PEDOT-modified flexible carbon-based electrode for supercapacitor and fuel-cell applications
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Abstract
Poly(3,4-ethylenedioxythiophene) (PEDOT) is a good candidate for electrochemical applications because of its high stability among all conducting polymers. [1, 2] In this study, we used flexible carbon cloth (CC) as the first conducting and porous substrate. To further improve the surface area of CC, graphene paper (GP) was prepared on CC to form a second substrate, GP/CC. The electrodeposition of PEDOT was carried out on these two substrates. The capacitance of PEDOT on both substrates was measured for supercapacitor applications. With the adsorption of Pt colloidal nanoparticles, the methanol oxidation reaction (MOR) of Pt on these two substrates were also evaluated.

Introduction
In recent years composite nanomaterials have been used in energy storage and conversion devices. Graphitic, activated, templated and carbide-derived carbons and nanocarbons have been tested as highly conducting, porous, electrochemically stable and cost effective EDLC materials for charge storage. [3, 4] However, oxidation of carbon during redox cycling and aging still limits the application of these carbon-based electrodes. On the other hand, electrically conducting polymers have been intensively investigated as electrode materials because of their excellent electrochemical reversibilities, fast switching between redox states, high conductivity in a doped state, mechanical flexibility, low toxicity, and low cost. [5, 6] Although having high specific capacitance, conducting polymers suffer from low mechanical strength and low porosity which inhibit their application as electrodes. Hence, graphene with mesoporous structure can be exploited due to the good electrical conductivity and high specific area. Because of their complementary electrical, electrochemical and mechanical properties, PEDOT and graphene, if combined, may offer the improved performance as electrochemical electrodes for supercapacitors and fuel cells.

Experimental
Graphene were chemically functionalized by ultrasonication in a mixture of sulfuric acid and nitric acid (3:1) for 6 hr. The resultant solution was filtered on carbon cloth (CC) to form graphene paper (GP) on it, named GP/CC. Both CC and GP/CC were used as two substrates for the electrodeposition of PEDOT. With these two substrates, PEDOT was potentiostatically grown on CC and GP/CC under 1.2 V vs. Ag/Ag+ in acetonitrile solution to obtain PEDOT-modified CC and GP/CC. The capacitance of these composite materials has been investigated using cyclic voltammetry (CV) in 1M H2SO4. Furthermore, PEDOT/CC and PEDOT/GP/CC electrodes were immersed in size-selected Pt colloidal solution [7] for 24 hr. The methanol oxidation reaction (MOR) of these electrodes with Pt were studied using cyclic voltammetry (CV) 0.5 M H2SO4 + 1 M CH3OH, respectively.

Results and discussion

Figure 1. Scanning electron microscopy images of PEDOT/CC with the deposition time of 120 min.

Figure 2. IR spectra of commercial PEDOT nanotubes (Aldrich) and PEDOT/CC with different deposition time.

Figure 3. Cyclic voltammograms of PEDOT/CC with different deposition time: 0, 10, 30, and 60 min. The scan rate is 50 mV/s and the electrolyte is 1 M H2SO4.

Figure 4. Specific capacitance of PEDOT/CC with the different deposition time of 10, 20, 30, 40, and 50 min.

Figure 5. Cyclic voltammograms of PEDOT/GP/CC with the different deposition time of 10, 20, 30, and 40 min. The scan rate is 50 mV/s and the electrolyte is 1 M H2SO4.

Figure 6. Specific capacitance of PEDOT/GPCC with different deposition time of 10, 20, 30, and 40 min.

Figure 7. X-ray diffraction patterns of Pt/PEDOT/CC and Pt/PEDOT/GP/CC.

Figure 8. TEM images of Pt colloidal nanoparticles.

Figure 9. Electrooxidation of methanol of Pt/PEDOT(10 min)/CC and Pt/PEDOT/CP (inset, ref. 8).

Figure 10. Cyclic voltammograms of Pt/PEDOT/CC in 1 M H2SO4.

Figure 11. Electrooxidation of methanol of Pt/PEDOT(10 min)/GP/CC.

Figure 12. Cyclic voltammograms of Pt/PEDOT/GP/CC and Pt/PEDOT/CP (inset, ref. 8) in 1 M H2SO4.

Conclusion
In this study, PEDOT/CC and PEDOT/GP/CC electrodes were investigated for supercapacitor and fuel-cell applications. With the control of electrodeposition time, the specific capacitance of PEDOT on CC decreases from 136.28 F/g to 89.34 F/g along time increases with high reversibilities. There is the same trend for PEDOT/GP/CC. Moreover, the highest specific capacitance of PEDOT on GP/CC is raised to 237.54 F/g. Using PEDOT/GP as support for Pt colloidal nanoparticles, the peak current of MOR is 5 times higher than all reported in the literature. [8] With GP/PEDOT/CC, the current is approximately 10 times higher than the reported data, indicating the excellent adsorption of Pt colloidal nanoparticles on the mesopores of PEDOT on GP/CC.

References