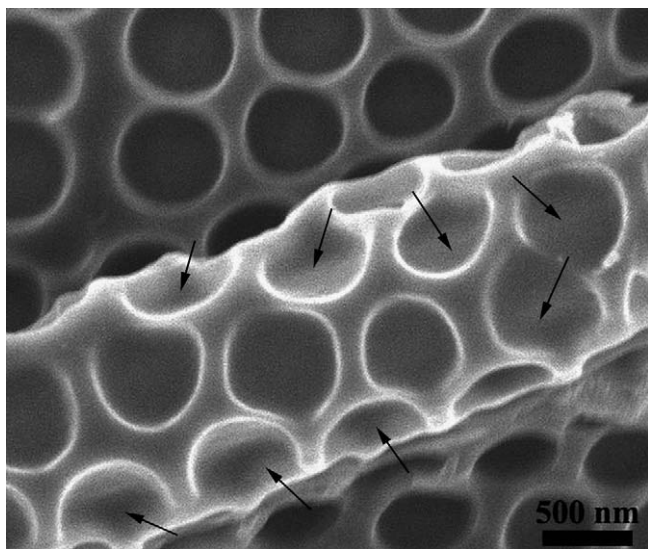


Fig. 3. SEM image of a curved porous PVA film. It is noticeable that the bottom area of holes is not open; thus, there is still a thin layer of the PVA film left (indicated by the arrows).

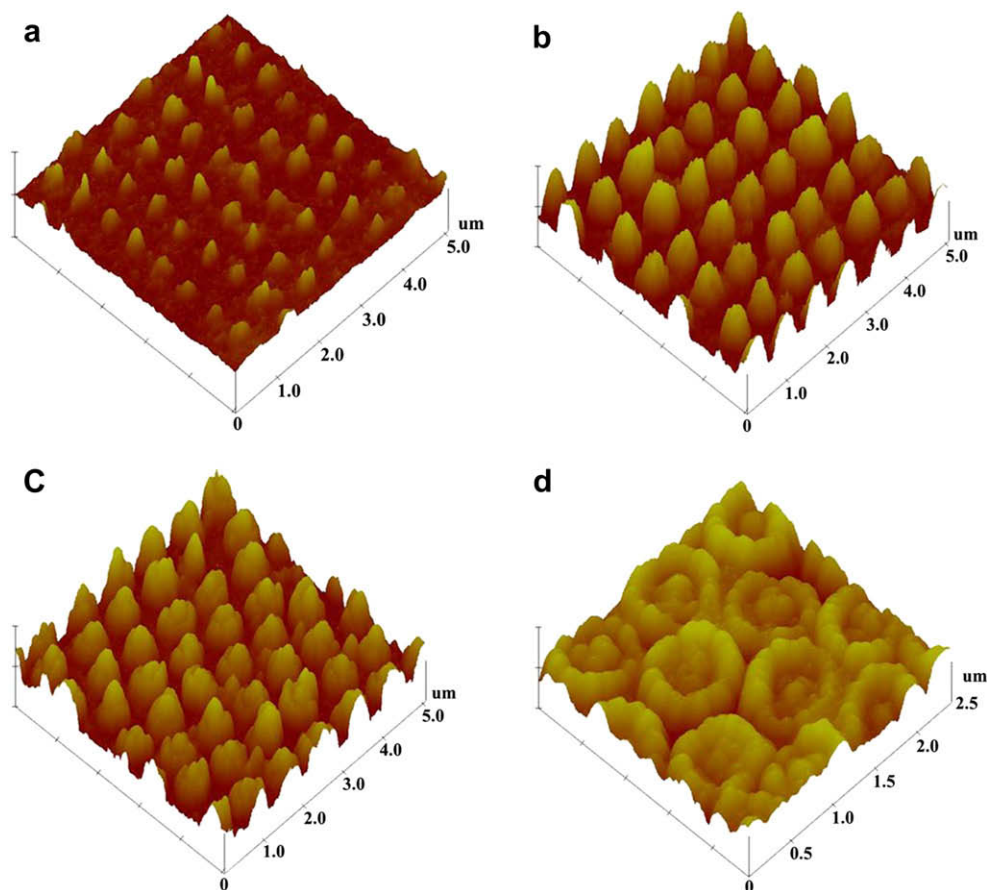


Fig. 4. AFM images of the PPy patterns which are electrodeposited with different charge densities: (a) 20 mC/cm², (b) 25 mC/cm², (c) 30 mC/cm² and (d) 60 mC/cm²; the morphologies of micropatterns evolve from hill to volcano. The z-scale is 200 nm in all the images.

Regarding our PVA patterns, the place where the holes located is the thinnest area of the PVA film; the polymerization took place and went on with much easier pyrrole monomer feeding. Thus, when the charge density was low, the hill-like micropattern was observed at the original hole place due to the fast accumulation of PPy. When the charge density was increased, more pyrrole monomer diffused

into the PVA film; therefore, the polymerization around the hill took place more efficiently, leading to the formation of the volcano-like morphology.

In order to prove the mechanism proposed, we fabricated an identical PDMS stamp but swelled by 50 wt% toluene in an acetone solution. Similar experiments were carried out to investigate the relationship between the lattice spacing of the template array together with the charge density and the formation of the PPy patterns with different morphologies. Fig. 6a and b shows the SEM images of the silica sphere pattern (a) and the corresponding porous PVA pattern (b) with the lattice spacing of 650 nm.

Fig. 6c displays the PPy pattern with a hill-like morphology obtained with a charge density of 16 mC/cm². The bottom size of the PPy microstructure is about 260 nm; thus, the hills are separated from each other. This charge density used is almost the same as that for Fig. 4a, because the polymerization only took place at the spots where holes located. The effect of the lattice spacing of the template array on the size of hill-like morphology was noticed. When the charge density was kept the same, the bottom size of hill-like morphology usually increased with the increase of the lattice spacing of the template array. When the charge density was fixed at 22 mC/cm², the bottom size of the hill-like PPy micropattern increased from 370 nm to 410 nm and to 430 nm, when the PDMS stamp was swelled by 0 wt%, 50 wt% and 100 wt% toluene solution, respectively. The reason may be related to the fact that the larger the lattice spacing, the less the area of holes and the more pyrrole monomer polymerization in the hole area.

In Fig. 6d, the PPy micropatterns with the volcano-like morphology connect with each other and are ready to form a continuous film;

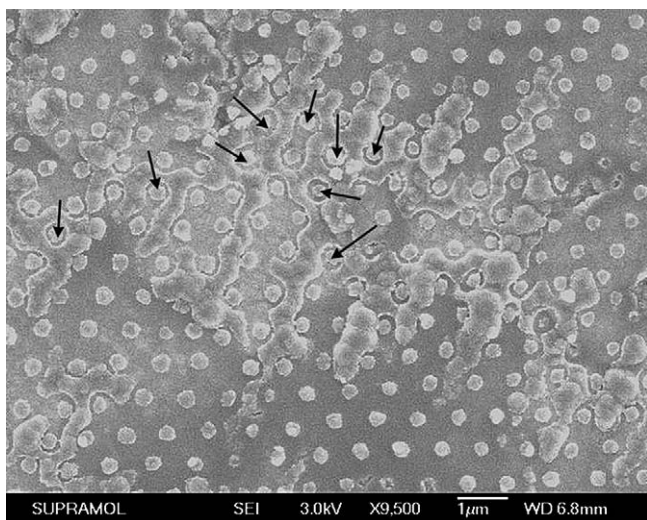


Fig. 5. SEM image of PPy micropattern existing at the place where the pre-existing holes located; examples are highlighted by black arrows.

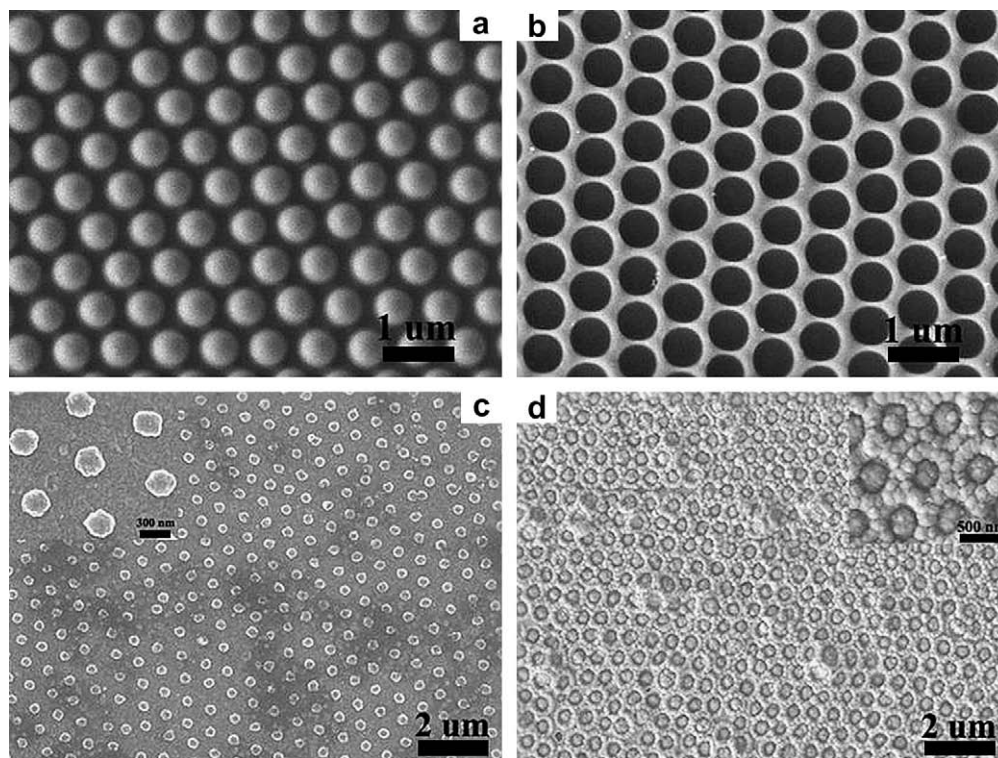


Fig. 6. SEM images of a silica array (a); a corresponding porous PVA array (b); a PPy pattern with the hill-like morphology (c) and a PPy pattern array with the volcano-like morphology (d). The two insets in Fig. 6c and 4d, with large magnification, demonstrate that both the lattice arrangement and lattice spacing of the PPy pattern are similar to those of the corresponding silica sphere array.

however, the charge density used for this morphology was dramatically reduced to 45 mC/cm^2 . Such difference of the charge density applied for the formation of the volcano-like microstructure shown in Figs. 4d and 6d was caused by the difference of the lattice spacing of the template presented in Figs. 2b and 6b. When the charge density was further increased to 60 mC/cm^2 , a continuous PPy film appeared with the disappearance of the PPy pattern array with volcano-like micropatterns.

4. Conclusion

An effective and reliable approach was developed for the preparation of unique PPy patterns with tunable morphologies including hill-like and volcano-like from one identical template. The various morphologies were achieved with different charge densities. The possible mechanism was investigated. The capability of swelling of a PVA film coated on the ITO glass, by the electrolyte, plays a vital role in the present engineering process. When the charge densities were kept the same, the size of the hill-like micropatterns increased with the increase of lattice spacing of the template array. The charge density needed for the formation of the volcano-like micropattern reduced with the decrease of the lattice spacing of the template array. Therefore, with the same charge density, the lattice spacing of the template array affects the formation of the hill-like and volcano-like morphologies. The synthetic strategy investigated here should be able to apply to make other interesting nanostructures of different conducting polymers, which may facilitate their potential applications in various areas such as microelectric devices, sensor arrays and microelectrodes.

Acknowledgments

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