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Electrosynthesis of poly(3,4-ethylenedioxythiophene) microcups in the aqueous solution of $LiClO_4$ and tri(ethylene glycol)

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Abstract

In this paper, we report a novel route for electrochemical growth of poly(3,4-ethylenedioxythiophene) (PEDOT) microcups with diameters in the range of 1–4 μm. In the process, 3,4-ethylenedioxythiophene (EDOT) was dispersed as microdroplets in the aqueous solution of $LiClO_4$ and tri(ethylene glycol) (TEG) by sonication. Then, the microdroplets were assembled on the indium tin oxide (ITO) glass electrode modified with multilayers poly(diallyldimethylammonium chloride) (PDDA) and poly(4-styrenesulfonic acid) (PSS), and polymerized into microcups. The well-ordered microcups stand on the working electrode surface in a density of about 10^6 units cm^{-2}.

Keywords: PEDOT; Electrochemical polymerization; Microcups

1. Introduction

Since poly(3,4-ethylenedioxythiophene) (PEDOT) was first synthesized in the early 1990s by Heywnag and Jonas [1], extensive work has been devoted to this polymer. This is mainly due to that PEDOT is one of the most successful conducting polymers for its excellent environmental stability, high conductivity and transparency in thin oxidized films [2–7]. On the other hand, micro- and nano-structured conducting polymeric materials have also attracted increasing attention [8–10], mainly due to their potential applications in catalysis, optics, drug delivery system, and microelectronics [11–15]. Nanowires and nanotubes of PEDOT also have been reported [16–19]. Recently, we used 'gas bubbles' as the soft templates for growing polypyrrole (PPy) microcontainers with diameters around 100 μm [20–23]. The unique conductive properties and the abundant structures of these microcontainers show that they have potential applications in encapsulations and the fabrication of sensors [24,25]. However, in these cases, the size of the microcontainers is about 100 μm and the fabrication of smaller microcontainers of about several micrometers in diameter is not possible by this technique.

In this paper, we report that PEDOT microcups with diameters in the range of 1–4 μm can be prepared by direct oxidation of EDOT at a modified multilayer polyelectrolyte ITO electrode in an aqueous solution of $LiClO_4$ and tri(ethylene glycol) (TEG). The microcups are generated through the use of a monomer droplet guided growth approach. The polyelectrolyte multilayers of poly(diallyldimethylammonium chloride) (PDDA) and poly(4-styrene sulfonic acid) (PSS) coatings on the working electrode can electrochemically catalyze the polymerization. This results in the formation of solid PEDOT layers around the droplets before they coalesce into a thin film.

2. Experimental

2.1. Chemicals

3,4-Ethylenedioxythiophene (EDOT) was purchased from Bayer AG (USA) and was used as received. Poly(4-styrenesulfonic acid) (PSS) and poly(diallyldimethylammonium chloride) (PDDA) with molar masses of 70,000 and 300,000 g, respectively, were purchased from Aldrich and also used directly. $LiClO_4$ (AR) was bought from Beijing Yili Fine Chem. Co. Ltd (Beijing, China). The ITO glass plates were purchased from Asahi Beer Optical, Ltd (Japan) and were used after being washed in acetone, ethanol and pure water with sonication and drying with nitrogen stream.

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2.2. Layer-by-layer deposition of polyelectrolytes on ITO electrode

The process of multilayer formation was as follows [26]: alternate dipping the ITO substrate in aqueous solutions of PDDA (1 mg mL^{-1}) and PSS (1 mg mL^{-1}) for 5 min, with intermediate water rinsing and N_2 drying. The dipping was repeated until the desired number of bilayers (each bilayer repeat unit consists of one PDDA layer and one PSS layer) was achieved.

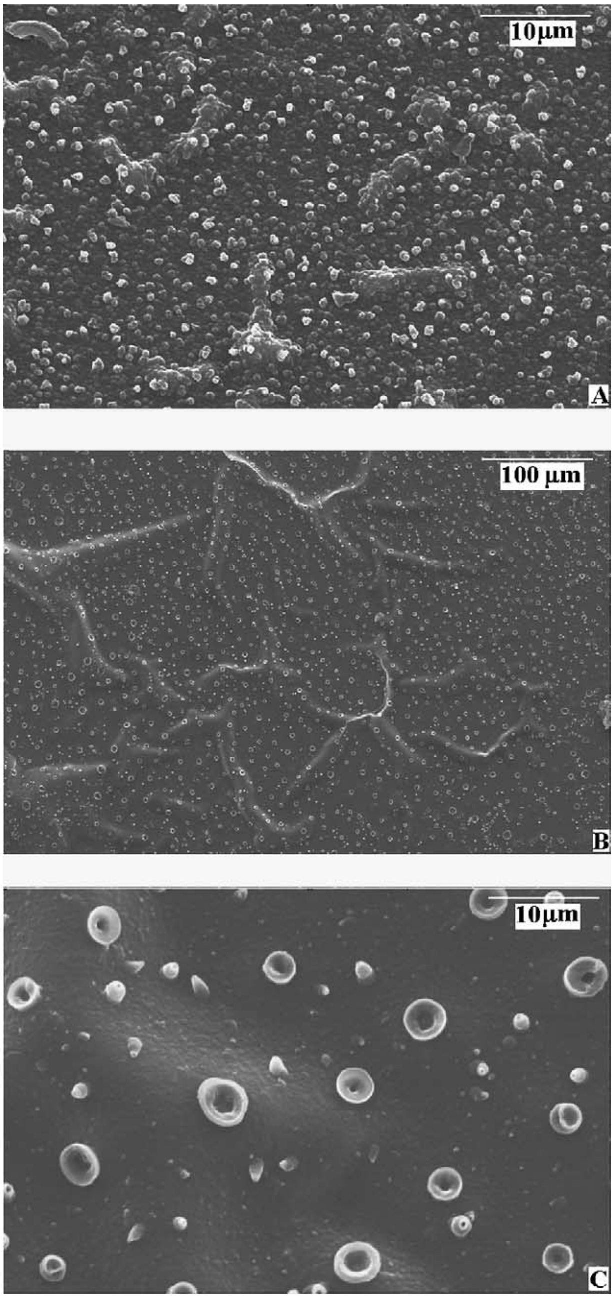

Fig. 1. SEM images of the PEDOT films formed on a bare (A) or a six bilayers PDDA/PSS modified ITO electrode (B) by electrolysis at a constant potential of 1.2 V for 300 s each in the aqueous solution of 9 mmol L^{-1} EDOT, 0.10 mol L^{-1} $LiClO_4$ and 0.68 mol L^{-1} TEG. (C) is a regional magnified view of pane B.

2.3. Electropolymerization

The growth of PEDOT microcups was carried out at room temperature in a one-compartment cell by the use of a model 283 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control. A stainless steel sheet (AISI 321) with an area of 0.5 cm × 3.0 cm was used as the counter-electrode, the polyelectrolyte modified ITO was used as the working electrode. The working and counter electrodes were placed 0.5 cm apart. All potentials were referred to Ag/AgCl. The typical electrolyte was an aqueous solution of 9 mmol L^{-1} EDOT, 0.10 mol L^{-1} $LiClO_4$ and 0.68 mol L^{-1} tri(ethylene glycol). Before each experiment, the electrolyte was sonicated in a water bath for 5 min to disperse the monomer as small drops. The electrolyte was deoxygenated by bubbling dry nitrogen gas.

2.4. Characterizations

The morphology of the microstructures was studied using a KYKY2800 scanning electron microscope (Beijing Scientific Instrument Co.) after sputter-coating with thin gold layers. Raman spectra were recorded by using a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, England) employing a 633-nm laser beam at 0.1 mW and a CCD detector with 4 cm^{-1} resolution. The spectrum was accumulated three times for 30 s each. A polarized optical microscope model BH-2 (Olympus, Japan) was used to watch the shape and size of EDOT drops disperse in the solution of 9 mmol L^{-1} EDOT, 0.1 mol L^{-1} $LiClO_4$ and 0.68 mol L^{-1} tri(ethylene glycol) after sonication for 5 min. Water contact angles were measured using a contact angle system, OCA 20, made by Dataphysics Instruments GmbH (Germany); the size of water droplet was 4 μL.

3. Results and discussion

Fig. 1 shows the scanning electron micrographs (SEM) of the PEDOT microcups prepared by electrochemical oxidation of 9 mmol L^{-1} EDOT in the aqueous solution of 0.10 mol L^{-1} $LiClO_4$ and 0.68 mol L^{-1} TEG at a constant potential of 1.20 V for 300 s. As can be seen from Fig. 1(A), a PEDOT film composed of particles was formed on the bare ITO electrode. Its morphology is similar to that of the electrosynthesized

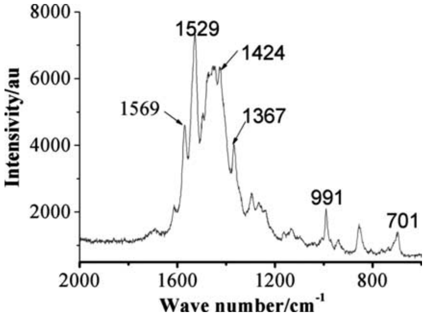

Fig. 2. Microscopic Raman spectrum of a PEDOT microcup.

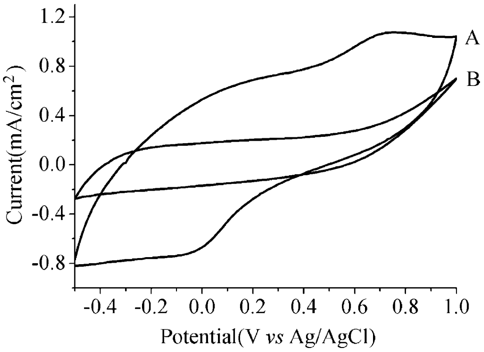

Fig. 3. Cyclic voltammograms of the PEDOT film with (A) or without microcups in an aqueous solution of 0.1 mol L^{-1} $LiClO_4$ at a potential scan rate of 50 mV s^{-1}. The PEDOT films with and without microcups were grown for 0.9 C cm^{-2} each under the conditions the same to those of Fig. 1(A) and (B), respectively.

PEDOT films reported previously [27,28]. However, on an ITO electrode modified by six bilayers of PDDA/PSS, a PEDOT film with many microcups was generated (Fig. 1(B) and (C)). Most of the microcups have opened mouths and their diameters are in the range of 1–4 μm. The number density of the microcups (including the small sized microcups with diameters around 1 μm) was calculated to be approximately 10^6 units cm^{-2} according to Fig. 1(C). The walls of microcups were made of PEDOT as confirmed by using confocal microscopic Raman spectroscopy. Fig. 2 is a 633-nm excited Raman spectrum recorded by focusing the laser spot on a microcup. The spectrum exhibits typical bands of PEDOT at 1569, 1529, 1424, 1367, 991, 701 cm^{-1}, respectively, [29].

The cyclic voltammogram of the PEDOT film with microcups (Fig. 3(A)) showed a couple of strong and broad redox waves in the potential range of −0.5 to 1.0 V. Their wave currents were much stronger than those of the normal film deposited on bare ITO glass (Fig. 3(B)). This is mainly due to the fact that the surface area of the PEDOT film with microcups is much larger than that of a normal film, which resulted in much higher film/electrolyte double-layer capacitive charges.

The microcup growth process was studied by SEM images recorded during electrochemical polymerization. As shown in pane A of Fig. 4, at the initial stage of electrochemical deposition (60 s), a few microcups were formed and located sparsely on the electrode surface (pane A). The number of microcups increased with the increase of deposition time and it reached maximum as the deposition time increased to 180 s (pane B). In this case, the microcups located densely and covered the whole surface of the working electrode. Simultaneously, the thickness of the microcups also increased with the deposition time. At 1800 s (pane C), some of the microcups' mouths were sealed and at 3600 s, most microcups were changed into microballs (pane D).

The concentration of TEG in the electrolyte affects strongly on the morphology of the microcups. In the system without TEG, few microcup can be produced (Fig. 5(A)). It was found

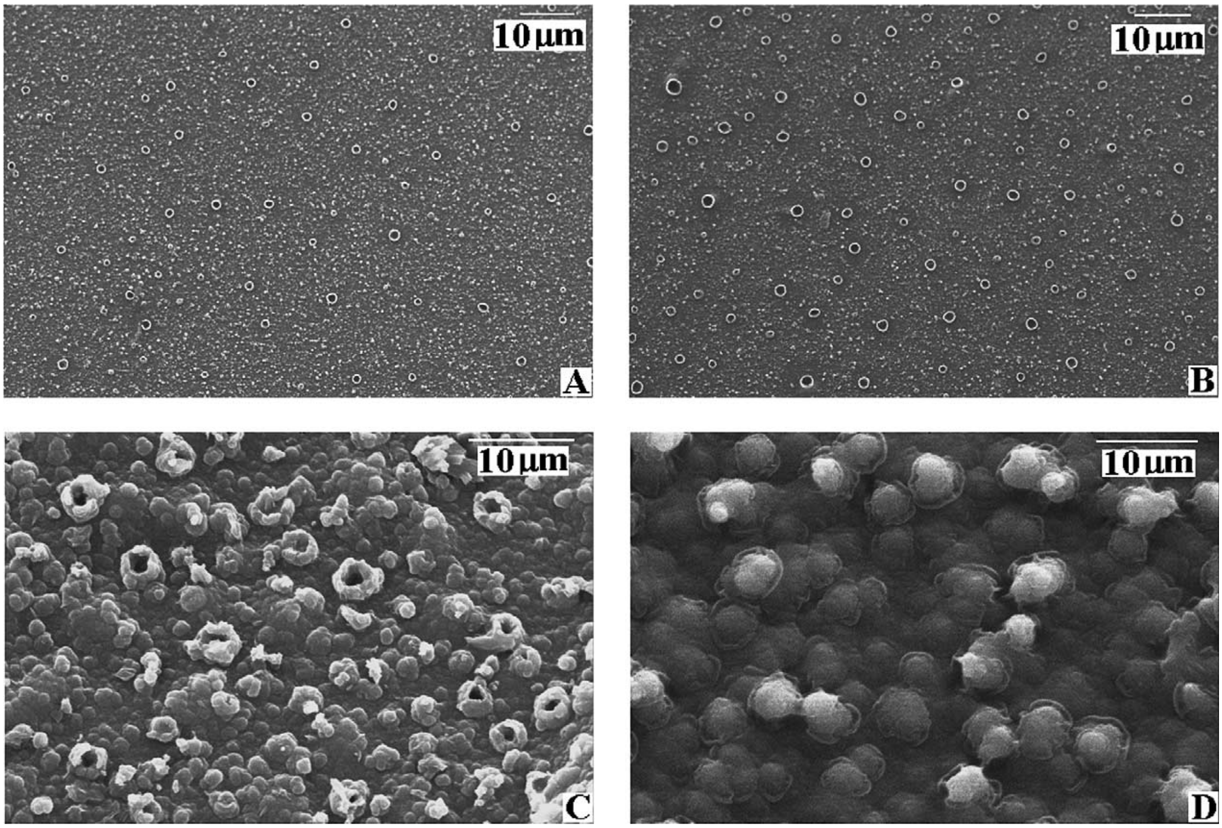

Fig. 4. SEM images of the PEDOT deposited on a ITO electrode modified with six bilayers of PDDA/PSS at 1.2 V for 60 s (A), 180 s (B), 1800 s (C) and 3600 s (D). The other conditions are the same to Fig. 1.

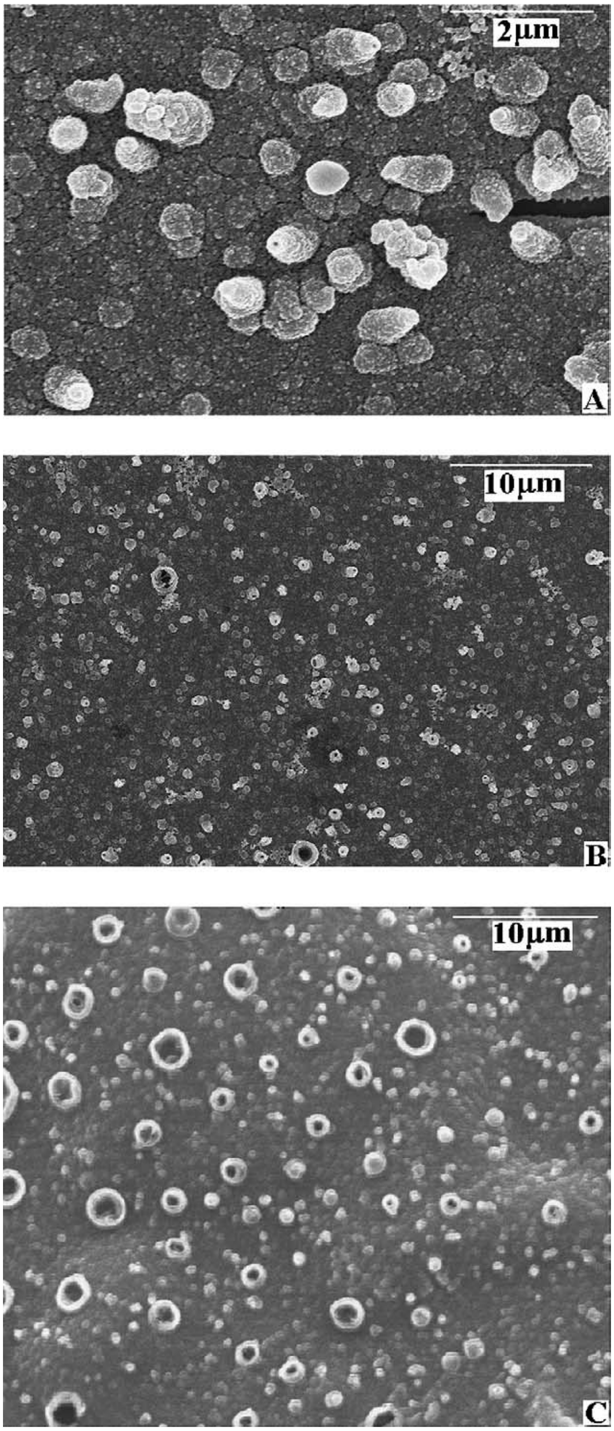

Fig. 5. SEM images of the PEDOT microcups formed on an ITO electrode modified with six bilayers of PDDA/PSS from the electrolyte contained 0 (A), 0.36 (B) or 1.25 (C) mol L^{-1} TEG. The other conditions are the same to Fig. 1.

that the solubility of EDOT in water was fairly low, the monomer was found to deposit to the bottom of the electrochemical cell during the process of electrochemical polymerization. The increase of TEG concentration resulted in the increase of the number and size of the microcups (Fig. 5(A)–(C)). The optimum concentration of TEG for growing unform microcups in high number density was tested to be around 0.68 mol L^{-1} as shown in Fig. 1. TEG was used as a dispersion agent of EDOT to increase the stability of the monomer droplets in the aqueous media [30]. Transmission polarized optical microscopy image also demonstrated that the monomer was dispersed in the electrolyte as droplets with diameters smaller than 4 μm (SI, Fig. S1). Their sizes are comparable to those of the microcups. These results imply that the microcups were formed through a droplet template guided growth route.

The morphology of the microcups also depends on the concentration of EDOT (C_{EDOT}). The microcups with opened mouths and uniform sizes were formed in the media with low EDOT concentration of 9 mmol L^{-1} as shown in Fig. 1. As C_{EDOT} was increased up to 18 mmol L^{-1}, the sizes of the microcups were decreased dramatically from 1 to 4 μm to about 500 nm (Fig. 6(A)). Further increase C_{EDOT} to 27 mmol L^{-1}, almost all the mouths of the cups were sealed (Fig. 6(B)). This is mainly due to the increase of monomer concentration accelerated the polymerization rate and also shortened the electrolysis time for sealing the microcups. The contact angle of a clean ITO electrode surface was measured to be about 69°, a little higher than that of a six multilayer polyelectrolyte coated ITO electrode surface (50°). The normal PEDOT film prepared by electrolysis of 9 mmol L^{-1} EDOT in the aqueous solution of 0.1 mol L^{-1} $LiClO_4$ showed a contact angle of about 45° (SI, Fig. S2A). However, the contact angle of the film deposited on the modified electrode from a medium

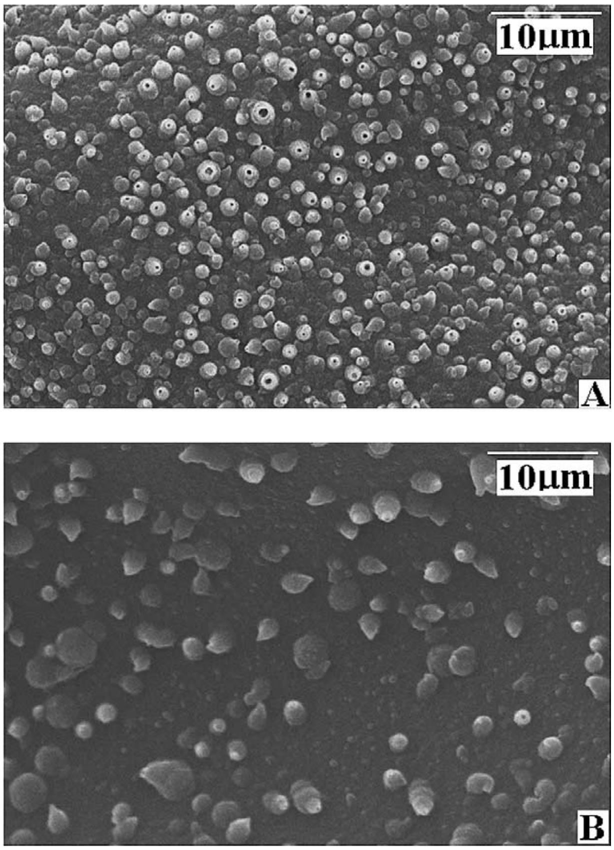

Fig. 6. SEM images of the PEDOT deposited on an ITO electrode modified with six bilayers of PDDA/PSS in the media contained 18 (A) or 27 (B) mmol L^{-1} EDOT. The other conditions are the same to Fig. 1.

without TEG (as shown in Fig. 5(A)) was decrease to be around 20° (SI, Fig. S2B). However, on the surface shown in Fig. 6(A), a water droplet of 4 μL spread out quickly within 2 s, the contact angle of the surface was measured to be close to 0° (SI, Fig. S2C). This is mainly due to the capillary effect of the microcups enhanced the hydrophilic property of the surface. Therefore, this technique developed a super-hydrophilic surface of conducting polymer.

The microcups of PEDOT were formed through a self-assembled monomer droplet template guided growth route as described above. In a neutral electrolyte, the organic monomer is insoluble and can be dispersed as droplets with diameters of several micrometers, and the droplets can be stabilized by TEG. During the process of electropolymerization, the microdroplets assembled onto the surface of working electrode. Because of the insolubility of EDOT, only the outmost layers of the droplets contacted to the electrolyte could be polymerized. After drying their contained monomer, PEDOT microcups were observed. The polymerization started from the domains of droplets in contacted with the electrode surfaces and extended uprightly. With the increase of polymerization time, the thickness and height of the PEDOT cups increased and finally the mouths of the cups were sealed.

The multilayer polyelectrolyte coating on the ITO electrode is also crucial for the formation of PEOT microcups. Fig. 7 illustrates the polarization curves of 9 mmol L^{-1} EDOT in an aqueous solution of 0.10 mol L^{-1} $LiClO_4$ and 0.68 mol L^{-1} TEG at a bare (A) or a six bilayer PDDA/PSS modified ITO electrode (B), respectively. It is clear from this figure that the oxidation potential of the monomer at the electrode with polyelectrolyte coating (B) is lower than those at a bare electrode (A). Furthermore, at a given applied potential (e.g. 0.8 V), the polymerization current densities on curve B is also much higher than those on curve A. This is mainly due to that the PSS layers of the polyelectrolyte coating acted as the dopants of the resulting polymer and electrochemically catalyzed the polymerization.

The anodic polarization curve of 9 mmol L^{-1} EDOT at a platinum electrode in the aqueous solution of 0.10 mol L^{-1} $LiClO_4$ + 0.68 mol L^{-1} TEG + 0.10 mol L^{-1} PSS indicates the oxidation potential of the monomer is about 0.69 V (Fig. 8(A)). This value is close to that measured in the medium of 0.68 mol L^{-1} TEG + 0.10 mol L^{-1} PSS (Fig. 8(B)), however, which is much lower than that measured in the solution of 0.68 mol L^{-1} TEG + 0.10 mol L^{-1} $LiClO_4$ (0.75 V, Fig. 8(C)). Furthermore, at a given applied potential (e.g. 0.8 V), the polymerization current densities on curves A and B are also much higher than those on curve C. These results also confirm that PSS can electrochemically catalyze the polymerization of EDOT.

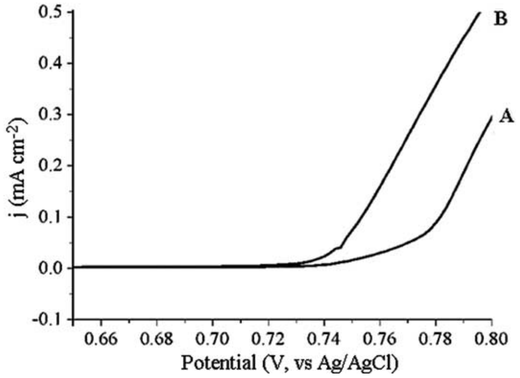

Fig. 7. Anodic polarization curves of 9 mmol L^{-1} EDOT at a bare ITO (A) and the ITO electrode modified with six bilayers of PDD/PSS (B) in the aqueous solution of 0.10 mol L^{-1} $LiClO_4$ and 0.68 mol L^{-1} TEG. Potential scan rate = 50 mV s^{-1}.

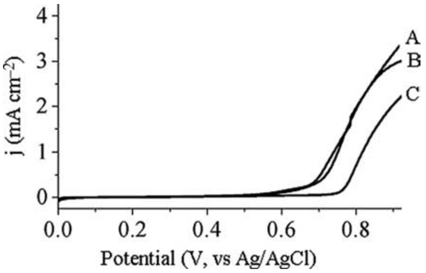

Fig. 8. Anodic polarization curves of 9 mmol L^{-1} EDOT at a platinum electrode in the aqueous solutions of 0.68 mol L^{-1} TEG + 0.10 mol L^{-1} $LiClO_4$ + 0.10 mol L^{-1} PSS (A), 0.68 mol L^{-1} TEG + 0.10 mol L^{-1} PSS (B) and 0.68 mol L^{-1} TEG + 0.10 mol L^{-1} $LiClO_4$ (C), respectively. Potential scan rate = 50 mV s^{-1}.

On a bare ITO electrode, the microdroplets on the electrode surface coalesced into a monomer film before forming PEDOT cups because of a low polymerization rate. In contrast, the polymerization rate at a polyelectrolyte modified electrode is high enough to form PEDOT cups before droplet coalescence. If the aqueous electrolyte solution was replaced by a viscous ionic liquid solution, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]), PEDOT microcups also can be grown on a bare ITO electrode (Fig. S3). This is mainly due to the high viscosity of ionic liquid reduced the diffusion rate of monomer microdroplets and also decreased the droplet number assembled on the electrode surface at the same time. This resulted in decreasing the possibility of monomer droplet coalescence on the electrode surface during the polymerization. A very thin polyelectrolyte film supports the formation of PEDOT film, possibly due to the coating is too porous to prevent the coalescence of monomer droplets. However, a very thick polyelectrolyte coating reduces the amounts of microcups. This is mainly due to that the thickness increase of polyelectrolyte coating also increases the resistance of the electrode and lowering the polymerization rate. A film of six bilayers of PSS/PDDA was tested to be the most suitable coating for generation PEDOT microcontainers in high number density. The observations described above strongly supported that the microcups were formed through a droplet template guided growth route proposed above.

4. Conclusions

We described a method for the fabrication of PEDOT microcups by combination LBL technique and electrochemical deposition. The PEDOT microcups with diameters in the range of 1–4 μm were generated by direct oxidation of EDOT in the aqueous solution of $LiClO_4$ and tri (ethylene glycol) on the ITO electrode with a PSS/PDDA multilayer coating. They were arranged upright on the working electrode surface in a density of 10^6 units cm^{-2}. The technology developed by this study can be extended to synthesize other conducting polymers such as polypyrrole (to be reported elsewhere) with similar microstructures.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2006.05.021.

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