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Electrochemical syntheses of highly ordered macroporous conducting polymers grown around self-assembled colloidal templates

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Three-dimensional highly ordered macroporous conducting polymer films were prepared using a self-assembled colloidal template based on poly(styrene) latex spheres. Poly(pyrrole), poly(aniline) and poly(bithiophene) were polymerised electrochemically and the polymer grown through the interstitial spaces between poly(styrene) latex spheres (0.5 μm or 0.75 μm in diameter) self-assembled in a close-packed array on gold substrates. The latex sphere template was subsequently removed by dissolution in toluene. Regular pore sizes and interconnected channels within the conducting polymer films were evident from scanning electron microscopy studies. The pore sizes for the conducting polymers studied were related to the dimensions of poly(styrene) spheres used as the template. Evidence for shrinkage of the structure was found for some polymers studied.

Introduction

Since the first electrochemical synthesis of 'pyrrole black' by Dall'Olio *et al.*,[1] conducting polymers have been used for numerous specialized applications including energy conversion and storage,[2,3] electrochromism,[4] cation sensors,[5] pH sensors,[6,7] gas sensors,[8] enzyme transistors[9,10] and as drug delivery systems.[11] Their widespread popularity arises not only because of their electrical conductivity, but also because it is possible to modify their properties through chemical substitution on the polymer chain. Furthermore, these materials can be synthesized using electrochemical means. Short fabrication times, ease of preparation and the ability to control both the growth rate and the amount of polymer deposited are significant advantages of electropolymerisation.

Many of the applications of conducting polymers rely directly, or indirectly, on the redox properties of the polymer. Conducting polymers can be reversibly reduced and oxidized using chemical or electrochemical means. This redox switching depends on both electron transfer processes, as well as counter-ion doping processes; the latter being essential for charge balance. There is strong evidence to suggest that the redox switching process is limited by low ion mobility within some conducting polymers.[12,13] Hence, the ability to increase mass transport in the film may result in an enhancement of the performance of conducting polymers in their current applications.

Interest in macroporous polymers first arose in the field of ion-exchange resins where enhanced mass transfer kinetics between the liquid and solid phases was desired.[14] Methods for preparation of macroporous polymers such as poly(styrene), poly(acrylates), and poly(vinyl chloride) are now well established. These materials are used in applications such as catalysis, and as adsorbents, supports and carriers in chromatography.[14] The preparation of these macroporous polymers involves the use of dispersion polymerisation in which the solution contains the monomer, large amounts of a cross-linking agent and a porogen. The cross-linking agent ensures that the growing polymer is rigid and does not coalesce during, or after, growth. The porogen is either a simple organic solvent or a different polymer, which remains within the growing polymer and ultimately forms the pores within the macroporous polymer.

In order to prepare three-dimensional ordered macroporous conducting polymers, it was necessary to use close-packed assemblies of poly(styrene) latex sphere as templates; these are the equivalent of the 'porogen' described above. The polymer was grown electrochemically through this template, from the conductive metal electrode surface onto which the template was assembled. The poly(styrene) template was then removed by dissolution in toluene to leave behind a highly ordered macroporous conducting polymer structure with interconnected channels. It is possible, by employing different sizes of poly(styrene) latex spheres, to grow conducting polymers with different pore sizes. Additionally with the use of electropolymerisation, we are able to control the growth rate and the amount of polymer formed. Hence this novel process for the preparation of three-dimensional ordered macroporous conducting polymer films is experimentally simple and widely applicable.

Self-assembled poly(styrene) latex templates have been used to prepare highly ordered three-dimensional macroporous platinum, cobalt and palladium metal films by our group.[15] Braun and Wiltziuz have described the synthesis of three-dimensional macroporous films of semiconducting cadmium selenium (CdSe) by electrochemical deposition in the interstitial spaces in a close packed array of poly(styrene) latex spheres assembled on the surface of an indium tin oxide substrate.[16] Other authors have prepared regular metal meshes[17] and macroporous metal alloys[18] using polystyrene and poly(methyl methacrylate) spherical templates, respectively. However, we are not aware of any reports of this method being applied to prepare macroporous conducting polymer films. Nolte *et al.*[19] have similarly electrodeposited poly(pyrrole) within the interstitial spaces of a latex sphere template in their sensor fabrication process. However, no attempt to remove the sphere template was made which is necessary for the preparation of a macroporous structure described here.

Martin synthesized poly(pyrrole), poly(3-methylthiophene) and poly(aniline) with regular fibular morphologies and showed that these materials were more conductive.[20] They have also demonstrated higher charge transport rates in fibular poly(pyrrole) as compared to conventional poly(pyrrole).[13] In

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this study Martin grew the conducting polymer within the pores of an Anopore (Al_2O_3) membrane and then dissolved away the membrane using sodium hydroxide.[13] The diameter of the fibrils was determined by the diameter of the pores in the host membrane. Unlike the conducting polymer fibres prepared by Martin, the macroporous polymers reported here comprise a continuous matrix of pores with inter-connected channels.

Experimental

Materials

All solvents and chemicals were of reagent quality and were used as received unless otherwise stated. Pyrrole (Aldrich, 99%) was filtered through a Brockmann Grade 1 aluminium oxide (BDH) column before each use. Aniline (99.5%, Aldrich) was distilled under vacuum prior to use and stored under argon at 4 °C. Tetrabutylammonium tetrafluoroborate (Fluka, >99%) was dried under vacuum at 120 °C in the presence of molecular sieves (Aldrich, 4 Å). Acetonitrile (Aldrich, HPLC grade) was dried over molecular sieves (Aldrich, 4 Å). Poly(styrenesulfonic acid) (Aldrich), poly(vinylsulfonic acid) sodium salt (25% in water, Aldrich), sulfuric acid (BDH, AnalaR grade, >98%), 2,2′-bithiophene (Aldrich, 97%) and butane-1-sulfonic acid sodium salt (Aldrich, 98%) were used as received. The monodispersed poly(styrene) latex spheres with diameters of 0.50 or 0.75 μm were obtained from Alfa Asear as a 2.5 wt% solution in water. All aqueous solutions were freshly prepared using water purified by a Whatman RO 50 and a Whatman 'still plus' system.

Self-assembled colloidal template synthesis

Working electrodes were prepared by deposition of a 10 nm chromium adhesion layer followed by 200 nm gold layer onto thin glass microscope slides. The slides were cleaned by sonication in propanol for one hour and rinsed with deionised water immediately before use. The poly(styrene) latex sphere templates were prepared by sticking a 1.0 cm diameter Teflon ring onto the gold substrate using double-sided tape. The solution of 0.50 or 0.75 μm diameter poly(styrene) spheres was diluted to 0.5 wt% and a volume of *ca.* 0.3 cm^3 was spread over the area of the gold electrode defined by the Teflon ring (0.785 cm^2). The electrode was then placed in a controlled humidity chamber and the water was allowed to evaporate slowly over a period of three days.

Instrumentation

The electropolymerisation of the conducting polymers was carried out using an EG&G 283 potentiostat in a three-electrode cell configuration with a large area platinum gauze as the counter electrode and homemade saturated calomel (SCE) or silver/silver nitrate, 0.01 mol dm^{-3}, in acetonitrile (Ag/$AgNO_3$) reference electrodes for aqueous and non-aqueous experiments respectively. The macroporous conducting polymers were prepared for scanning electron microscopy by sputtering a thin layer (8 to 10 nm) of gold onto the surface. An analytical scanning electron microscope (JEOL 6400) was used to study the morphology and structure of the conducting polymers.

Electropolymerisation of macroporous conducting polymer films

Electropolymerisation of macroporous conducting polymer films was carried out on gold electrodes coated with the poly(styrene) latex templates. Deposition of poly(aniline) doped with either poly(vinyl sulfonate) (PANI/PVS) or poly(styrene sulfonate) (PANI/PSS) was carried out from a solution containing 21.5 wt% in water of poly(vinylsulfonic acid) or poly(styrenesulfonic acid) in 1.88 mol dm^{-3} sulfuric acid and 0.44 mol dm^{-3} aniline. Poly(aniline) doped with sulfate (PANI/S) was deposited from a solution containing 0.1 mol dm^{-3} aniline and 1.0 mol dm^{-3} sulfuric acid. Poly(pyrrole) (PPY/BSA) doped with butanesulfonate was deposited from an aqueous solution containing 0.1 mol dm^{-3} pyrrole and 0.1 mol dm^{-3} butanesulfonic acid. Poly(bithiophene) doped with tetrafluoroborate (PBT/TFB) was deposited from an acetonitrile solution containing 0.1 mol dm^{-3} bithiophene and 0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate. In each case the electropolymerisations were carried out by stepping the potential to an appropriate anodic value: +0.9 V *vs.* SCE for the deposition of poly(aniline) films, +0.85 V *vs.* SCE for poly(pyrrole) and +0.85 V *vs.* Ag/$AgNO_3$ for poly(bithiophene).

After the electrochemical deposition was complete, the poly(styrene) template was removed by soaking the conducting polymer films for 24 hours in toluene.

For the measurements of the polymer resistance the polymers were grown across a 10 μm gap between two 10 μm wide on 500 μm long Pt microband electrodes patterned onto a Si substrate. The resistance measurements where made using a digital multi-meter (Keithley Model 197).

Results and discussion

Figs. 1, 2 and 3 show scanning electron micrographs of the 3-dimensional ordered macroporous structures obtained for poly(pyrrole)–butanesulfonate, poly(aniline)–sulfate, poly(aniline)–poly(styrene sulfonate) and poly(aniline)–poly(vinyl sulfonate). From these SEM micrographs, and others not shown here, it is clear that the macroporous conducting polymer films show high regularity in pore size and that their morphologies are independent of the polymer type. Long-range regularity was observed as long as the growth of polymer did not exceed the template thickness. Fig. 1a shows an example of a poly(pyrrole) film in which some of the polymer material protrudes through the template layer. Note that the template thickness can be controlled by the amount of latex solution applied during the template preparation, whereas the polymer thickness is controlled by the amount of charge passed during the deposition so that it is possible to avoid this effect if one wishes. However, it was noted that the thickness of the polymer layer did not remain constant over the entire sample. Fig. 2 demonstrates two images of different areas of the same templated poly(aniline)–poly(vinyl sulfonate) film. Fig. 2(a) shows an area estimated from the SEM image to be 3 spheres thick while Fig. 2(b) shows an area of the film only 1 radius thick. This non-uniformity of the film thickness is more dramatic in the polymer cases reported here than the metal films reported earlier.[15]

An interesting general observation for these macroporous conducting polymers was the presence of small concave triangular gaps or spandrels between each pore within the macroporous structure, see for example, Fig. 2. These gaps appear to be the result of preferential growth of the polymer around the latex particle during polymer growth leading to a 'skin effect'. Martin[20] has made similar observations for conducting polymer films grown within track etch membrane templates. In these cases the growth of conducting polymers occurred preferentially along the pore walls of the poly(carbonate) membrane, giving rise to hollow polymer fibres. Since the poly(styrene) latex particles that are employed here have surface carboxylate groups in order to electrostatically stabilize the particle solutions, one can postulate that the growth of polymer was 'guided' by electrostatic interactions between these carboxylate groups and the oligomeric or polymeric cations formed during the polymerisation. The occurrence of these concave triangular gaps was less common for poly(aniline)–poly(styrene sulfonate) films as compared to

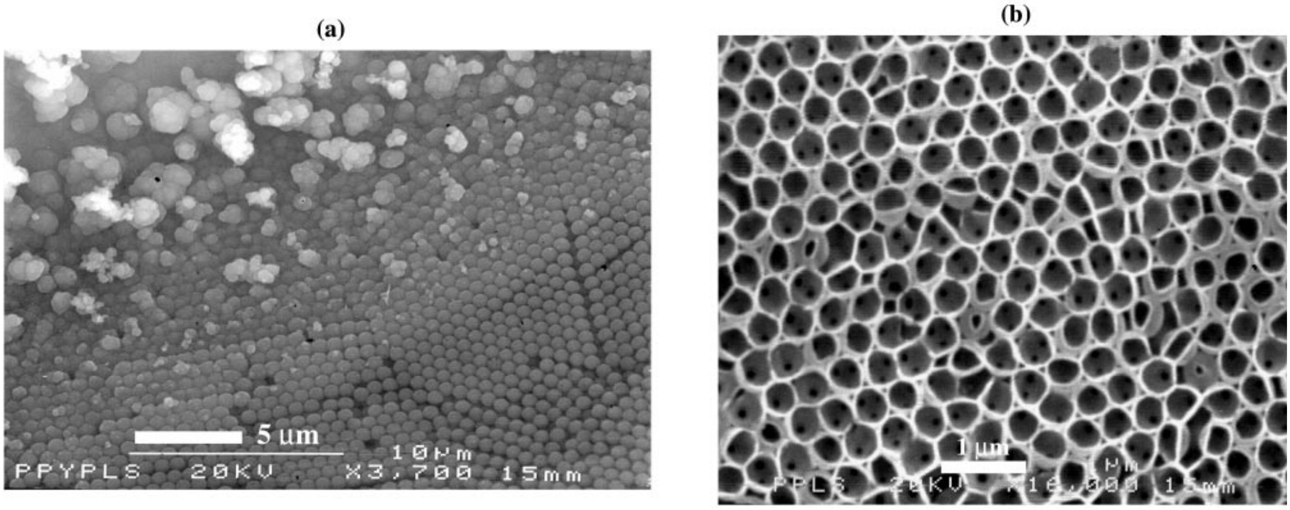

Fig. 1 SEM micrographs of (a) poly(pyrrole) doped with butanesulfonate grown through a poly(styrene) latex sphere template (0.75 µm spheres) before removal of poly(styrene) template. Growth deposition charge density 430 mC cm^{-2} (b) A macroporous film of poly(pyrrole) doped with butanesulfonate after removal of the poly(styrene) template (0.5 µm spheres). Growth deposition charge density 53 mC cm^{-2}.

poly(aniline) films doped with either sulfate or poly(vinyl sulfonate). Clearly more studies are needed in order to establish the effect of the anions on the growth of these three-dimensional ordered macroporous polymers. Further analysis of the SEM images showed that both poly(pyrrole) and poly(aniline) films are remarkably similar in appearance largely irrespective of the thickness of the film once the film was grown above the radii of the sphere templates. In order to explore this effect further we grew graded films of poly(aniline)–sulfate in which the thickness of the polymer film increases steadily from one end of the templated gold substrate to the other. This was achieved by allowing the deposition solution to drain out of the electrochemical cell during deposition of the templated polymer onto an electrode held vertically in the solution. Examination of the resulting graded film by SEM showed only two types of surface morphology: one in which the pore sizes were similar to the size of the template spheres used (Fig. 3a) and the other where there are no evident pores in the surface. Fig. 3b shows that the polymer films, when thicker than a single sphere layer, are interconnected to layers below. This can be seen as small holes connecting the upper layer in Fig. 3b to the lower layer.

Fig. 4 shows the distribution of pore mouth areas for poly(pyrrole) and poly(aniline) macroporous polymer films. It is interesting to note that the pore mouth area is largely uniform but less than that expected from the diameter of the template used. As an example Fig. 4a shows that the most common pore mouth area for a film grown from a 0.5 µm sphere template was 0.1 μm^2 (filled circles). This corresponds to a template diameter of 0.36 µm instead of the expected 0.5 µm template from which the sample was fabricated. Similarly for a film fabricated from a 0.75 µm diameter template an average pore diameter of 0.6 µm was found (triangles). Higher uniformity in pore mouth area for poly(aniline)–poly(vinyl sulfonate) can be seen for regions of the film that are about one template sphere radius thick (see Fig. 4a, triangles). However, even for these regions the pore mouth diameter is smaller than expected. In regions of the film which are thicker than a single template sphere layer the distribution of pore mouth areas becomes less well defined but tends to a smaller pore mouth area (see Fig. 4b). These results contrast strongly with our observations for the deposition of metals within this type of template where we find that the size of the mouth of the pore depends on the thickness of the metal film relative to the size of the template spheres.[15] In principle for the poly(aniline) and poly(pyrrole) films we expect to see a variation in the size of the mouth of the pore in a similar fashion to the metal, in practice this was not observed. Rather it appears that as the polymer dries it shrinks and this shrinkage, coupled with the "skin effect" causes any partially closed pores to tear open to their widest diameter. In addition to this difference in behaviour when compared to metals, the pore mouths are smaller than the template and the appearance of slight hexagonal holes (see Fig. 3b and Fig. 2b) suggests strain on the polymer structure.

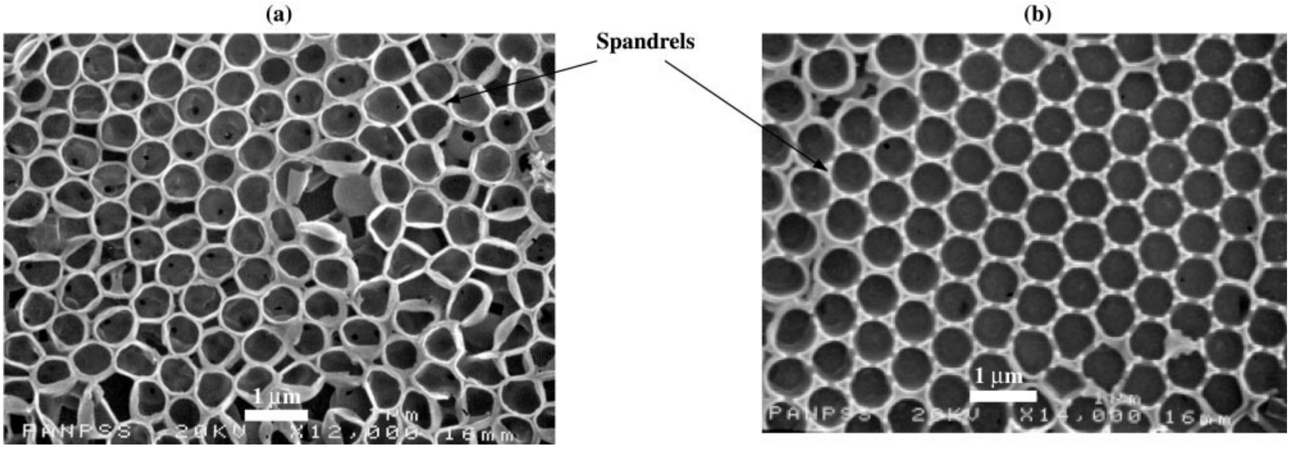

Fig. 2 SEM micrographs of (a) macroporous poly(aniline)–poly(vinyl sulfonate) (0.75 µm sphere template), film thickness approximately 6 sphere radii; (b) portion of the same sample showing a thin area corresponding to *ca.* 1 sphere radius.

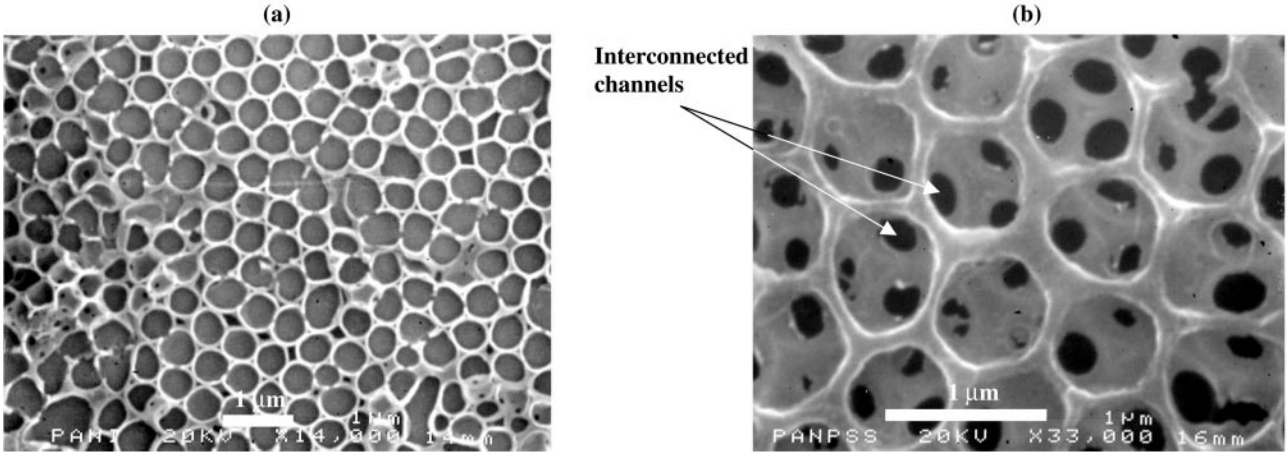

Fig. 3 SEM micrographs of (a) macroporous poly(aniline)–sulfate (0.5 μm sphere template), growth deposition charge density 29 mC cm^{-2}; (b) macroporous poly(aniline)–poly(styrene sulfonate) (0.75 μm sphere template) showing interconnected channels, growth deposition charge density 31 mC cm^{-2}.

Support for this idea can be found in Fig. 2a where close examination shows the presence of excess polymer in folds around the rims of some of the pores, as well as broken polymer links between pores of the type expected if there is shrinkage of the polymer on drying. Yanagida *et al.* recently reported changes in pore diameter of poly(pyrrole) films grown through a silica template.[21] In this case Yanagida *et al.* observed that changes in the electrode potential employed in depositing the films were associated with the pore mouth diameter variation. Although the results produced by Yanagida *et al.* were obtained under different conditions to those reported here and were only for poly(pyrrole) it is apparent that pore mouth variation can occur for these materials.

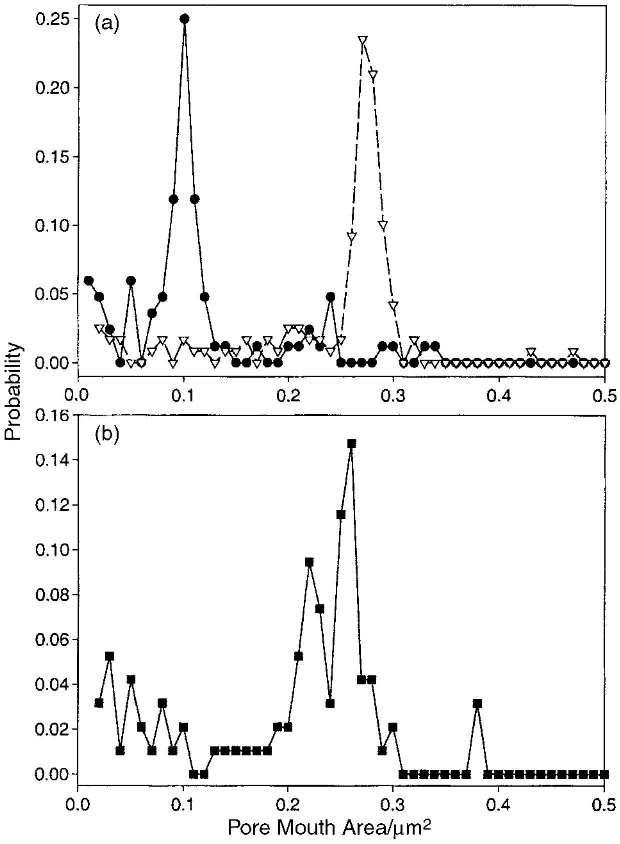

Fig. 4 Plot showing the probability of pore mouth area as a function of pore mouth area (a) ● poly(pyrrole) doped with butanesulfonate; deposition charge 53 mC cm^{-2} 0.5 μm diameter template, data from 84 measurements; ▽ poly(aniline)–poly(vinyl sulfonate), for a portion of a film corresponding to 1 sphere radius thickness, 0.75 μm diameter template, data from 119 measurements; (b) poly(aniline)–poly(vinyl sulfonate) for a portion of a film corresponding to 6 sphere radii, 0.75 μm diameter template, data from 95 measurements.

In contrast, for poly(bithiophene) doped with tetrafluoroborate, a different type of behaviour was observed, see Fig. 5. In this case it appears that the polymer does not shrink on drying so that, because of the "skin effect", a collection of hollow polymer spheres is produced. This difference in the extent of shrinkage depends on several factors: including polymer cross-linkings,[22] type of counter-ions used[23] and solvents[24] employed. It is also interesting to note that the poly(aniline) and poly(pyrrole) were grown from aqueous solutions and then exposed to toluene. This is in contrast to the poly(bithiophene) films, which are solely treated with non-aqueous solvents. Clearly more work is required in order to understand the cause of the changes in the morphology of macroporous conducting polymers.

All of the three-dimensional ordered macroporous conducting polymer films exhibited electronic conductivity as determined by measurements of the resistance of macroporous polymer films grown across a 10 μm gap between two platinum microband electrodes. Table 1 compares resistance measurements in air for a set of conducting polymers grown under the same conditions, and for the same total charge passed both in the absence and in the presence of the latex sphere templates. A detailed comparison of the resistivities of the different polymer films is complicated by the fact that the thicknesses of the polymers will be different and by the fact that the presence of the template may alter the Faradaic efficiency for polymer deposition. Nevertheless it is clear from the preliminary results

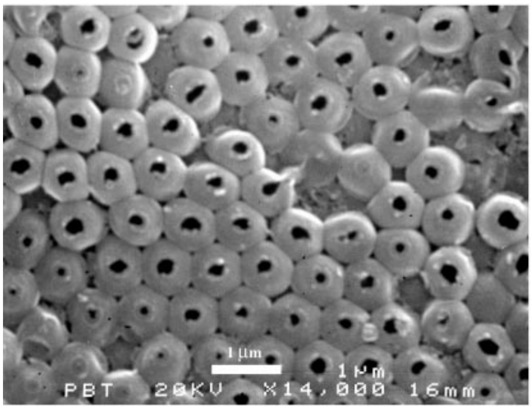

Fig. 5 SEM micrographs of macroporous poly(bithiophene) doped with tetrafluoroborate (0.75 μm sphere template).

Table 1 Resistances of a set of platinum dual microband coated with different templated and non-templated conducting polymers

Polymer/counter-ion	Deposition charge/mC	Resistance across device/Ω^a		
		Normal	Macroporous + spheres^b	Macroporous^b
PANI/PVS	1	125 (1)	66 ± 11 (2)	67 ± 11 (2)
	3	86 (1)	72 ± 1 (2)	71 ± 4 (2)
PPY/BSA	1.4	4000 ± 2200 (2)	2800 ± 200 (2)	2700 ± 300 (2)
	0.7	1700 ± 600 (2)	2500 ± 900 (2)	2600 ± 900 (2)
PBT/TFB	0.5	122 (1)	67 (1)	114 (1)

[a] The numbers in brackets show the numbers of devices tested in each case. [b] "Macroporous + spheres" denotes the polymer films before removal of the polystyrene latex template and "Macroporous" denotes the same devices after removal of the template.

in Table 1 that in all cases the templated films are electronically conducting and that their conductivities are similar to, if not greater than, those for the corresponding non-templated polymer film. The data in Table 1 also show that the removal of the polystyrene latex template by dissolution in toluene does not adversely affect the conductivity of the polymers. In addition, by cycling the potentials of the macroporous poly(pyrrole) and poly(aniline) films in 0.1 mol dm^{-3} sodium butanesulfonate and 1 mol dm^{-3} sulfuric acid respectively, we have also confirmed that these macroporous conducting polymers are electroactive.

Conducting polymers have interesting electronic, electrochromic, electrochemical and electrocatalytic properties which arise out of their ability to switch between conducting and insulating states. The ability to control the polymer porosity and morphology has many implications in terms of kinetic studies, control of polymer properties and the possible improvement of performance in many of their current applications. In addition the ability to make three-dimensionally ordered macroporous structures with these materials should lead to new applications.

Conclusions

We have demonstrated a general method for the preparation of three-dimensionally ordered macroporous conducting polymer films. These films remain electroactive and, in the appropriate redox state, electronically conducting. The final structure obtained from this preparation depended on the particular polymer. With the poly(aniline) and poly(pyrrole) polymers grown and treated under the conditions stated, it was apparent that shrinkage of the resultant structure occurred. Conversely the poly(bithiophene) film remained largely as grown.

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