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Preparation and Electrochemical Performances of Cellulose Nanofiber/Graphene Nanosheet/Polyaniline Composite Film via in-Situ Polymerization

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This study demonstrates that green and renewable cellulose nanofiber can be applied in the production of electrode materials for energy-storage supercapacitors. We prepared cellulose nanofiber/graphene nanosheet/polyaniline (CGP) composite films through in-situ polymerization and vacuum filtration and studied the effect of aniline amounts on the electrochemical properties of CGP films. The composite films were characterized using FT-IR, XRD, XPS, Raman, SEM, and EDX, and the results show that their specific capacitance initially increased and then decreased as the amount of aniline increased. Among the films studied, the CGP_{1: 15}(1 : 15 is the mass ratio of GNS to aniline in the feedstock)films achieved a specific capacitance of 430.78 F/g at a current density of 1 A/g and a charge transfer resistance of 1.65 Ω . After 1000 charge-discharge cycles, 79.33% of the specific capacitance was maintained at 5 A/g.

Keywords: cellulose nanofiber, graphene nanosheet, polyaniline, electrochemical performance

1. INTRODUCTION

Portable and wearable electronic devices, especially flexible, ultra-light, and portable energystorage equipment, have attracted extensive attentions of researchers in recent years. Among these devices, flexible supercapacitors in particular have gained notice because of their high energy density, high power density, long cycle-life, and fast current response [1, 2]. Carbon materials such as graphene and carbon nano-tubes (CNT) have exceptional conductivity, large specific surface area, good magnification performance, and remarkable cycle stability, and they are frequently used in the preparation of supercapacitor electrodes [3]; however, these materials have low capacitance. On the other hand, polyaniline (PANI) is a low-cost, stable, conductive polymer with high specific capacitance, and it shows promise as electrode materials of supercapacitor[4, 5]. Unfortunately, polyaniline inevitably expands and contracts in the charge–discharge process, resulting in poor cycle stability and limiting its application in supercapacitors [6].

In a recent innovation, graphene was incorporated into a polyaniline matrix as a hybrid electrode material for supercapacitors, in order to enhance both the intrinsic electrochemical performance and cycling stability of polyaniline [7, 8]. However, polyaniline is very brittle, while graphene is expensive and readily agglomerative; these factors have limited the applications of the hybrid material in the supercapacitor field. In addition, the pulverized hybrid material requires a conductive agent and binder to form an electrode, and these additions change the structure of the material in a way that is unfavorable to its electrochemical performance and application in high-performance energy-storage materials [9-11].

Cellulose, the most enriched natural polymer, is colorless, non-toxic, and renewable. Cellulose nanofiber, obtained through mechanical or chemical treatments, has a large length–diameter ratio, a large specific surface area, good biocompatibility, and high flexibility, qualities that have led it to be extensively studied in the context of preparing flexible energy-storage materials [12-15]. For example, Liu et al. prepared a flexible electrode material of supercapacitor through in-situ polymerization of aniline on the surface of a cellulose nanofiber films, but the specific capacitance was as low as 120 F/g. Liu et al. also prepared a flexible electrode material of supercapacitor with a specific capacitance of 220 F/g through in-situ polymerization of aniline on cellulose nanofiber and cellulose-derived carbon-sheets (CCS) [10]. Yang et al. prepared a flexible CNF/CNT/PANI films electrode and an aerogel electrode through vacuum filtration and freeze drying follow by cold pressing respectively. The films electrode had a low specific capacitance (207.2 F/g), while the aerogel electrode had a high specific capacitance (343.31 F/g at the current density of 1 A/g) and great cycle stability (80.72% retention after 1000 cycles) [16, 17].



Figure 1. Diagram for the preparation of CGP composite

To date, composites consisting of graphene, cellulose nanofiber, and polyaniline and

functioning as flexible supercapacitor electrode applications have been rarely reported. In this paper, a cellulose nanofiber/graphene nanosheet/polyaniline (CGP) composite films was prepared via facile insitu polymerization and vacuum filtration (Fig.1). Then, this films was used to fabricate a binder-free flexible composite electrode. The effects of polyaniline content on the structure and electrochemical properties of the films were studied. The results demonstrate that cellulose nanofiber can be applied successfully in energy-storage materials.

2. EXPERIMENTAL SECTION

2.1 Materials

Sisal pulp was produced according to kraft pulping technology[18]. Graphene nanosheets (GNS) (0.2 to 1 μ m in diameter and 20 nm in thickness) were purchased from Ashine Technology Co., Ltd, Shanghai City. Sodium chloroacetate was purchased from Huihong Composite Material Co., Ltd, Suzhou City. Ethanol (EtOH), ammonium persulfate (APS), hydrochloric acid (HCl), and sulfuric acid (H₂SO₄), aniline (An), sodium hydroxide (NaOH) were purchased from Xilong Chemical Co., Ltd, Shantou City. Aniline was purified through vacuum distillation. Other chemicals were used as received, without purification or other modifications.

2.2 Preparation of CNF

CNF was prepared according to the procedure outlined in our previous work [19]. First, 6 g of sisal pulp was immersed in 18 mL of a 7.69 wt% NaOH aqueous solution at room temperature for 30 minutes. Then, 120 mL of anhydrous ethanol was added. The mixture was stirred and then heated to 75°C. Subsequently, 1.848 g of sodium chloroacetate was added and left to react for 3 h. The product of the reaction was repeatedly washed with deionized water until it reached a neutral pH. A 0.6 wt% suspension was then prepared with deionized water. The suspension was intensely stirred for 10 minutes in order to derive a transparent, gelatinous CNF solution. Unreacted microfibers were removed with 1000-mesh filter cloth, yielding a 0.4 wt% CNF solution.

2.3 Preparation of CNF/GNS/PANI composite films

24.822 mg of GNS was added to 25 g of the 0.4 wt% CNF solution. The mixture was homogenized for 5 min and sonicated for 30 min to derive a CNF/GNS suspension. A certain amount of aniline and ammonium persulfate was added to a 1 mol/L HCl solution. The solution was added to the CNF/GNS suspension, and the mixture was homogenized for 1 min and then placed at room temperature for 5 h. Then, the CNF/GNS/PANI solution changed from gray to dark green.

An excess of ammonia solution was added to the CNF/GNS/PANI dispersion for dedoping, and the pH was neutralized through dialysis. A CNF/GNS/PANI composite films was then derived through vacuum filtration. The films was denoted according to the mass ratio of CNF/GNS to aniline. Herein,

the cellulose nanofiber/graphene nanosheet/polyaniline composite is denoted by CGP. And, the notation $CGP_{1: 15}$ indicates that the mass ratio of CNF/GNS to aniline in the feedstock for the preparation of the films was 1 : 15.

2.4 Characterizations

Fourier transform infrared spectroscopy (FT-IR) was performed with an NICOLETNEXU 470 infrared spectrometer (Perkin-Elmer Co., Ltd, USA) with a resolution of 4 cm⁻¹. Raman spectroscopy was performed with a Thermo Nicolet NEXUS 670 spectrometer (Thermo Fisher Scientific DXR; Thermo Electron Corporation, USA), using a He-Ne laser with a wavelength of 532 nm. X-ray diffraction (XRD) was conducted at 40 kV and 30 mA with an X`Pert PRO X-ray diffractometer (PANalytical B.V.) equipped with a Cu target. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250Xi photoelectron spectrometer (EPS) equipped with an Al K α X-ray source (hv = 1486.6 eV) (Thermo Electron Corporation, USA). Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed with a JSM6380-LV field emission scanning electron microscope (Thermo Electron Corporation, USA) at an accelerating voltage of 3 kV.

2.5 Test of electrochemical performance

The electrochemical performance of the CNF/GNS/PANI composite films was tested with a ternary-electrode system in a CHI690I electrochemical workstation (Chenhua Co., Ltd., Shanghai City). The three-electrode system employed a platinum electrode as the counter electrode, Ag/AgCl as the reference electrode, and the composite films as the working electrode. Specifically, the composite films was divided into 1 cm \times 1 cm squares and pressed on a 1 cm \times 4 cm stainless steel mesh at 10 MPa for 20 s. The electrochemical performances were tested with cyclic voltammetry (CV), the galvanostatic charge–discharge method (GCD), electrochemical impedance spectroscopy (EIS) and cycle stability. CV was carried out separately at scanning rates of 10, 20, 50, 100, and 200 mV/s in a potential range of -0.2 to 0.8 V. GCD was performed separately at current densities of 1, 2, 3, 4, 5, and 10 A/g in a voltage range of 0 to 0.8 V. EIS was carried out in a 1 mol/L H₂SO₄ solution with an open circuit voltage amplitude of 5 mV in a frequency range of 0.01 Hz to 100 kHz. Cycle stability was carried out at current densities of 5A/g with charge-discharge 1000 times.

3. RESULTS AND DISCUSSION

3.1 Structure and morphology of the CGP composite films

3.1.1 The stability of CGP dispersion

The digital images of CGP dispersion after one month of storage is shown in Fig.2. After the incorporation of CNF, the dispersion of $CGP_{1:1}$ did not coagulate, probably because the PANI and CNF

formed by in-situ polymerization were entangled together, while the abundant CNF carboxyl groups stabilized PANI, CNF, and GNS. In addition, when the amount of aniline was increased from $CGP_{1:1}$ to $CGP_{1:30}$, the data indicate that CNF, PANI, and GNS maintained a stable dispersion system. This finding suggests that it is possible to prepare CGP composite films through vacuum filtration in order to produce flexible electrode materials.



Figure 2. Stability of CGP dispersion

3.1.2 FT-IR spectroscopy

The functional groups of the composite films were characterized by FT-IR, and the results are shown in Fig. 3. In the CNF curve (Fig. 3a), the bands at 898, 1061, 1374, and 3345 cm⁻¹ correspond to the deformational vibration of C–H, vibration of C–O–C in the pyranose ring, deformational vibration of –OH, and stretching vibration of C–H [20].

The results of the GNS curve depict the stretching vibration of secondary alcohols, bending vibration of -OH, and vibration of the benzene ring at 1176, 1400, and 1176 cm⁻¹, respectively. The -OH groups form during GNS's mechanical stripping process, and they have a positive effect on the wetting of the electrode material and the activation of ion transport channels [21].



Figure 3. FT-IR spectra of the CNF, GNS, PANI, CNF/GNS and CGP_{1:15} composite film

The characteristic bands of both CNF and GNS were observed in the CNF/GNS test. For the $CGP_{1:15}$ composite films, the band at 1588 cm⁻¹ corresponds to the deformation vibration of the quinone ring. The band at 1495 cm⁻¹ corresponds to the stretching vibration of N=C=N, and the bands at 1303 and 1144 cm⁻¹ correspond, respectively, to the stretching vibration of C–N and the flexural vibration of C–H in the quinone ring. These characteristic bands are consistent with the characteristic bands of PANI, indicating that PANI was successfully in-situ polymerized on CNF and GNS.

Compared with PANI, the characteristic bands of $CGP_{1:15}$ shifted from 1592, 1498, 1304, and 1145 cm⁻¹ to 1588, 1495, 1303, and 1144 cm⁻¹, respectively. The intensity of these bands also decreased, indicating a strong interaction among CNF, GNS, and PANI [22].

3.1.3 Raman spectroscopy

The Raman spectra of GNS, PANI, and CGP composite films are shown in Fig. 4a. In the GNS curve, the bands at 1350 and 1581 cm⁻¹ correspond to the characteristic bands D and G of grapheme[23]. In the PANI curve, the bands at 1186, 1256, 1511, and 1620 cm⁻¹ correspond to the bending vibration of the quinone ring, the C–N vibration of the quinone ring and benzene ring, the stretching vibration of C = N in the quinone ring, and the stretching vibration of C = C in the quinone ring, respectively. For the CGP composite films also include the characteristic bands of GNS and PANI, indicating that PANI was successfully polymerized onto the CNF/GNS composites.

3.1.4 XRD spectroscopy



Figure 4. Raman (a) and XRD (b) spectra of the CNF, GNS, PANI and CGP composite

The XRD results for the CGP composite films are shown in Fig. 4b. The CNF pattern includes two intense peaks at 2 θ of 15.3° and 23.1°, which correspond, respectively, to the 110 and 200 diffraction planes of cellulose I [24]. In the GNS pattern, the peak at 26.5° corresponds to the 002 diffraction plane of grapheme[25]. In the PANI pattern, the peak at 2 θ of 23.6° corresponds to the 200 plane of polyaniline crystal in the form of aniline salt [26].

The pattern from the CGP composite films includes the characteristic GNS peak at 2θ of 26.5°

and the characteristic CNF peaks at 2 θ of 15.3° and 23.1°. However, these characteristic peaks weaken with increased PANI content in CGP films. These results suggest that PANI and CNF were entangled and dispersed on the surface of GNS, and the strong hydrogen-bond and π - π interactions decreased the crystallinity of CNF and GNS [27].

3.1.5 XPS spectroscopy

The chemical states of the elements in the CNF/GNS and CGP_{1:15} composite films were characterized by XPS, and the results are shown in Fig. 5a. A peak in N1s is present in the spectrum of the CGP_{1:15} composite films, indicating that PANI was successfully incorporated into the CNF/GNS nano-composite. The –OH groups in CNF adsorbed aniline monomers and functioned as active sites for PANI nucleation [10]. Based on the N1s and O1s peaks, the N/O ratio of the CGP_{1:15} films is 0.88; this finding indicates that most of the aniline monomers were adsorbed in the vicinity of CNF in order to polymerize and form PANI nano-wires entangled with CNF. This result is consistent with the morphology revealed in the SEM results, which will be discussed later.



Figure 5. XPS spectra of CNF/GNS and CGP_{1:15} composite film (a),the C1s region of CNF/GNS (b),the O1s region of CNF/GNS (c),the C1s (d), N1s (e) and O1s (f) region of CGP_{1:15} composite film.

In Fig. 5b, the C1s spectrum of the CNF/GNS composite films exhibits three intense peaks: sp^2 of the aromatic ring at 282.44 eV, the oxygen atom in C–O–C at 286.24 eV, and the oxygen atom in O–C=O at 284.10 eV [28]. Fig. 5c shows that the O1s spectrum of the CNF/GNS films exhibits two intense peaks at 532.51 (C=O) and 533.48 eV (C–OH) [29]. Fig. 5d shows four intense peaks in the C1s spectrum of the CGP_{1:15} composite films, at 284.63, 284.54, 285.69, and 286.86 eV; these peaks correspond to C–C, C–OH, C=O, and O–C=O, respectively. The sp^2 intensity of the aromatic ring is more significant than the sp^2 intensity of CNF/GNS, which may result from the stronger π - π

interactions between CNF, GNS, and PANI.

Fig. 5e shows three peaks in the N1s spectrum of the CGP_{1:15} composite films; the most intense peak at 398.55eV corresponds to -NH- in aniline, while the other peaks at 397.46 and 400.34 eV correspond to -N= and $-N^+-$, respectively [30]. The O1s spectrum of the CGP_{1:15} composite films is depicted in Fig. 5f. The peaks at 532.22 and 530.49 eV correspond to C–OH and C=O, respectively. These O1s peaks are shifted compared to those in the CNF/GNS films, which may be attributed to the hydrogen-bond and π - π interactions between PANI, CNF, and GNS.

3.1.6 SEM characterization

The SEM images of $CGP_{1:1}$, $CGP_{1:15}$, and $CGP_{1:30}$ are shown in Fig. 6. The findings indicate that PANI was polymerized and coated the CNF/GNS surface (Fig. 6a).

As shown in Fig. 6b-d , when the concentration of aniline monomers increased, more aniline cations were attracted to the GNS layers for polymerization because of the electronic induction effect [31] and –OH in CNF. Therefore, GNS was peeled and evenly distributed, combining with PANI to form conductive circuits. More aniline monomers were attracted by the oxygen-containing functional groups of CNF and polymerized in the vicinity of CNF. Then, PANI was entangled with CNF and dispersed on the GNS surface. PANI nano-wires became entangled with CNF rather than coating CNF, resulting in the porous structure of the CGP_{1:15} composite films. These pores promote the permeation of electrolytes and shorten the path of charge transport [32-34].

As shown in Fig. 6e–f, excess aniline in the $CGP_{1:30}$ composite films leads to the agglomeration of PANI and a decrease in porosity. The large amount of agglomerated PANI between the GNS layers isolates GNS, breaking the conductive network with PANI.



Figure 6. FE-SEM images of CGP_{1:1} composite(a),CGP_{1:15} composite(b-d), and CGP_{1:30} composite film(e-f).

The large-area of SEM images and EDS results for the $CGP_{1:15}$ films are illustrated in Fig. 7a– d. CNF and PANI are uniformly dispersed, and the distributions of N atoms and O atoms are



Figure 7. Large-area SEM image of CGP_{1:15} composite (a), and its corresponding EDS element images of C (b), O (c), and N (d).

3.2 Effect of PANI content on the electrochemical performance of the CGP film

3.2.1 CV curve

Fig. 8a shows the effect of the aniline amount on the CV curve of CGP films at a scan rate of 10 mV/s. The CV profiles are approximately rectangular and exhibit two pairs of redox peaks within the range of 0.2 to 0.6 V, which are related to the PANI conductor–semiconductor transition and the benzoquinone–amine quinine transition. These findings indicate that the CGP films has both double-layer capacitance and pseudocapacitance [35]. The CV profile of the CGP_{1:15} composite films contains the largest area, indicating that CGP_{1:15} composite film has the best electrochemical performance.

CV profiles of the $CGP_{1:15}$ films at different scanning rates are shown in Fig. 8b. As the scanning rate increases, the redox peaks gradually shift to both sides simultaneously [36]. In the range from 10 to 200 mV/s, the CV profiles gradually become more symmetric, indicating that the composite films has good reversibility and a fast charge transport capacity [37].

3.2.2 GCD curve

The GCD curve of CGP composite films with different aniline contents at a current density of 1 A/g are shown in Fig. 8c. These profiles take the shape of isosceles triangles, indicating that the CGP films has ideal capacitance behavior. In addition, the discharge profiles of the composite films exhibit

two flat segments, probably due to the presence of PANI pseudocapacitance. The specific capacitance of the electrode material in a galvanostatic charge–discharge process can be calculated according to the following equation [38]:

$$C_m = \frac{i \times \Delta t}{\Delta V \times m}$$

where C_m is the specific capacitance (F/g); *i* is the galvanic current (A); Δt is the discharge time (s); ΔV is the potential difference (V); and *m* is the mass of electrode material (g).

Based on this equation, the specific capacitances of the CGP_{1:1}, CGP_{1:5}, CGP_{1:10}, CGP_{1:15}, CGP_{1:20}, and CGP_{1:30} composite films are 30, 190, 292, 431, 422, and 407 F/g, respectively. The specific capacitance reaches a maximum with CGP_{1:15}, at 14.37 times the value for the CGP_{1:1} films, which can come to as high as 431 F/g, such high specific capacitance is remarkable compared with some reported CNF-based or PANI-based composite electrode materials (Table. 1) This large specific capacitance of CGP_{1:15} composite mainly attributed to the strongly interaction between CNF , GNS and PANI.



Figure 8. (a) CV curves of CGP composite film at the scan rate of 10mV s⁻¹; (b) CV curves of CGP_{1:15} composite films at different scan rates; (c) GCD curves of CGP composite films at a current density of 1A g⁻¹; (d) Specific capacitance of CGP composite films within 1-10 A g⁻¹ current density range.

The high specific capacitance of $CGP_{1:15}$ films is mainly attributed to the following process: As the aniline amount increases, PANI tends to become entangled with CNF, and it is uniformly dispersed

on the surface and in the vicinity of GNS, thereby enhancing the interactions among CNF, PANI, and GNS. Simultaneously, GNS is uniformly distributed to create a conductive networks with PANI, forming a high double-layer capacitance and high PANI pseudocapacitance. Moreover, the porous structure formed by the entangled PANI and CNF can preserve electrolytes and accelerate the transport of charges, allowing PANI to be fully utilized [42].

Table 1.	Comparison	of various	materials in	terms of specific	capacitance performance
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Composite	Potential	Electrolyte	Capacitance (F/g)	Ref.
CGP _{1:15}	0-0.8V	$1 \text{ M H}_2 \text{SO}_4$	431, 1 A/g	This work
CNF/GNS/PANI(GNS:6%)	0-0.8V	$1 \text{ M H}_2 \text{SO}_4$	343, 1A/g	22
CNF/CCS/PANI _{2:4:1}	-0.2-0.8V	$1 \text{ M H}_2 \text{SO}_4$	220, 1 mA/cm ⁻²	10
CNF/MWCNTs/PANI aerogel	0-0.8V	1 M H ₂ SO ₄	343, 1 A/g	16
CNF/MWCNTs/PANI film	0-0.8V	$1 \text{ M H}_2 \text{SO}_4$	207, 0.2 A/g	17
3D porous graphene/polyaniline	0-0.8V	1 M H ₂ SO ₄	331, 1 A/g	39
PANI / reinforced cellulose-acetate	0-0.8V	1 M H ₂ SO ₄	402, 0.3 A/g	40
PPY/RGO/bacterial cellulose	0-1V	1 M NaNO ₃	235, 2 mA/cm ⁻²	41

The rate capability of the CGP composite films were tested with GCD at different current densities, and the results are shown in Fig. 8d. The CGP_{1:15} composite films exhibits a good rate capability; when the current density was increased from 1 to 10 A/g, 78% of the specific capacitance was maintained. In contrast, only 45% of the specific capacitance of the CGP_{1:1} composite films was retained. The high retention of specific capacitance for the CGP_{1:15} films is mainly explained by the porous structure, which results in the rapid transport of charges and ions at a high current density. However, when the aniline amount is further increased, excess PANI in the CGP_{1:30} composite films begins to agglomerate and the aggregates block a proportion of pores, decreasing the porosity and thereby decreasing the transport rate of ions in the electrolytes. Therefore, the rate capability declined.

3.2.3 EIS curve

The effect of aniline content on the EIS of CGP composite films shows the enlargement of the high-frequency zone. The semicircle in the high-frequency zone corresponds to the charge transfer internal resistance (Rct), which represents the factors limiting both charge transfer and the

electrochemical performance of the electrode. The straight line in the low-frequency region represents the diffusion capacity of charges in the pores of the composite films [43]. The Rct value (1.65 Ω) of the CGP_{1:15} films is lower than those of other films, indicating increased porosity due to the entanglement of PANI with CNF. In comparison to coating, entanglement enhances contact with electrolytes and the diffusion of ions. In addition, the CGP_{1:15} films exhibits a vertical line in the lowfrequency region, reflecting the electrode material's superior capacitance behavior [44].

3.2.4 cycle stability

The effect of the aniline amount on the cycle stability of CGP composite films is studied. The CGP_{1:15} composite films in particular shows excellent cycle stability. At a current density of 5 A/g and after 1000 charge–discharge cycles, this films retained 79.33% of its initial specific capacitance; this is superior to the retention rates of the CGP_{1:1} (72.82%) and CGP_{1:30} (71.43%) composite films. The exceptional cycling stability of the CGP_{1:15} composite films is mainly due to the entanglement of PANI and CNF inside the composite films, as well as the synergistic effect between CNF, GNS, and PANI. These effects restrain the volume variation of PANI during the cycling charging and discharging process. In addition, the porous structure inside the composite films enhances the permeation of electrolytes and shortens the transport distance of ions, thereby improving cycle stability.

4 CONCLUSIONS

In this study, flexible CGP composite films were prepared via in-situ polymerization and vacuum filtration. The effects of aniline amounts on the structure and properties of these films were then studied. The electrochemical results show that the specific capacitance of the CGP conductive films initially increases and then decreases with increasing aniline content. The specific capacitance of the CGP_{1:15} films is as high as 430.78 F/g at a current density of 1 A/g, and its internal resistance is as low as 1.65 Ω . At 5 A/g and after 1000 charge–discharge cycles, the films retained 79.33% of its specific capacitance. According to the results of characterizations, significant hydrogen-bonding and π - π interactions are present among CNF, GNS, and PANI in the CGP_{1:15} films. The conductive films is porous, which promotes the fast transport of ions and permeation of electrolytes. GNS and PANI are uniformly distributed and form a connected conductive network, improving the electrochemical performance of the CGP_{1:15} films. This flexible, recyclable composite films can be applied to produce flexible supercapacitors.

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