Electrochemical preparation of macroporous polypyrrole films with regular arrays of interconnected spherical voids

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Polypyrrole films possessing regular macropores interconnected through size-controlled holes have been prepared by electrochemical oxidation in the presence of ordered arrays of silica spheres as templates.

Ordered porous ceramics, metals and polymers have attracted much attention currently because of their applications in catalysis, separation films, porous electrodes and photonic crystals. For synthesis of these materials, useful methods using emulsions[1] or colloidal crystals, which are comprised of submicron-sized monodisperse lateces[2–8] or silica particles,[9–12] as templates have been successfully developed. The advantages of the template-directed methods are mainly due to their size tunability and the simple procedure involving impregnation of the interstitial channels of templates with the desired precursors, reactions and subsequent removal of the templates.

Thus obtained macroporous materials generally possess two types of characteristic void closely related to the applications mentioned above. One is a macropore that is well controlled by the size of the particles that constitute the templates. The other is a smaller hole, which forms at each contact point between the nearest neighbor particles of templates and three-dimensionally connects each macropore. The size of these holes as well as the macropores strongly influence the mass transportation in the bulk of the porous materials. Therefore, the size control of these holes is the critical issue in the fields that require easy access to the high internal surface area of the materials and designed diffusion pathways. However, its control is more difficult than that of the macropores. This is because their size is sensitive to the degree of filling of the channels of the original templates which depends on the viscosity and concentration of precursors and shrinkage of materials when the precursors react. Consequently, there have been only a few reports in which the control of the interconnecting hole size has been achieved through changing the viscosity of the precursor which depends on temperature,[11] repetitions of the filling process[3] or sintering of templates to give larger contact areas between original particles.[9,10]

Recently, electrodeposition has been applied to colloidal template-directed synthesis toward complete impregnation of interstitial channels with group II–VI semiconductors.[13] The electrochemical technique should be an effective route not only for complete filling but also for governing the growth and volumes of materials being deposited in the complex channels *via* parameters such as potential and current that are easy to vary and monitor.

Here we describe the size control of the small interconnecting holes as well as the macropores in template-directed electrochemical synthesis of macroporous polypyrrole. This new material should be of practical value for electrochemical capacitor and battery material applications.

According to a convective self-assembly technique by Jiang *et al.*[14] which relies on capillary forces, we prepared silica colloidal crystals supported on F-doped SnO_2 coated glasses (OTE). An OTE was dipped into ethanol containing monodisperse silica spheres with a mean diameter of 238 nm. Because rapid ethanol evaporation led to poor uniformity of the thickness of the colloidal crystals, the OTE dipped into silica/ethanol dispersion was covered by a 200 mL beaker to slow the evaporation rate. After ethanol was evaporated for 5 days, opalescent colloidal crystals of 3.0 μm average thickness were deposited on the conducting surface. These colloidal crystals used as templates were hydrothermally treated at 473 K for 3 h at a heating rate of 2 K min^{-1} leading to slight necking between silica particles which mechanically stabilizes the templates.[9,10] The necking also resulted in a shrinkage of *ca.* 2% of the thickness compared to the as-grown crystals. Finally, the templates were washed with ethanol several times and kept in a vacuum desiccator until use. The electropolymerization was potentiostatically performed using 0.1 M pyrrole and 0.1 M $LiClO_4$ in acetonitrile solutions with a BAS 100W apparatus (Bioanalytical Systems, Inc.). The counter electrode was Pt wire and the reference electrode was Ag/Ag^+. After electropolymerization of pyrrole, the templates were dissolved by immersing in 20% HF aqueous solutions for 48 h. The polypyrrole films which were peeled off from the OTE were washed with deionized water and characterized by SEM (Hitachi S-800) without the requirement for deposition of metal because of the conductivity of polypyrrole.

Fig. 1 shows chronoamperometric responses of pyrrole polymerization at applied potentials of 0.55, 0.75 and 0.85 V *vs.* Ag/Ag^+. Transition points (marked by the arrows), where the current rapidly increased were observed and shifted toward shorter times at higher potentials. Similar transition points have been observed in template synthesis using membranes with topologically simple cylindrical pores.[15] These rapidly increased currents were suggested to be mainly caused by a rapid increase of the electrochemical reaction area when the growing surface of materials reached the membrane/bulk solution interface. In our case, the surfaces of the colloidal crystals were almost fully covered with cauliflower-like polypyrrole at

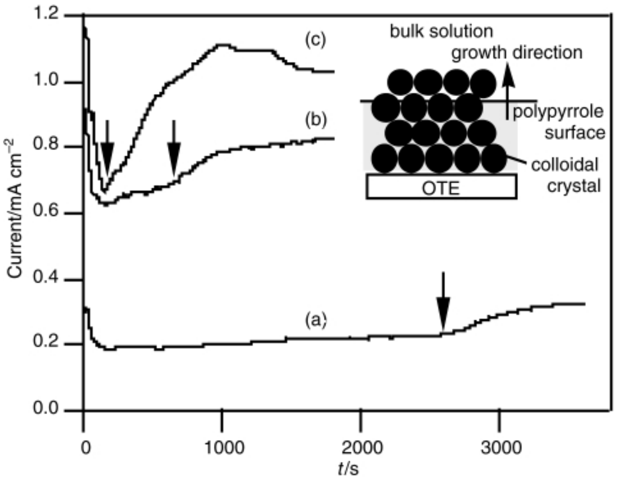

Fig. 1 Chronoamperometric responses of pyrrole electropolymerization in channels of silica colloidal crystals by applying (a) 0.55 V, (b) 0.75 V and (c) 0.85 V. The inset shows a schematic represetation of colloidal crystals and the growth direction of polypyrrole.

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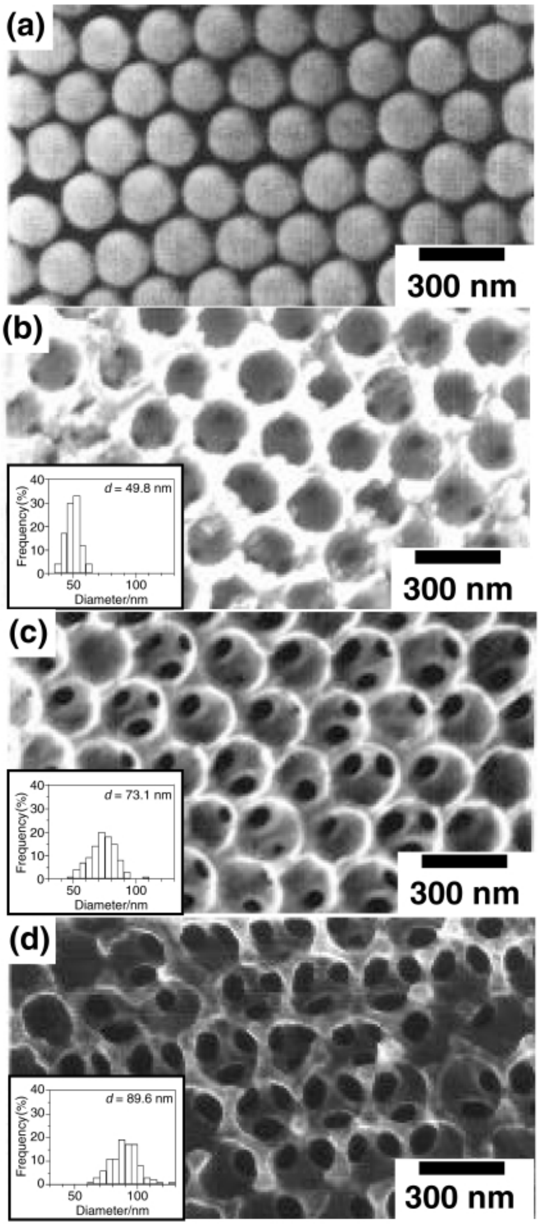

Fig. 2 SEM imges of (a) the original templates and the macroporous polypyrrole films prepared by applying (b) 0.55 V, (c) 0.75 V and (d) 0.85 V. The insets show the hole size distributions corresponding to each SEM image. The size distributions were determined by counting more than 200 holes.

deposition times beyond the transition points (data not shown). Hence, in the present colloidal template synthesis, the transition points are considered to appear according to a similar phenomenon as above. These transition points also should enable us to avoid covering the pores of the top surface of the films with excess polypyrrole.

Fig. 2 shows typical SEM images of the original templates and the macroporous polypyrrole prepared at various potential with electropolymerization stopped before each transition point. Fig. 2(b), (c) and (d) demonstrate that the polypyrrole films had honeycomb macroporous structures mirroring the ordered channels of the original templates [Fig. 2(a)] and smaller holes inside each macropore were clearly observed. As shown in the insets of Fig. 2, their average size increased with increasing polymerization potential from 49.8(5.68) to 73.1(10.6) to 89.6(11.2) nm (esds in parentheses) at 0.55, 0.75 and 0.85 V. These results demonstrated that simple potential change should allow the hole size to be controlled. At 0.55, 0.75 and 0.85 V, the center-to-center distances between the macropores were smaller by 0.1, 0.2 and 3% than the diameters of the original silica spheres, respectively. Taking into account the low shrinkage, the hole size is likely determined rather by incomplete filling during the electropolymerization process than by shrinkage of polypyrrole. The charges passed at each transition time were 0.8, 0.6 and 0.2 C at 0.55, 0.75 V and 0.85 V, respectively implying that smaller quantities of polypyrrole were deposited within the channels at higher potentials, which would decrease the degree of filling.

In conclusion, we have electrochemically prepared macroporous polypyrrole films using colloidal templates. Furthermore, we found that their smaller hole size could be controlled by changing the polymerization potentials. Preliminary experiments showed that this electrochemical control of the hole size can be extended to other templates with different diameters of silica spheres. More detailed mechanisms of the variation of the hole size and the growth of materials in three-dimensionally complex channels are under investigation by experiments with other conducting polymers and metals.

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