

Electrochemical polymerization of aniline inside ordered macroporous carbon†

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3D ordered macroporous multicomponent composite materials have been fabricated by electrochemical deposition of aniline on the inner surface of macroporous carbon; the maximum thickness of polyaniline (PANI) deposited is dependent on the concentration of the aniline as well as the dimension of the windows in the macroporous carbon

Materials with well-ordered porous structure are of considerable interest due to their extensive applications in catalysis,¹ separation, porous electrodes and photonic crystals.² In comparison with microporous and mesoporous materials, three-dimensionally (3D) ordered macroporous materials with pore sizes in the range of submicrometers are fabricated by the recently developed colloidal crystal template method, in which the colloidal crystals, self-assembled by a monodisperse polymer latex or inorganic beads, serve as the template. Besides application as photonic crystals,² another interesting application for 3D ordered macroporous materials is as host matrices to accommodate diverse guest molecules. For example, Jiang *et al.* used an ordered macroporous polymer as a host matrix to fabricate diverse colloidal arrays.³ Xu *et al.* utilized 3D ordered NiO macroporous materials to fabricate metal sphere photonic crystals.⁴ Similarly, our group have fabricated oxides with hollow spheres or ordered macroporous structure by introducing different precursors into the macroporous carbon.⁵

Recently multicomponent 3D ordered macroporous materials have been prepared by chemical precipitation of mixed precursors,^{6,7} sol-gel method⁸ and sequential electrostatic deposition.⁹ 3D ordered macroporous hybrids materials are expected to yield promising applications in optical devices based on photonic crystals. However, there have been few reports on the fabrication of such materials. In this communication, we report on a 3D ordered macroporous multicomponent composite material, which was fabricated by electrochemical polymerization of aniline on the inner surface of a macroporous carbon. This strategy is based on the conductivity of macroporous carbon itself and therefore provides a general approach to introduce diverse components in ordered macroporous carbon *via* an electrochemical method.

3D ordered macroporous carbon was fabricated by the previously reported method.¹⁰ The working electrode was prepared by affixing a slab of macroporous carbon to a copper wire with Ag paint. To prevent the aniline preferably polymerizing on the outside surface of the whole carbon electrode and make further polymerization inside the pore impossible, the working electrode was first immersed for 10 min in an infiltration solution containing 50% ethanol, 0.1 M aniline and 2.0 M H₂SO₄. The subsequent polymerization was performed in

a solution with an identical composition as the infiltration solution except the aniline is absent. Electrochemical polymerization was carried out in a three-electrode cell with a platinum wire as the counter electrode and Ag/AgCl as the reference electrode. Cyclic voltammetry was performed to induce polymerization of aniline. Voltammograms were recorded until successive current traces were constant. Then the working electrode was rinsed with deionized water and dried at 50 °C. By repeating the multiple procedure of infiltration, polymerization and drying. The thickness of the PANI can be increased layer-by-layer inside the pores of the carbon.

Due to the conductivity of carbon, the inner surface of each pore serves as an electrode and induces PANI deposition on the inner surface. In this respect, the working electrode is essentially composed of numerous microelectrodes. By comparing the cyclic voltammograms of the 677 nm macroporous carbon and the corresponding composite, it can be clearly seen that the aniline has been polymerized on the inner surface of the carbon. Moreover, with repeated cycles of infiltration, polymerization and drying, the intensity of the main oxidation and reduced peak also increase, suggesting the thickness of PANI increases layer-by-layer in the macroporous carbon. In addition, concomitant with the change of polymerization number, the oxidation peak shifts to more positive potential while the reduction peak shifts to more negative potential. This is the result of the change of the status of the microelectrode surface during aniline polymerization. For 677 nm macroporous carbon, the first layer of PANI is deposited on the inner surface of carbon, and the second to the ninth layer may deposit on the surface of PANI and carbon, and eventually on the PANI alone. The difference of potentials between PANI and the carbon will decrease the reversibility of microelectrodes. From the IR spectrum of cross-sections of the sample, we know the peak at 1303 cm⁻¹ corresponds to the C–N stretching modes of the leucoemeraldine component and the peaks at 1494 and 1562 cm⁻¹ correspond to the C=N stretching modes of the quinoid moiety in the permigraniline component. The peak at 1143 cm⁻¹ is due to the C–H in-plane bending mode of permigraniline and that at 1240 cm⁻¹ is related to the protonated C–N⁺ group. Thus the PANI formed on the inner surface of the macroporous carbon was emeraldine rather than solely the leucoemeraldine or permigraniline forms. This is consistent with the result on the fabrication of 3D macroporous PANI.¹¹

Fig. 1A displays the dependence of oxidant peak current on the polymerization number in the 677 nm macroporous carbon. Curve *a* and *b* are obtained by infiltrating the macroporous carbon with 0.1 and 0.2 M aniline solution, respectively. The increase of oxidant current reflects the increase of the thickness of PANI on the inner surface of the macroporous carbon. It is interesting that in the initial polymerization, the current increases linearly with the increase of polymerization number, which is indicative of a linear change of the thickness of PANI. However, for curve *a*, when the polymerization number reaches 9, the current increases little further and the curve tends to a

† Electronic supplementary information (ESI) available: Cyclic voltammograms of the 677 nm macroporous carbon and the corresponding composite, infrared spectrum of PANI, SEM images of 490 nm and high magnification SEM images of 677 nm composite materials. See <http://www.rsc.org/suppdata/cc/b1/b111727k/>

limiting value at a given polymerization number (denoted maximum polymerization number). For the same polymerization number, when the concentration of the aniline solution is increased from 0.1 M (curve *a*) to 0.2 M (curve *b*), the oxidation current should theoretically increase twice. However, it was found that the current of curve *b* is less than double that of curve *a*. This is because the higher concentration of aniline will enhance the diffusion velocity from the macroporous carbon to the blank electrolyte solution. The higher the concentration of aniline the more the aniline diffuses into the blank solution.

The existence of a maximum polymerization number and the appearance of a flat region in Fig. 1A are directly related to the microstructure of the macroporous carbon. Fig. 2 shows a cross-sectional scanning electron microscopy (SEM) image of the 677 nm macroporous carbon (A) and the corresponding PANI-doped carbon (B). The 3D hexagonal arrays of pores are connected by the windows in each pore, which can be clearly seen as three dark areas in the higher magnification images of the upper inset of Fig. 2A. These windows provide the necessary channels for the infiltration solution to flow through the whole macroporous carbon. After polymerization a layer of PANI was formed on the inner surface of both the pores and the windows. It is envisioned that with the increasing of the thickness of PANI layer, the dimensions of these windows gradually decrease and eventually close. At this point the aniline monomer can no longer be infiltrated into the carbon because of the blocked channels, resulting in little change of oxidation current with a further increase in polymerization number. Fig. 2B shows the SEM image of PANI-doped macroporous carbon

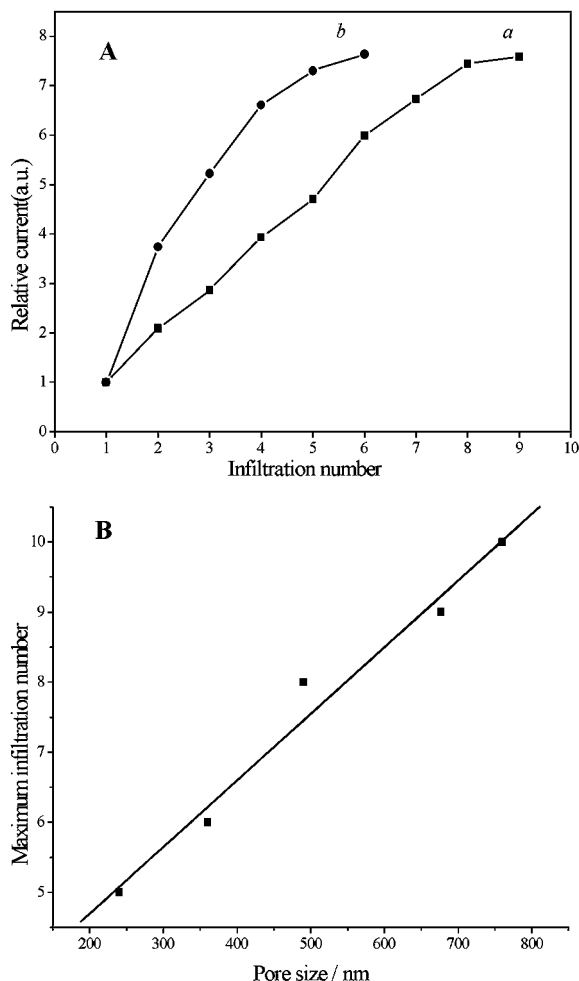


Fig. 1 (A) Plot of relative oxidation current vs. the polymerization number of a 677 nm macroporous carbon using 0.1 M (*a*) and 0.2 M (*b*) aniline as the infiltration solution. (B) The dependence of the maximum polymerization number on the diameter of the macroporous carbon using 0.1 M aniline as the infiltration solution.

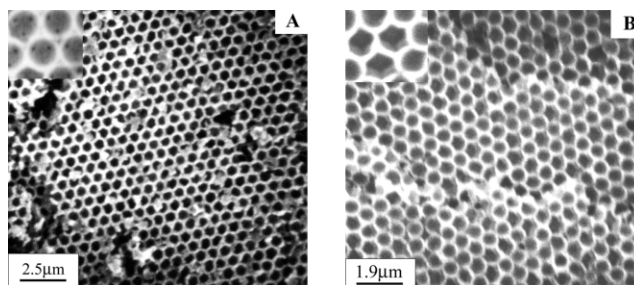


Fig. 2 Cross-sectional SEM images of the 677 nm macroporous carbon (A) and the corresponding PANI-doped macroporous carbon (B). The windows clearly observed in the upper inset of (A) are no longer be seen in the upper inset of (B) after repeating the process of infiltration, polymerization and drying 9 times.

after a polymerization number of 9 using 0.1 M aniline solution as the precursor. The resulting macroporous carbon modified with PANI has the same structure as that of the initial macroporous carbon, confirming the polymerization process did not destroy the long-range ordered structure of the carbon. However, by carefully comparing the high magnification images in the upper inset of Fig. 2A and B, it can be clearly seen that these windows in each pore have been blocked by PANI after maximum infiltration and polymerization.

The fact that the closing of the windows leads to the maximum polymerization number and the appearance of a flat region in Fig. 1A can also be confirmed by choosing a macroporous carbon with different pore size as the working electrode. Fig. 1B shows the relationship between the maximum polymerization number and the pore size of macroporous carbon. Because the dimension of the windows is dependent on the pore diameter of the carbon, when the diameter of carbon is increased from 240 to 760 nm, the maximum polymerization number correspondingly increases from 5 to 10. The increase of the maximum number is the result of the expanded dimension of the windows.

In conclusion, using 3D ordered macroporous carbon as a host matrix, we have demonstrated the feasibility to deposit PANI on the inner surface of the macroporous carbon. 3D ordered macroporous multicomponent composite materials are of considerable interest because they combine the benefits of each component. The host carbon can serve as a support, while the introduction of organic functional groups may produce promising applications in photoelectron devices and therefore, provide the possibility for the further modification. In addition, many other conductive polymers and metal particles can also be introduced to fabricate 3D ordered macroporous composite materials *via* a similar electrochemical method.

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