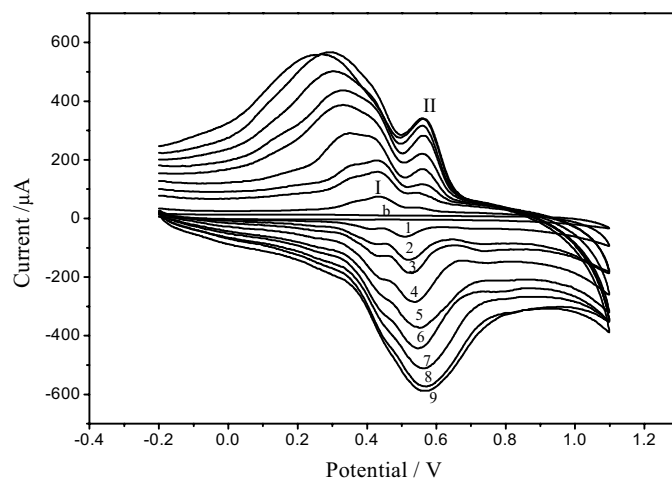


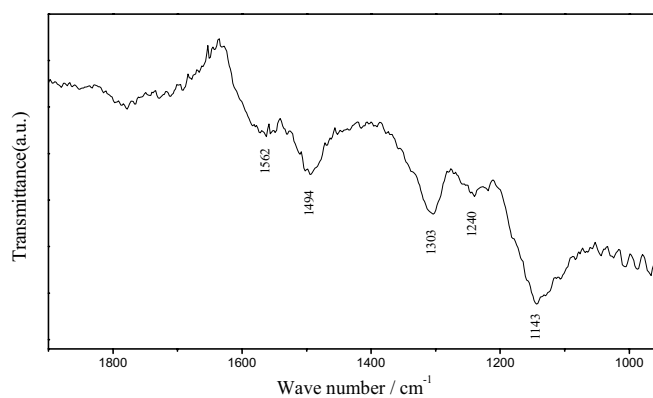
1 Experimental section

3D ordered macroporous carbon was fabricated by the previously reported methods. The working electrode was prepared by affixing a slab of macroporous carbon of different diameter to copper wire with Ag paint. The facet of carbon with Ag paint was then covered by insulating tape and other facets were left to allow the aniline solution to infiltrate the inner pores. It should be noted that if the working electrode was directly put into the electrolyte solution containing aniline, the polymerization process would conduct not only on the inner surface of pore but also on the outside surface of the whole carbon electrode. With the polymerization continued, the outside surface of carbon will be completely covered by the PANI layer, which prevents the aniline solution from flowing through the inner pore and make the further polymerization inside the pore impossible. To overcome this disadvantage, the working electrode was firstly immersed for 10 min in infiltration solution containing 50% ethanol, 0.1M aniline and 2.0M H₂SO₄. The subsequent polymerization, however, was performed in the solution with identical composition as the infiltration solution except the aniline is absent. After putting the working electrode in infiltration solution, the solution will fill the macroporous carbon immediately under the capillary force. The excess aniline solution on the surface of carbon was then removed by suction using filter paper. Electrochemical polymerization of aniline was carried out in three-electrode cell with platinum wire as counter electrode and Ag /AgCl as reference electrode. The scan potential was in the range of -0.2~1.10V and the scan rate was 30mV·s⁻¹. Cyclic voltammetry was used to induce aniline to polymerize. The voltammogram was recorded when the successive two peaks current are constant, which is indicative of the complete polymerization of aniline inside the pore of carbon. After complete polymerization, the working electrode was rinsed with deionized water and then 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 pore of carbon.

2 Fig. 1 Cyclic voltammograms of blank 677nm macroporous carbon(curve *b*) and the PANI deposited on the inner surface of 677nm carbon with the polymerization number increased from 1 to 9(curve 1 to 9). The infiltration solution containing 50%ethanol, 0.1M aniline and 2.0M H₂SO₄.



3 Fig. 2 IR spectrum of PANI deposited on the inner surface of macroporous carbon.



4 Fig. 3 Cross-sectional SEM images of 490nm macroporous carbon(A) and PANI-doped macroporous carbon, (B) 490nm, (C) and (D)677nm. The windows can no longer be seen in (B)–(D) after repeating the process of infiltration, polymerization and drying for 8 and 9 times respectively.

