

Synthesis and modification of corncob-based carbon as high performance negative material for supercapacitor

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Abstract: Porous carbons derived from agricultural waste biomass are ideal active materials for eco-friendly and low-cost supercapacitors electrode materials. However, the challenge remains to further functional modification of biomass-based carbon to achieve high specific capacitance. Herein, PPD-modified porous carbon (MPC) was synthesized by KOH soaking coupled with facile carbonization method of natural corncob and covalently graft of p-phenylenediamine. The MPC exhibits a high specific capacitance of 393 $F \cdot g^{-1}$ at a scan rate of $5 mV \cdot s^{-1}$ in a three electrode system in a 1 M KOH aqueous electrolyte solution. MPC was expected to become promising active materials for high performance negative electrode materials.

1. Introduction

Benefiting from large specific surface area and excellent electrical conductivity, carbon materials have been extensively researched as supercapacitor electrode materials [1,2]. Carbon materials have low preparation cost and wide source of raw materials. Activated carbon materials can be obtained through coconut husk, corn husk, wood, etc[3,4]. Natural biomass materials can also provide a small amount of heteratom doping in the process of carbonization. However, the specific capacitance of carbon is greatly limited by the electrical double-layer charge storage behavior. The specific capacitance of electrical double-layer capacitance are strongly depended on the surface area of porous carbon. However, the ion transport is also one of the important confounding factors for excellent electrochemical performance, which may be affected by large pore tortuosity and poor pore connectivity. Fortunately, mesoporous carbons with high electrical conductivity often have high power density of EDLC due to their fast ion/electron transport within the electrode particles. KOH activation during carbon possessing can fabricate

extremely large surface areas, which means large accessible surface area and high specific capacitance [5].

Carbon-based materials with high specific surface area as supercapacitor electrodes can be well combined with other components. For instance, there have been some reports that the combination with redox active additives such as p-phenylenediamine (PPD), potassium iodide and hydroquinone can introduce redox reactions to offer additional pseudocapacitance[6]. However, improve of poor rate performance and simplify the preparation still needs to be done.

Herein, a easy but efficient method to produce PPD-modified porous carbon (MPC) was presented, as shown in Fig. 1. In this method, hierarchical porous carbon-based supercapacitor negative electrode materials have been synthesized by pyrolysis methods with mixture of corncob and KOH, the PPD were covalently grafted on the porous carbon. By comparing the microstructure of PC and MPC, PPD modification has no effect on morphology. After the hierarchical porous structure can act as a reservoir for electrolyte ions and PPD molecules, leading to a high specific capacitance ($393 F \cdot g^{-1}$ at $5 mV \cdot s^{-1}$) and low resistance.

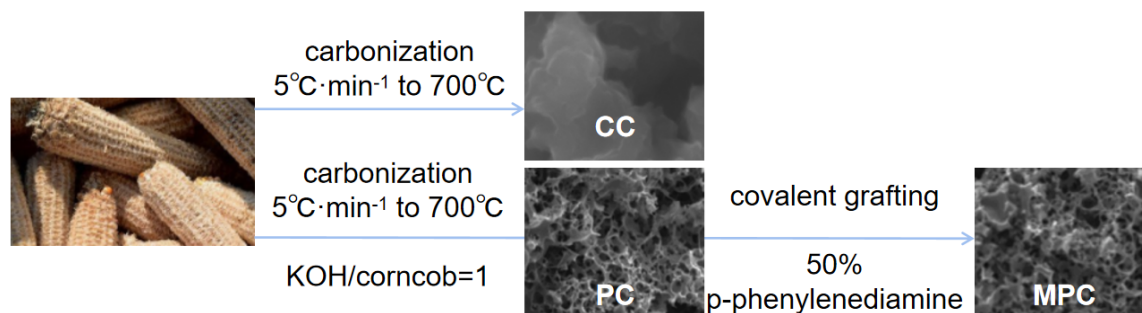


Fig.1 Preparation process diagram of CC, PC and MPC

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2. Test Results and Discussions

2.1 Characteristic method

The X-ray diffraction (XRD) pattern of MPC and PC was shown in Fig.2. Two characteristic peaks at 24° and 43° are respectively related to the (002) and (101) lattice planes of amorphous carbon. Meanwhile, the diffraction intensity at 43° exhibits no obvious change after

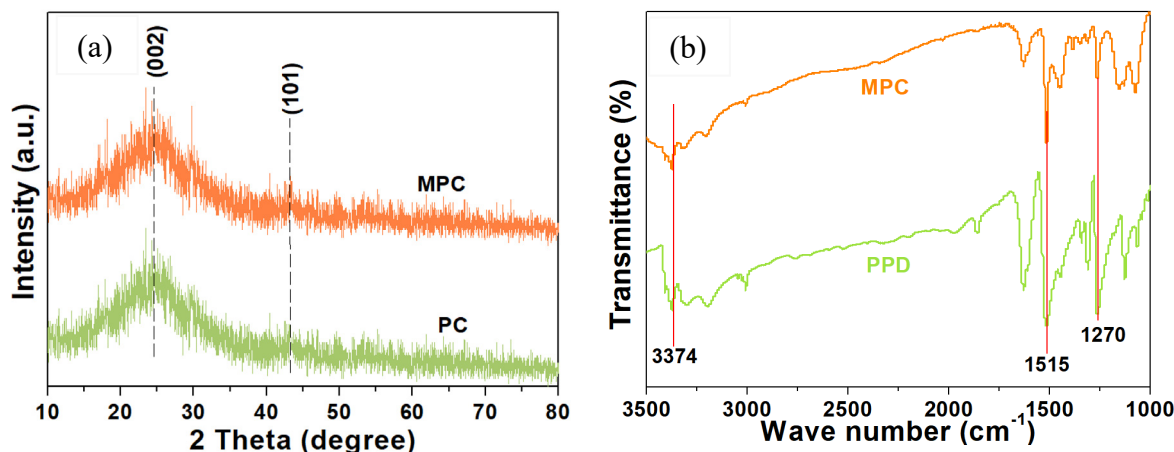


Fig. 2 (a) XRD pattern of PC and MPC, and (b) FTIR spectra of PPD and MPC

Fourier transform infrared spectroscopy (FTIR) of PPD and MPC is compared in Fig. 3, which can further demonstrate the covalent grafting between PPD and PC. For MPC with PPD chemical modification, three characteristic peaks emerged at 3374, 1515, and 1270 cm^{-1} corresponding to the N-H stretching vibrations, N-H bending vibrations, and C-N stretching vibrations, respectively^[7]. Meanwhile, those characteristic peaks are good matching with the FTIR spectrum of PPD. Analysis from the point of view of intramolecular bonds following three different types: the hydrogen bond between the oxygen-containing functional group of MPC and PPD molecule (C-OH... H₂N-X), ionic bonding between protonated PPD and MPC at the negatively charged position (-COO-H₃⁺N-X), and the covalent bond between the amino group (NH₂) and the oxygen-containing functional group in MPC: the reaction of the carboxyl group (COOH) and the nucleophilic substitution reaction of the epoxy group (C-O-C).

2.2 Electrochemical Measurements

The working electrodes were prepared by facial coating method, nickel foam ($1 \times 1 \text{ cm}^2$) was used as negative current collector. The mixture slurry was prepared by mixing of active material, carbon black, poly binder

modification, indicating that PPD modification make no difference to the degree graphitization of carbon materials. Generally, the amorphous carbon has more ion transport channels than the graphitized carbon, which is also more conducive to the rapid electrolyte ions transportation.

(polytetrafluoroethylene) and ethanol. The three-electrode system was made up of 1 M KOH aqueous electrolyte, working electrode, platinum counter electrodes and Hg/HgO reference electrode.

2.3 Electrochemical Performance

Typically, the electrochemical performances of CC, PC and MPC were measured in a three-electrode system in the potential window of -1~0 V (vs. Hg/HgO), 1 M KOH was used as electrolyte. The comparison of CV curves can confirm the different energy storage mechanism of electrochemical reactions. For comparison, the CV curves of the CC and MPC electrode are shown in Fig. 3. Typically, CC exhibits irregular shapes within a potential window from -1 to 0 V, mainly due to poor electrical conductivity and pore structure. Fortunately, after one-step activation and PPD modification, rectangular shapes and redox peaks without obvious graphical changes, demonstrating its efficient charge transfer kinetics and fast redox reaction dynamics. Besides, MPC exhibits large area of CV curves at same scan rate, indicating additional faradaic pseudocapacitance and high specific capacitance.

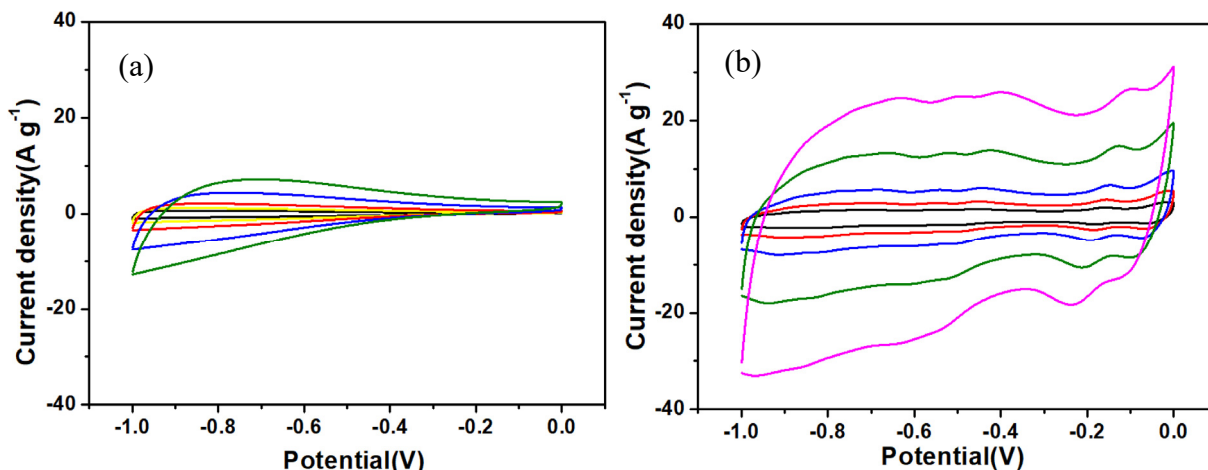


Fig. 3 CV curves of (a) CC and (c) MPC electrode

Fig. 4 exhibits the comparison of galvanostatic charge/discharge curves at 10 A g^{-1} in the potential range of $-1 \sim 0 \text{ V}$. Obviously, both of the galvanostatic charge/discharge profiles exhibit excellent symmetrical characteristic, indicating a good electrochemical reversibility. It can be seen that the highly symmetrical triangle without obvious IR drop curves belongs to MPC. Thus, MPC was defined as ideal supercapacitor negative electrode materials with negligible overall resistance [8]. Furthermore, MPC shows no obvious plateau from -1 V to 0 V . Moreover, the curve of MPC is not a perfect straight line, which is matched with the several redox peaks in CV curves, indicating corresponding pseudocapacitance process in the potential range of $-1 \sim 0 \text{ V}$. Correspondingly, the longer discharge time of MPC is related to a higher specific capacitance.

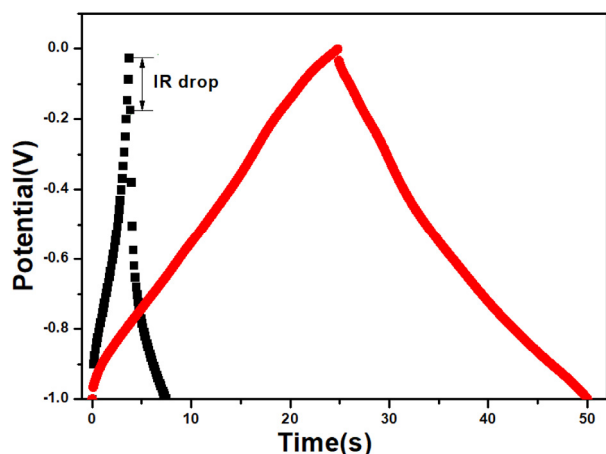


Fig. 4 The galvanostatic charge/discharge curves of CC and MPC

To further analyse the electrochemical performance of CC, PC and MPC electrode As shown in Fig. 5, the CV diagram of PC after one step activation presents an approximate rectangular shape, while the rectangular area of MPC after PPD modification increases, and an obvious redox peak appears, showing extremely excellent random energy. Obviously, the electrochemical performance of MPC was changed by intramolecular bonds between PPD molecules and carbon materials.

Consequently, MPC exhibits rapid redox reaction kinetics and high specific capacitance as supercapacitor negative electrode materials.

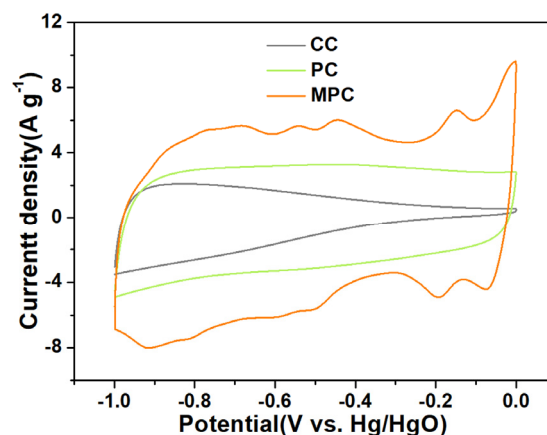


Fig. 5 CV curves of CC, PC, MPC at $20 \text{ mV} \cdot \text{s}^{-1}$

The gap in the electrochemical performances of the CC, PC and MPC can be compared more intuitively from Fig. 6. It can be seen that at the initial scanning rate at $5 \text{ mV} \cdot \text{s}^{-1}$, CC exhibits a rather low specific capacitance as $104 \text{ F} \cdot \text{g}^{-1}$. Obviously, PC shows two-fold increasing specific capacitance ($216 \text{ F} \cdot \text{g}^{-1}$) which is related to the increasing accessible surface area by KOH activation. Moreover, MPC exhibits $393 \text{ F} \cdot \text{g}^{-1}$ at $5 \text{ mV} \cdot \text{s}^{-1}$, increased 3.76 times compared with the original carbon material, indicating the covalent CO-NH bonding between PPD and the carbon. During the charging and discharging process for reversible electrochemical reaction, the specific functional group can introduce additional redox reaction in the alkaline solution for high specific capacitance.

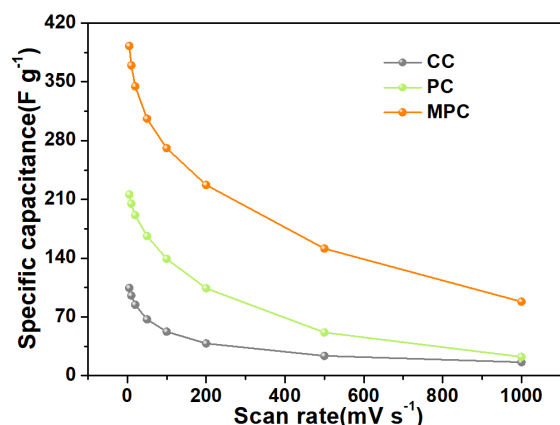


Fig. 6 specific capacitance of CC, PC and MPC electrode

Fig. 7 shows the nearly perpendicular line with ideal capacitive behavior of MPC in the low frequency region, which can be also testified by good symmetry of redox peaks of CV curves. Meanwhile, MPC electrode exhibits the smallest semicircle at relative high frequency, demonstrating that the porous structure that obtained from natural corncob is beneficial for efficient and fast charge transfer. Furthermore, the solution resistance (R_s) towards the intrinsic resistance of electrode materials, ionic resistance of electrolyte and contact resistance between electrode and current collector. The R_s value of MPC, CC and PC are respectively 0.428 Ω , 0.495 Ω and 0.833 Ω , MPC shows lowest R_s value and best electrochemical performance.

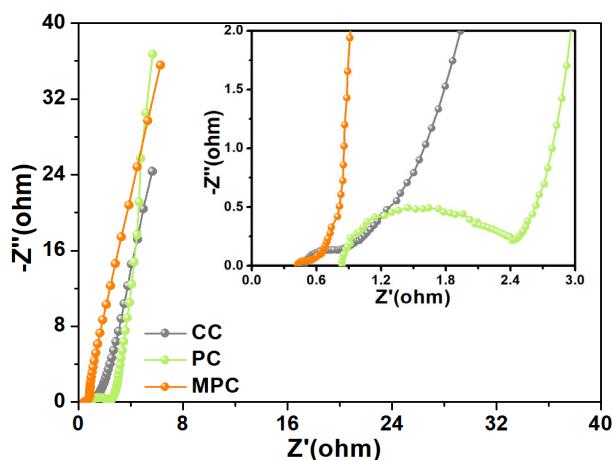


Fig. 7 Nyquist plots of CC, PC and MPC electrode.

3. Conclusion

Based on the previous summary and discussion of the results, the conclusions are obtained as below:

(1) A facile and low-cost method to synthesize high performance supercapacitor negative electrode carbon materials was developed by KOH activation and PPD modification.

(2) The specific capacitance of MPC increased 3.76 times compared with CC. Obviously, the addition of PPD can introduce pseudocapacitance and increase specific capacitance of the carbon negative electrode material.

(3) MPC shows lowest R_s value and the smallest semicircle, indicating that porous framework with PPD covalent grafting is beneficial for efficient charge transfer during electrochemical reactions.

Acknowledgments

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