

Electrochemical synthesis of PEDOT and PPP macroporous films and nanowire architectures from ionic liquids

Timo Carstens · Alexandra Prowald ·
Sherif Zein El Abedin · Frank Endres

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Abstract We report on the electrochemical synthesis of macroporous films and on nanowire architectures of conducting polymers from ionic liquids. The electrodeposition of poly(3,4-ethylenedioxythiophene) (PEDOT) and of poly(*para*-phenylene) (PPP) from the air and water stable ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)amide ([EMIm]TFSA) and from 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([HMIm]FAP) within the voids of a polystyrene opal structure on gold and on platinum substrates yield macroporous films. For this purpose, polystyrene spheres with an average diameter of about 600 nm were applied onto the employed electrodes by a simple dipping process resulting in a layer thickness of about 10 μm . The macroporous films turn into yellow, orange, blue, and green colors owing to the Bragg reflection of the incident artificial white light. PPP and PEDOT nanowires were electrochemically prepared in a track-etched polycarbonate (PC) membrane with an average pore diameter of 90 nm. One side of the membrane was sputtered with a thin gold film to serve as a working electrode. Electrodeposition occurs along the pores of the template. Nanowires with an average diameter of 90 nm and a length of up to 17 μm can be easily synthesized by this electrochemical template-assisted method. Such materials

are of interest as catalyst in metal/air batteries and as cathode material in, e.g., microbatteries.

Introduction

Conducting polymers are used in numerous fields like, e.g., supercapacitors [1], light-emitting diodes [2, 3], electrochromic displays [4], energy conversion and storage [5, 6], sensors [7, 8], and catalysis [9, 10] to mention a few. A great deal of attention has been dedicated to poly(3,4-ethylenedioxythiophene) (PEDOT) because of its high electronic conductivity and its good chemical resistance in the oxidized state. Further advantages are the low oxidation potential of the monomer and the relatively well-ordered structure of the polymer layers resulting from polymerization. This is attributed to the fact that in the monomer 3,4-ethylenedioxythiophene (EDOT), the 3 and 4 positions of the thiophene ring are blocked; thus, cross-linking reactions are effectively prevented [11]. Conducting polymers like PEDOT are known as catalyst for oxygen reduction [12] and interesting as gas diffusion electrodes in metal/air batteries. Furthermore, 3D-structured electrodes such as nanowire architectures and macroporous films ensure large energy density. The charge capacity of PEDOT as a possible cathode material in batteries was given as almost 700 mAh/g [13].

The conducting polymer poly(*para*-phenylene) (PPP) is of particular interest due to its high air stability even at high temperatures and due to its ability to emit light in the visible region [14–16]. Therefore, it was discussed as a material not only for the fabrication of, e.g., blue polymer light-emitting diodes in the past [14, 17, 18] but also for secondary batteries [19] and electrochemical actuators [20]. If made and cycled electrochemically in ionic liquids, both the cation and the anion take part in the charge compensation during electrochemical oxidation and reduction [21]. We showed recently that template-assisted electrochemical synthesis in ionic liquids is

T. Carstens · A. Prowald · S. Zein El Abedin · F. Endres (✉)
Institute of Particle Technology,
Clausthal University of Technology,
38678 Clausthal-Zellerfeld, Germany
e-mail: frank.endres@tu-clausthal.de

T. Carstens · A. Prowald
Energy Research Centre of Lower Saxony (EFZN),
38640 Goslar, Germany

S. Zein El Abedin
Electrochemistry and Corrosion Laboratory,
National Research Centre,
Dokki,
Cairo, Egypt

a feasible method for the synthesis of nanostructured materials such as Si, Ge, $\text{Si}_x\text{Ge}_{1-x}$, Ag, and Al nanowires [22–25] and of highly ordered macroporous films of Ge, $\text{Si}_x\text{Ge}_{1-x}$, Al, Li, and PPP [26–30]. For an overview on template electrodeposition, we refer to [31]. In an earlier paper, we could show the initial steps of PEDOT polymerization with the STM [32]. The deposition of PEDOT on Au(111) starts well below the potential of the bulk deposition observed in the cyclic voltammograms. The observation of nucleation corresponds to a type of an underpotential deposition as it is well known for metal deposition. Such a type of an underpotential deposition was also observed for the electrochemical polymerization of benzene to poly(*para*-phenylene) [33]. Due to their wide electrochemical windows in the anodic regime together with extremely low vapor pressures (10^{-11} – 10^{-10} mbar) around room temperature, ionic liquids are interesting solvents for the electropolymerization of organic molecules. Especially PPP could be an interesting cathode material for batteries. The main focus of the present paper is the synthesis of templated conducting polymer structures.

Experimental methods

The ionic liquid 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([HMIm]FAP) was purchased in a custom made quality from Merck KGaA. All impurities are guaranteed by the supplier to be below 10 ppm. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm]TFSA) was purchased in the highest available quality from Iolitec. The ionic liquids were used after drying under vacuum at 100 °C to a water content of below 1 ppm. Benzene (>99.5 %, FLUKA) and EDOT (>98.0 %, TCI Europe) were used as delivered. The track-etched polycarbonate (PC) membranes were purchased from Ion Track Technology for Innovative Products (IT4IP, Belgium). The thickness of the

membranes is 21 μm with an average pore diameter of 90 nm and a pore density of 10^9 cm^{-2} . One side of the membrane was sputtered with a $\sim 125\text{-nm}$ thick film of gold and stabilized with more gold deposited electrochemically on the sputtered gold layer to be used as a working electrode during the electrochemical synthesis for this fundamental study. The electrodeposition of PEDOT and PPP from the air and water stable ionic liquids [EMIm]TFSA and [HMIm]FAP within the voids of a polystyrene opal structure on gold and on platinum substrates yield macroporous films. For this purpose, polystyrene spheres with an average diameter of about 600 nm (Thermo Scientific, USA) were applied onto the employed electrodes by a simple dipping process resulting in a layer thickness of about 10 μm . After deposition, the PS template was removed by tetrahydrofuran (THF). The electrochemical cell was made of polytetrafluoroethylene (Teflon) and clamped onto the template with a Teflon-covered O-ring (Viton), yielding a geometric surface area of 0.6 cm^2 . A platinum ring was used as a counter electrode, and a Pt wire was used as a quasi-reference electrode. Its electrode potential was calibrated vs. ferrocene/ferrocinium and reveals sufficient stability during the experiment. The redox couple ferrocene/ferrocinium has a value of $550 \pm 50 \text{ mV}$ vs. the Pt quasi-reference electrode [34]. The electrochemical measurements were performed by using a Parstat 2263 (Princeton Applied Research) potentiostat/galvanostat controlled by PowerSuite software. For analysis of the obtained polymer films, SEM experiments were performed (Carl Zeiss DSM 982 Gemini).

Results and discussion

The air and water stable ionic liquids [HMIm]FAP and [EMIm]TFSA allow the electrochemical polymerization of conducting polymers at room temperature under very mild conditions. A track-etched PC membrane and polystyrene

Fig. 1 Ten successive cyclic voltammograms of the potentiodynamic polymerization of 0.2 mol l^{-1} EDOT to PEDOT in [EMIm]TFSA on gold at room temperature. Scan rate, 10 mV s^{-1}

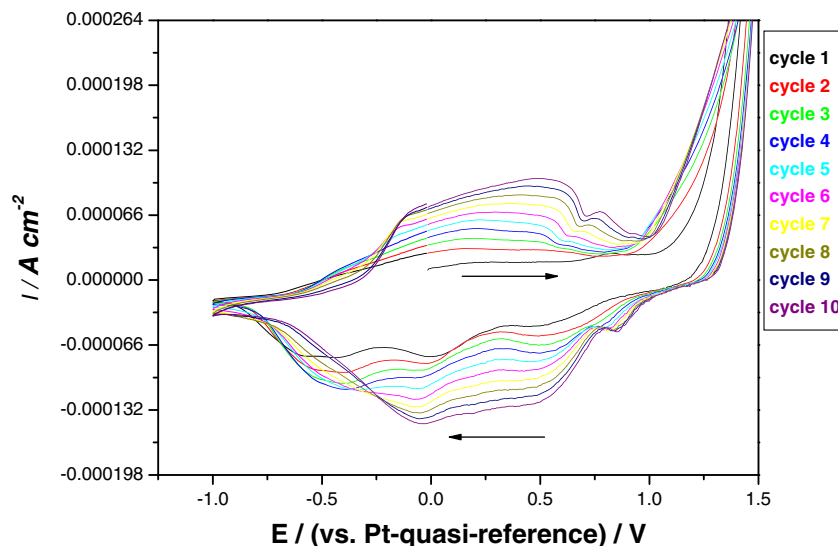
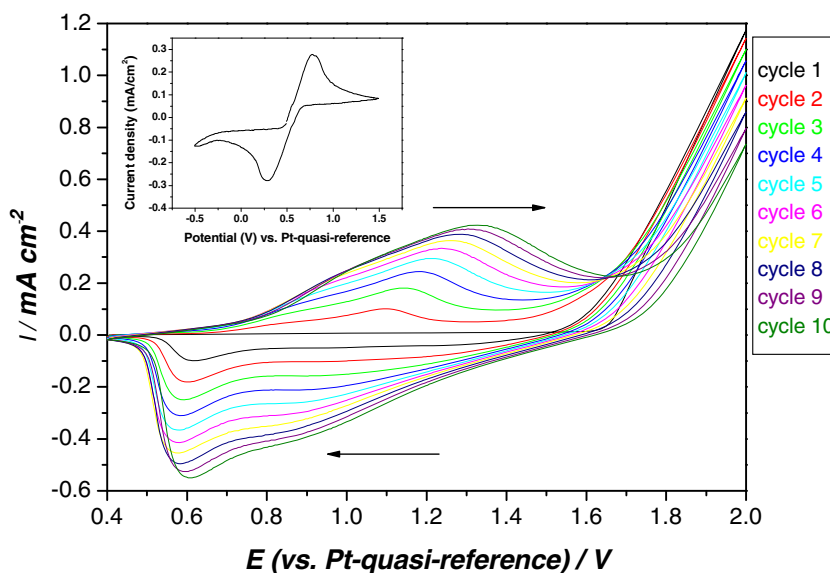


Fig. 2 Ten successive cyclic voltammograms of the potentiodynamic polymerization of 0.2 mol l^{-1} benzene in [HMIm]FAP on platinum at room temperature. Scan rate, 10 mV s^{-1} *Inset:* Cyclic voltammogram of ferrocene (0.1 mol l^{-1}) in [HMIm]FAP. Scan rate of each cycle, 10 mV s^{-1} . The redox couple ferrocene/ferrocinium has a value of $550 \pm 50 \text{ mV}$ vs. the Pt quasi-reference electrode



opal structures are simple and efficient templates for the preparation of highly ordered three-dimensional macroporous films and of nanowire architectures of PPP and PEDOT.

The electrochemical polymerization (Fig. 1) at room temperature of 0.2 mol l^{-1} EDOT in [EMIm]TFSA starts at around 1.1 V vs. Pt quasi-reference-electrode. As already mentioned in the experimental section, the Pt quasi-reference electrode potential was sufficiently stable in the course of the experiments. On the back scan (black cycle), three reduction waves at 0.5 , 0.0 , and -0.5 V can be observed. The second cycle and the following ones reveal a wide oxidation wave between -0.2 and 0.6 V and a small one at 0.8 V . The observed reduction process is represented by a wide oxidation wave between 0.6 and -0.2 V and by a

small peak preceding the wave at 0.8 V . The numerous processes can be explained with the postulated structure or morphology of the PEDOT film which contains two types of coexisting zones: a compact and an open structure [35]. So far, EDOT shows the usual polymerization behavior in the employed ionic liquid.

Figure 2 shows 10 successive cyclic voltammograms of the potentiodynamic polymerization of 0.2 mol l^{-1} benzene in the ionic liquid [HMIm]FAP on platinum at room temperature. The ionic liquid [HMIm]FAP was chosen in this study because of the high stability of the FAP anion towards oxidation allowing the oxidative polymerization of benzene without any undesirable side reactions of the ionic liquid at the cathode. In the anodic scan of the first cycle, an anodic current starts to rise at an electrode potential of 1.65 V vs.

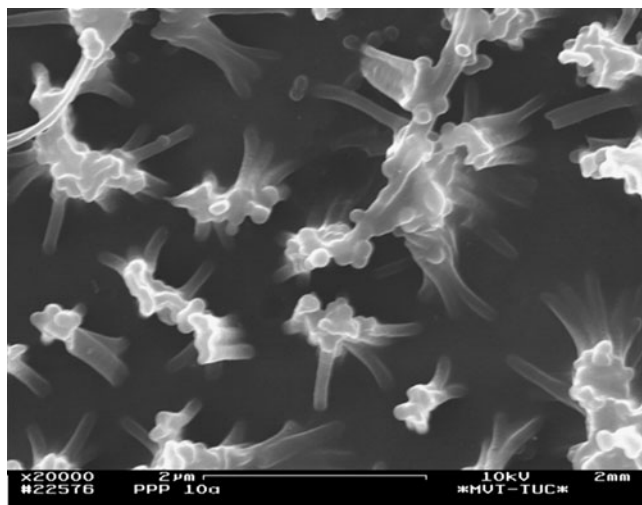


Fig. 3 A top view SEM micrograph of poly(*para*-phenylene) nanowire arrays obtained at a potential of 2.2 V vs. Pt quasi-reference for 45 min . After chemical dissolution of the membrane, vertically aligned PPP nanowire bunches were obtained

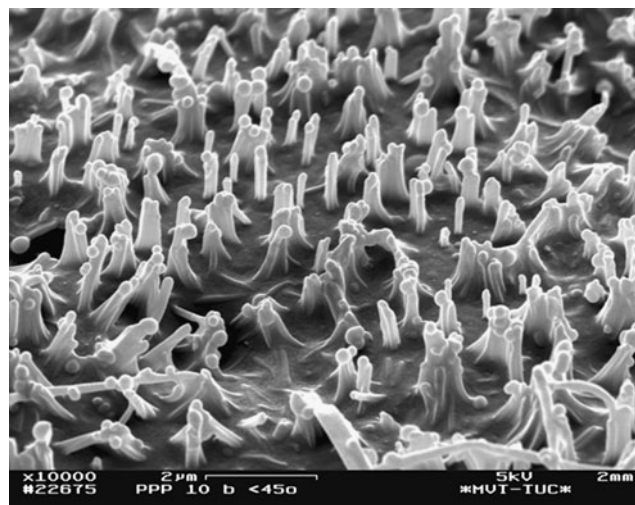
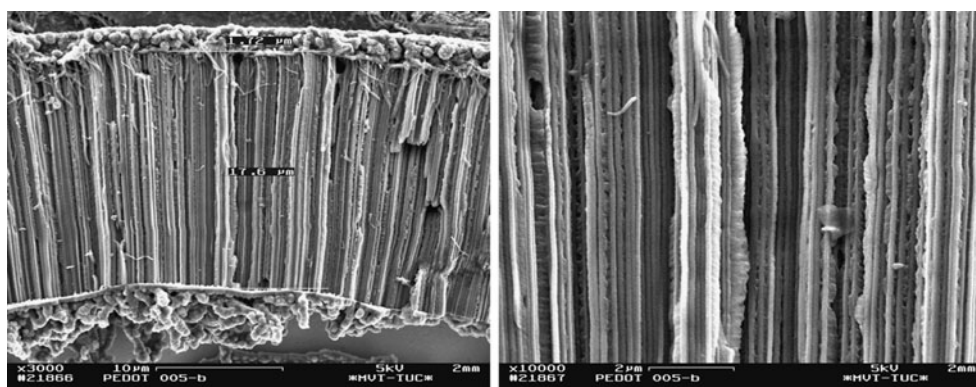


Fig. 4 A 45° view SEM micrograph of self-standing electrochemically prepared poly(*para*-phenylene) nanowires on the supporting gold layer obtained at an applied potential of 2.2 V vs. Pt quasi-reference for 45 min

Fig. 5 SEM micrographs of PEDOT nanowires after the removal of the polycarbonate membrane obtained in 10 successive voltammograms within the limits of -0.2 and 1.8 V on gold. Scan rate, 10 mV s^{-1}



the Pt quasi-reference electrode. The current rises strongly, indicating the polymerization of benzene. In the back scan, a reduction process at an electrode potential of 0.6 V is observed. In the second anodic cycle, an oxidation peak at an electrode potential of 1.1 V is recorded indicating the quasi-reversible behavior of the deposited film. With successive cycles, both anodic and cathodic currents increase as a result of the increasing thickness of the polymer film. After the first cycle, a yellowish film is clearly seen on the platinum working electrode. Then, the color changes from yellowish to brownish, and already after the third cycle, a black polymer film is obtained. Comparison of Figs. 1 and 2 shows that the electropolymerization of benzene to PPP seems to lead to a more uniform material than the one of EDOT to PEDOT.

Conducting polymer nanowires were electrochemically prepared in a track-etched PC membrane with an average diameter of 90 nm. A supporting gold film was deposited electrochemically on the sputtered gold layer to stabilize the working electrode. This is necessary in order to stabilize the polymer nanostructure after removing of the PC membrane with dichloromethane. Figure 3 is a top view of PPP nanowires prepared at a potential of 2.2 V vs. the Pt quasi-reference electrode for 45 min and after removal of the PC membrane by chemical dissolution in dichloromethane. This electrode potential delivered the best growth conditions in

this experiment. Vertically aligned poly(*para*-phenylene) nanowire arrays with bunch-like structures are obtained. The bottoms of the wires are well separated from each other, while the tops stick together to form shrub-like bunches. The PPP nanowire array shows a good connection to the supporting gold layer. The nanowire arrays only become less bunched at the edges of the electrode (Fig. 4). At the edges of the arrays besides bunch-like structures, single self-standing and isolated PPP nanowires in the micrometer regime can be obtained. Figure 4 is a 45° view of the sample after removal of the PC membrane by chemical dissolution in dichloromethane.

Figure 5 shows SEM micrographs of PEDOT nanowire structures obtained in 10 successive voltammograms within the limits of -0.2 and 1.8 V on gold at a scan rate of 10 mV s^{-1} . This electrode potential range delivered the best growth conditions in this experiment. The cyclic electro-polymerization of EDOT in [EMIm]TFSA leads to a complete filling of the pores of the membrane with the same concentration of the monomer and to the formation of a rough layer containing coarse PEDOT (upper part of Fig. 5) particles on the other side of the membrane, at too long deposition times. Nanowires with an average diameter of 90 nm and a length of up to $17 \mu\text{m}$ can be easily synthesized by this electrochemical template-assisted method, and the length is obviously only limited by the thickness

Fig. 6 SEM micrographs of macroporous PPP on platinum after the removal of the polystyrene template. Applied potential = 2.0 V for 30 min

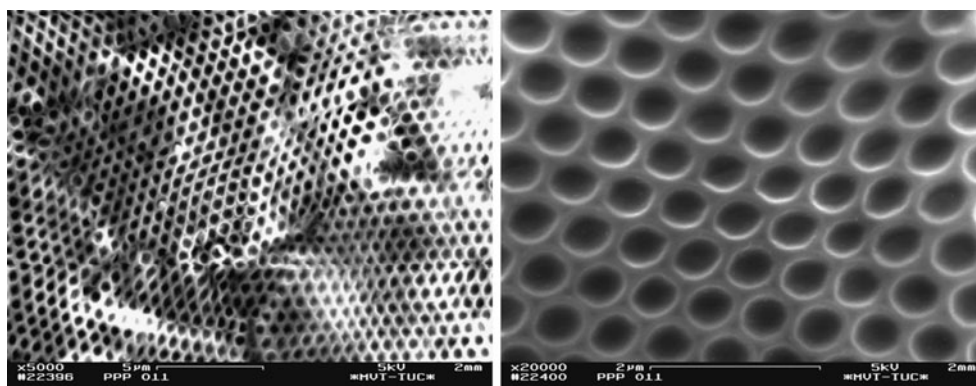
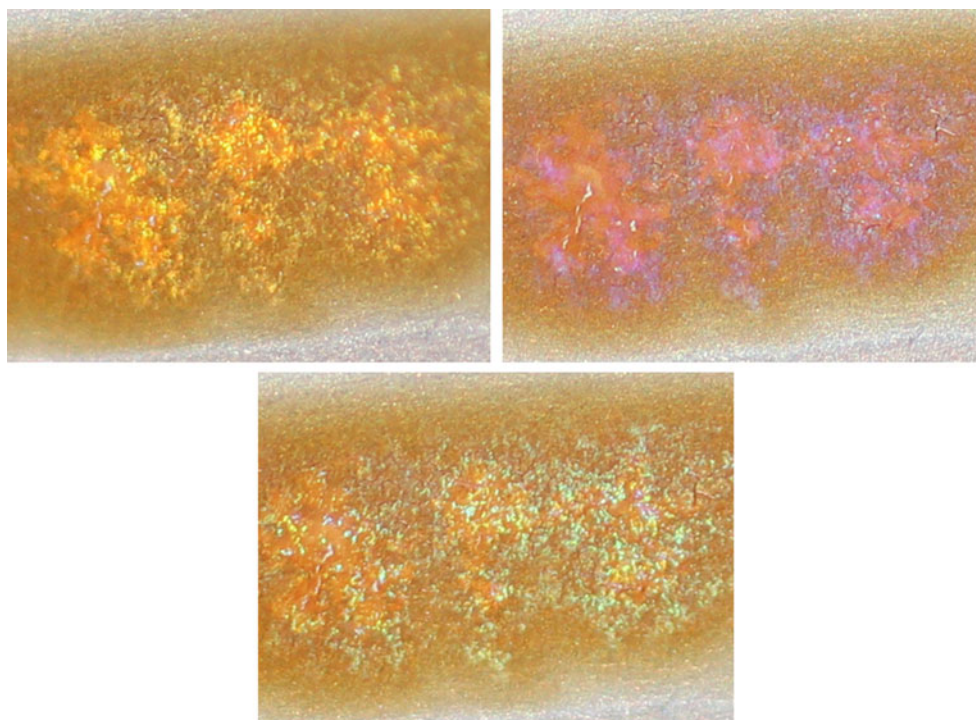


Fig. 7 Photographs of the macroporous PPP film deposited on platinum at different angles of incident light



of the membrane and the available monomer. Those PEDOT nanowires could be of interest for the application as actuators. Nanomaterials of conjugated polymers are found to have superior performance relative to conventional materials due to their much larger exposed surface area.

The described procedure is a facile method to make PPP and PEDOT nanowire architectures on an electrodeposited gold film through template-assisted electrodeposition in ionic liquids. The employed electrodeposition technique involves the electrodeposition of a thick supporting gold layer on a gold-sputtered surface of the template followed by nanowire growth within the pores of the membrane. After chemical dissolution of the membrane in dichloromethane, a three-dimensional PPP and PEDOT nanowire architecture on gold was obtained. It was shown that different mechanically stable nanowire structures, such as free-

standing nanowires, vertically aligned shrub-like arrays, and bunched nanowire films, could be made.

The electrodeposition of PPP from the air and water stable ionic liquid [HMIm]FAP within the voids of a polystyrene opal structure on platinum substrates yields macroporous films as shown in Fig. 6. In order to synthesize a macroporous PPP deposit, a potential of 2.0 V was applied (at room temperature) for 30 min and a yellow deposit starts to appear which turns brownish black with increasing time due to increasing thickness. The polystyrene spheres were simply removed by THF. The macroporous PPP film adopts somewhat the wavy surface of the platinum substrate. Therefore, the photographs show numerous colors on each picture at one and the same angle of incidence of light (Fig. 7). A very smooth gold substrate leads to a much smoother polymer film, and only one Bragg reflection for each angle of incident light is obtained (Fig. 9).

Fig. 8 SEM micrographs of macroporous PEDOT on gold after the removal of the polystyrene template. Applied potential = 1.3 V for 20 min

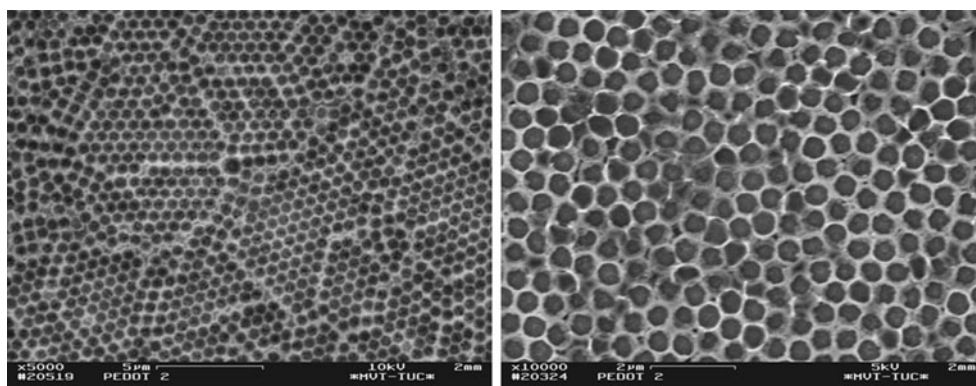
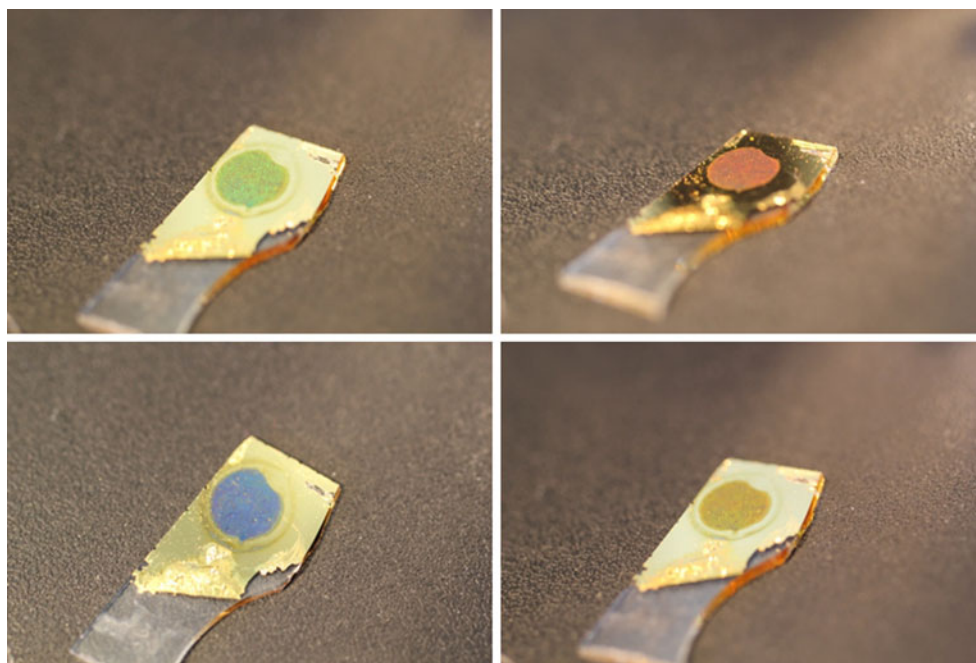


Fig. 9 Photographs of the macroporous PEDOT film deposited on gold. The PEDOT film turns green, red, blue, and orange with slight change of the angle of the incident visible light



The electrodeposition of PEDOT from the air and water-stable ionic liquid [EMIm]TFSA within the voids of a polystyrene opal structure on gold substrates yields macroporous films too, as shown in Fig. 8. The SEM image shows clearly that PEDOT grows through the voids of the polystyrene template, and after removal of the template, a macroporous PEDOT deposit as a well-ordered macroporous nanoarchitecture is obtained.

Figure 9 shows photographs of the macroporous PEDOT film deposited on gold after the removal of the PS template. The PEDOT film turns green, red, blue, and orange due to the Bragg reflection of the incident light. This macroporous structure yields different colors depending on the angle of incident light.

Conclusion

In this paper, we have presented a facile method to make PPP and PEDOT macroporous films within the voids of a polystyrene opal structure on gold and on platinum substrates. Polystyrene spheres with an average diameter of about 600 nm were applied onto the employed electrodes by a simple dipping process. The obtained macroporous films turn into yellow, orange, blue, and green colors owing to the Bragg reflection of the incident artificial white light. We have also shown that by using track-etched membranes with a definite pore size, free-standing nanowires of PPP and of PEDOT can be made. Both conducting polymers with a high surface area either as macroporous films or as nanowire arrays could, e.g., be doped with metal nanoparticles and then used as gas diffusion electrodes in metal/air

batteries or as cathode material in microbatteries. The three-dimensional architecture with its porosity might ensure a large energy density; furthermore, the open structure of the materials might minimize volume changes during charging/discharging.

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