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## Preparation of Cellulose-Polyaniline Composite Microspheres via Electron Beam Irradiation Grafting and It's Properties

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# Preparation of Cellulose-Polyaniline Composite Microspheres via Electron Beam Irradiation Grafting and It's Properties

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**Abstract.** In this study, a novel poly (acrylic acid-aniline)-grafted MCC conducting composite were synthesized by a simple two-step method. The radical copolymerization of MCC and AA was based on Electron Beam Irradiation Grafting. The synthesized MCC-AA matrix was further grafted with aniline through oxidative-radical copolymerization using APS in acidic media. The resultant MCC-PANI was characterized using X-ray diffraction, thermo gravimetric analysis, and electrical conductivity. It was found that acrylic acid was successfully grafted onto cellulose, and polyaniline was successfully coupled to modified cellulose. and the thermal stability of modified polyaniline composite cellulose was improved. The electrochemical activity of the composites was the best while the mass ratio of aniline monomer to MCC is 3:1. These novel nanorods are desirable for applications in supercapacitor devices.

## 1. Introduction

Conductive composite consisting of template and conductive polymers have received considerable attention for their diversified applications in biosensors, fuel cells, biomedical technology, environmental technology, and so on. For practical applications and to meet the requirements for the fabrication of flexible devices, these materials should demonstrate good conductivity and mechanical properties.

Polyaniline (PANI) has good biocompatibility, environmental stability, high electrical conductivity, and has many potential applications in various fields. There are many reports about the applications of composite containing PAN, such as regenerative processes in nerve cells, antibacterial materials, supercapacitors, and adsorption materials.

Cellulose must be modified due to its limited functional groups (only hydroxyl group) and poor adsorption capacity. Radiation-induced graft polymerization has been proved as a green, fast, effective, and environmentally friendly method in the modification of cellulose. Acrylic acid, is a versatile monomer. It could be easily grafted to different polymer substrates and it could be chemical modified easily to produce many functional materials.

Herein, MCC-PANI conductive composite was prepared by radiation-induced grafting of AC onto MCC, followed by amination of the grafted MCC. The structure and morphology of the obtained



hydrogels were characterized by FT-IR, XRD, and SEM. The thermal stability and conductivity of the composite hydrogels were investigated as well.

## 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 M $\Omega$  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<sup>-1</sup>, 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-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-co-PANI copolymer composite

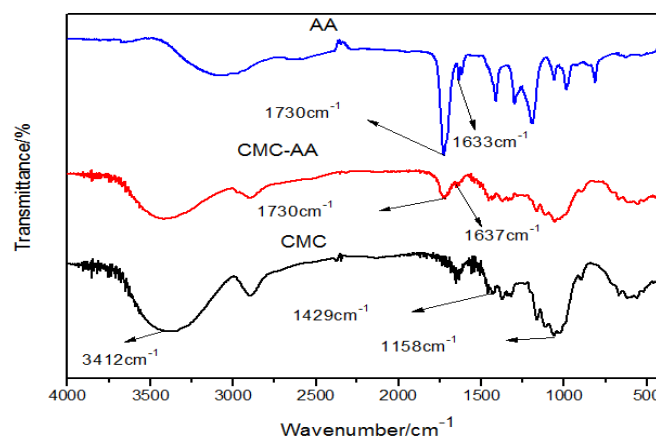
Firstly, the cellulose microspheres were packaged in polyethylene bags purged with nitrogen gas and radiated by an electron beam with doses of 100 kGy at the dose rate of 20 kGy/pass at room temperature by a 1 MeV electron accelerator (Wasik Associates, USA). Then 20ml of 20% acrylic solution was injected into the bags and sealed. Then it was placed in a water bath and heated to 60 °C for 4 h. Finally, the AC-grafted MCC microspheres were cleaned with ethanol and dried at 60 °C before use.

Conductive composite were prepared according to the following procedures: MCC-AA microspheres with 100ml hydrochloric acid (1M) was added into a 250mL three-necked flask fitted by continuous mechanical stirring at 0 °C water bath for 30min to obtain homogeneous solution. Then aniline monomer was added into the flask. The APS that dissolved in 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. 50 mL acetone was added to termination reaction after 4h. After extraction, the solid products were washed three times respectively with deionized water and ethanol and dried in vacuum oven at 60 °C overnight.

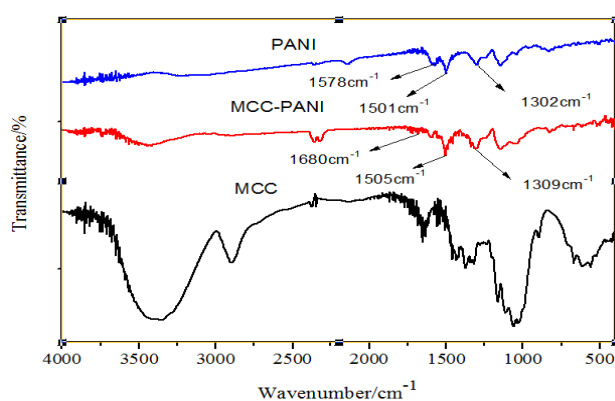
## 3. Results and discussion

### 3.1. IR spectra

The Infrared spectra of MCC, AA and MCC-AA are shown in Fig.1. All the samples exhibited some common peaks as shown in the figure. The broad peak at 3412 cm<sup>-1</sup> could be related to hydrogen-bonded -O-H stretching vibration and the peaks at 2900 and 1461 cm<sup>-1</sup> could be attributed to the C-H stretching and C-H bending from the -CH<sub>2</sub> group. The bands at 1050, 1242 and 1384 cm<sup>-1</sup> corresponds to the C-O-C stretching vibrations, C-OH stretching peak, O-H deformation of the C-OH group, respectively. For AA, The bands at 1730 cm<sup>-1</sup> corresponds to the C=O stretching vibrations of the -COOH group.



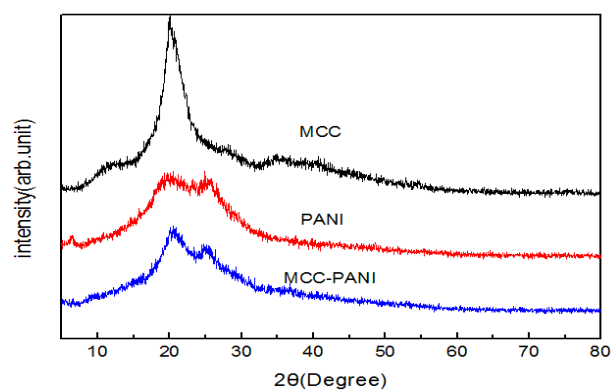
**Figure 1.** Infrared spectra of MCC; AA and MCC-AA



**Figure 2.** Infrared spectra of MCC; PANI and MCC-PANI

### 3.2. XRD analysis

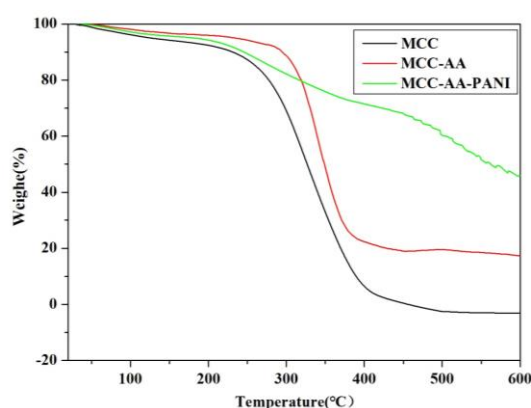
The XRD patterns of MCC, pure PANI and PANI/MCC nanorods are compared in Fig.3. It can be seen that diffraction of MCC shows a typical peak at  $20.6^\circ$ . The pure PANI has a primary characteristic peak at  $25.2^\circ$  attributed to the scattering from the periodicity perpendicular to PANI chains and the one at  $20.3^\circ$  to the alternating distance between layers of polymer chains. The diffraction peak of PANI/MCC composite is similar to pure PANI, and diffraction peak at about  $20.6^\circ$  of MCC appears, because the composite materials contains MCC and PANI.



**Figure 3.** XRD patterns of MCC, pure PANI, and PANI/MCC composites

### 3.3. Thermal properties

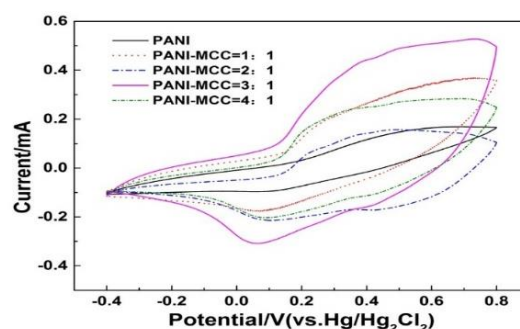
Thermal stabilities of MCC, MCC-co-poly(AA) and MCC-co-poly(AAANI) determined by TGA and results obtained were illustrated in Fig.4. MCC showed initial decomposition temperature at 188.6 °C and final decomposition temperature at 530.5°C. The initial decomposition temperature of MCC was higher than that of MCC-co-poly(AA) while, the final decomposition temperature was lower than that of MCC-co-poly(AA). The lower initial decomposition temperature of the MCC-co-poly(AA) and MCC-copoly(AA-ANI) may be ascribed to the creation of acidic and imide groups which indicates that crosslinking and graft copolymerization of AA and ANI onto the MCC and leading to more thermal stability. It was concluded from the above discussion that thermal stability of MCC-PANI copolymer was observed to improve when compared with MCC and MCC-AA. This may be attributed to the formations of enhanced intermolecular and intramolecular H-bonds in the graft copolymer structure due to the existence of plenty of hydroxy and amino groups in the MCC.



**Figure 4.** TGA spectra of (a) MCC, (b) MCC-AA, (c) MCC / PANI

### 3.4. Electrochemical properties

CV curves for various mass ratios of MCC to aniline are given in Fig. 6. As can be seen from the figure, when polyaniline is combined with microcrystalline cellulose, a significant reduction peak appears. When the mass ratio of polyaniline: cellulose crystallites is 1:1, 2:1, 3:1, 4:1, respectively, the reduction peak of the composite first becomes stronger and then weakens, and a maximum CV curve area of MCC-PANI is obtained when the mass ratio of polyaniline: cellulose crystallites is 3:1. The electrochemical window is the widest, indicating that the electrode can work stably over a wide range. When the mass ratio is 4:1, the cyclic voltammetry curve starts to approach pure polyaniline because the polyaniline content is too large and the electrocatalytic activity is close to pure polyaniline. The optimal mass ratio of aniline monomer to MCC for specific capacitance is 3:1.



**Figure 5.** Cyclic votammograms of a MCC-PANI electrode with different MCC content at a scan rate of 50 mV s<sup>-1</sup> in 1 M H<sub>2</sub>SO<sub>4</sub>.

#### 4. Conclusion

We have successfully synthesized conducting MCC-PANI composite based on Electron Beam Irradiation Grafting. With the help of FTIR, and XRD spectroscopic techniques we have confirmed the formation of graft copolymers. Thermal analysis of the samples has revealed that the grafting and crosslinking have increased the thermal stability. The electrical conductivity of the composite varied with the mass ratio of aniline monomer to MCC, and the conductivity increased first and then decreased slightly with increasing dosages because the condensed network restrained the absorption of PANI in the composite.

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