Preparation and Properties of Conducting Polymer/Microcrystalline cellulose composite

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Abstract. An irregular globules structured Polymer/ Microcrystalline cellulose composite is synthesized as a promising material for conductivity. In this work, the eco-friendly microcrystalline cellulose (MCC) were used as templates, and 1:1 mixture of aniline (PANI) and pyrrole (PPy) monomers in the presence of MCC were synthesized via in situ oxidative polymerization. The experimental results show that the conductive, thermal stability and hydrophobicity of the MCC/PPy-co-PANI composite are indeed optimized to enhance.

Keywords: microcrystalline cellulose, polypyrrole, polyaniline, electrochemical performance.

1. Introduction
Polyaniline (PANI) and polypyrrole (PPy) is widely used in fuel cell, electromagnetic shielding material, stealth material, super capacitor due to their remarkable electrochemical properties, simple and facile synthesis, low cost, good electrical conductivity and good environment stability. Over the last three decades, a large body of research has been amassed on intrinsically conducting polymers for their applications in sensors, batteries, supercapacitors, and biomedical engineering. PANI and PPy are probably the most studied conducting polymers, they are closely related to each other and both are prepared by the chemical oxidation of respective monomers or by their electro-polymerization. However, both PANI and PPy have low thermal stability, poor mechanical properties and processability, and easy to aggregate large particles, which limited their application range. To overcome these disadvantages, conducting polymers could be composited with some nanoscale particles with high mechanical properties and thermal stability. Great research interest has been attracted in finding suitable supports such as carbon nanotubes, land plant cellulose, and cladophora cellulose to explore the great potential of PPy and PANI for various applications.

Here, we report the preparation of morphology-controlled composites with an elegantly optimized synthesis protocol. The as-prepared MCC/PPy-co-PANI composites demonstrated outstanding electrical conductivities. The irregular globules structured hybrid composites were prepared by homogenously coating PPy-co-PANI layers around MCC via in situ oxidative polymerization of pyrrole and phenylamine in aqueous solution. The highly electrically conductive MCC/PPy-co-PANI
composites exhibited a high mass specific capacitance, showing great potential applications in the field of electrochemistry.

2. Experimental Section

2.1. Chemicals and Instrumentations
All reagents were purchased from commercial suppliers of analytical reagent grade and used without further purification, unless otherwise stated. Ultrapure water (18.2 MΩ cm) was provided by a Millipore water purification system and used in the whole experiment.

The FTIR spectra were measured on Shimadzu FTIR-650 spectrometer between 400 and 4000 cm⁻¹, using the KBr pellet method. A TESCAN VEGA3-SBH SEM was used to determine the morphology and composition of the products with samples previously coated with gold via vapour deposition. XRD analysis was carried out on a XRD-6100 X-ray diffract meter using Cu (40 kV, 30 mA) radiation. TG were performed on a TG209F3 using a temperature ramp from 30°C to 600°C at 10°C/min under nitrogen atmosphere. The electrochemical properties of the synthesized MCC/PPy-co-PANI were studied in a CHI660C electrochemical workstation by cyclic voltammetry in a three-electrode cell at room temperature.

2.2. Fabrication of MCC/PPy-co-PANI copolymer composite
Conductive composite were prepared according to the following procedures: 0.8g microcrystalline cellulose with 100ml hydrochloric acid (1M) was added into a 250mL three-necked flask fitted with a condenser, coupled with a mechanical overhead stirrer, by continuous mechanical stirring at 0°C water bath for 30min to obtain homogeneous solution. Then mixed pyrrole(5mM) and aniline(5mM) monomer 0.8g were added in the flask. The 50mL APS(2.28g) that dissolved in 50mL 1M hydrochloric acid was added drop-wise with continuous stirring for 30min. Then keep constant temperature stirring, the color of the solution begins to gradually change from white to purple, and finally to black. After reaction 4h, 50mL acetone was added to termination reaction. After extraction, the solid products were washed three times respectively with deionized water and ethanol. then dry 48 h under 60°C, get MCC/PPy-co-PANI composites (1:1), MCC/PPy-co-PANI composites (1:3) was prepared in the same procedure.

3. Results and discussion

3.1. Structure and morphology analysis
The morphology characterization of MCC/PPy-co-PANI composites was investigated using scanning electron microscope (SEM). Fig. 1 displays the irregular globules were formed by the accumulation of several fine spheres. This is due to the well-separated MCC were quickly coated with /PPy-co-PANI layers.

![SEM images of MCC/PPy-co-PANI composites](image-url)
3.2. IR spectra

Figure 2 shows the FT-IR spectrum of MCC, PPy/PANI and MCC/PPy-co-PANI. For the MCC/PPy-co-PANI composites was prepared under the optimized reaction conditions, their structures were further confirmed with FTIR spectroscopy. The bands at 1650 and 2380 cm$^{-1}$ are due to the ring-stretching modes of PPy-co-PANI. The above results demonstrate the existences of PPy and PANI in products.

3.3. XRD

The X-ray diffraction (XRD) pattern of pure MCC, PPy-co-PANI, MCC /PPy-co-PANI(1:1), and MCC /PPy-co-PANI(1:3) were shown in Figure 3. As shown, the two main peaks of pure MCC, located at 13.6° and 22.6° corresponding
respectively to the (1 1 0) and (2 0 0) diffraction planes of cellulose disappeared in MCC /PPy-co-PANI composites. However, the characteristic broad diffraction peak at 17.3° for amorphous PPy-co-PANI was clearly observed in the as prepared MCC /PPy-co-PANI composites. It is reasonable to conclude that the addition of PPy-co-PANI was not destroying the structure of microcrystalline cellulose.

3.4. TGA

Fig. 4. TGA spectra of (a) MCC, (b) PPy-co-PANI, (c) MCC / PPy-co-PANI(1:1), and (d) MCC / PPy-co-PANI(1:3).

The thermal stability of as-prepared MCC / PPy-co-PANI composite was studied by thermal gravimetric analysis (TGA). As shown in Fig. 4, the TGA trace of MCC a first slow weight loss corresponding to the elimination of ordered water around MCC fibers via hydrogen bonding in the samples at ~105 °C, a second weight loss between 300°C~395 °C involving the removal of small molecular fragments such as O–H and CH2–OH groups during this rapid degradation process, and a third process attributed to the decomposition of the cellulose backbone. The degradation TGA trace of PPy-co-PANI can be continued throughout the process. It is noted that the PPy-co-PANI acted as a protective barrier for the MCC against thermal degradation.

3.5. Super capacitor performance of MCC/PPy-co-PANI composites

Fig. 5 CVs of (a) PPy-co-PANI, (b) MCC / PPy-co-PANI(1:1) and (c) MCC / PPy-co-PANI (1:3). in 1.0 M H2SO4 solution recorded at scan rates of 0.1 V/s.
The potential applications of as-prepared PPy-co-PANI composites were explored by fabricating the samples into supercapacitor electrodes and characterizing with cyclic voltammograms (CVs). The composite showed a high degree of electroactivity, with the rectangular CV traces showing the transitions from reduced to oxidized forms, which demonstrates the retention of the important redox feature of conducting polymers in the as-synthesized MCC / PPy-co-PANI composites.

4. Conclusion
In summary, the composites of conductive structured MCC/PPy-co-PANI were designed and fabricated by a simple chemical oxidation method. The composites morphology evolved strongly with the reaction parameters including concentrations of oxidant and dopant, reaction duration, reaction temperature, and reaction medium. The electric conductivity, thermal stability, and well-controlled microstructure of MCC/PPy-co-PANI composites pave the way towards promising applications in various electronic devices.

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