Synthesize electrode material based on rGO/Polyacrylic acid prepared by a combination of direct ink writing technique and UV irradiation

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ABSTRACT

In this work, the rGO/polyacrylic acid (rGO/PAA) composite film was synthesized using the 3D direct ink writing technique with GO/acrylic acid (GO/AA) ink and UV irradiation. Results show that after a UV irradiation time of 3.6 seconds, GO was reduced into rGO, and AA was polymerized into PAA. The prepared material was characterized by using Fourier Transform Infrared Spectroscopy (FT-IR), Energy-dispersive X-ray spectroscopy (EDX), cyclic voltammetry (CV), and galvanostatic charge/discharge technique (GCD). The obtained composite film is applied as an electrode for the supercapacitor. The electrode has a specific capacity of 321 F/g at a current density of 1 A/g and retains 82% of its initial capacity after 5,000 charge/discharge cycles at a current density of 5 A/g.

Keywords: Composite; Graphene oxide; Polyacrylic acid; Capacitor.

1. INTRODUCTION

Energy storage devices known as supercapacitors can provide exceptionally high pulse power and capacitance densities. These devices have continuously received great attention in recent years. Supercapacitors are classified into two types based on their energy-storing principles: electrical double-layer capacitors, which store energy through adsorption/desorption of electrolyte ions on material surfaces, and pseudocapacitors, which store energy through faradaic reactions in electrodes [1].

Graphene has many unique characteristics, such as high electrical conductivity and thermal conductance; its surface area and large electronic mobility. Therefore, graphene has been studied for applications in a variety of fields, including electrode materials for supercapacitors [2]. However, making a film from powdered graphene is difficult, so the investigation of creating a composite with polymer has attracted many scientists. Composite films are typically created by spin-coating, drop-casting, and self-assembly techniques.

In recent years, 3D printing technology has advanced significantly, with a high level of automation making composite film design considerably simpler, faster, and more precise. 3D printing is classified into nine categories, with Direct ink writing (DIW) technology being the most suitable for electrode film fabrication [3]. Making ink from graphene is challenging because it is not diffuse; thus, scientists typically use graphene oxide (GO) and then reduce GO into rGO using various chemical and physical methods.

This work presents the result of making a composite film of rGO and PAA using a DIW technique and UV irradiation. Composite rGO/PAA is applied as an electrode for supercapacitors.

2. EXPERIMENT

2.1. Materials

- Graphite powder 99%, $KMnO_4$ 99%, H_2SO_4 98%, H_3PO_4 85%, and H_2O_2 30% was a pure chemical from Macklin Company, China, used to synthesize GO.

- Acrylic acid (AA), Benzophenone, $K_3[Fe(CN)_6]$, and $K_4[Fe(CN)_6]$ from Sigma-Aldrich used to synthesize ink and measure electrochemical properties

- The graphite papers were provided by Xiamen TOB New Energy Technology.

All chemicals were of analytical grade without further purification.

2.2. Materials characterization

The morphology was characterized using scanning electron microscopy (SEM) Hitachi S4800 instrument. An energy-dispersive X-ray (EDX) spectrometer instrument was attached to the SEM instrument. Fourier transform infrared (FT-IR) spectra were recorded by an FT-IR NEXUS 670 spectrometer, the composite film was analyzed using the Attenuated Total Reflectance technique, with wave numbers from 400 to 4000 cm^{-1}.

The electrochemical measurements for the sample are conducted on a Biologic VSP 300 multi-channel instrument using a standard three-electrode cell system with a saturated calomel electrode (SCE) as the reference electrode, Pt counter electrode, and rGO/PAA working electrode of the area of 1 cm^2, the mass of the active materials of 1 mg. All tests are performed at room temperature.

2.3. Experimental

Preparation of electrode materials

GO is synthesized from graphite powder by the Tour method [4]. Briefly, 1.0 g graphite powder is added into 100 mL of a mixture of concentrated H_2SO_4 and H_3PO_4 (volume ratio is 9:1) under vigorous stirring. Then 6.0 g $KMnO_4$ is added slowly. The oxidation reaction is carried out at 50 ^oC with continuous stirring for 12 h. After that, 100 mL 30% H_2O_2 is added to the mixture, and the suspension is centrifuged and washed several times with distilled water until the supernatant pH value is 7. The obtained gel GO is used directly for the ink preparation with a concentration of 8 mg/mL.

Prepare 20 mL GO concentration of 8 mg/mL, and add 1 M AA solution with a volume of 220 µL (corresponding to 10% wt. compared with GO). Add benzophenone with 1% wt. compared to AA one-hour ultrasound receives GO/AA ink.

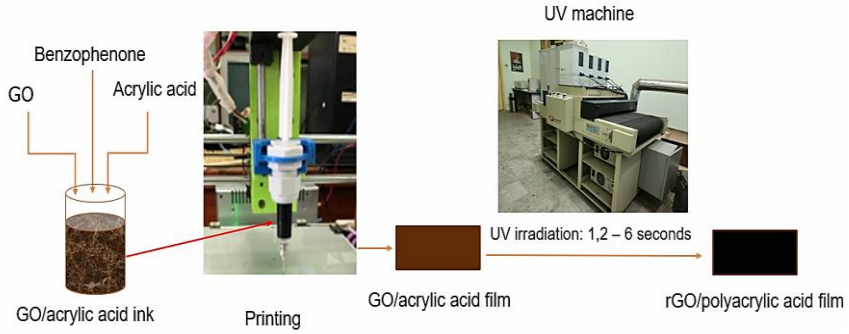

Figure 1. *Schematic illustration of rGO/PAA electrode using homemade DIW printer.*

GO/AA ink is directly printed onto a graphite paper substrate with a size of 10×20 (mm)

by using a homemade Direct ink writing (DIW) printer to form thin film electrodes. The DIW drawing process is the same as in previously published articles [5, 6]. The obtained GO/AA film is further UV irradiation treated using the FUSION UV device model F 300S (USA) at the Institute for Tropical Technology. The wavelength is 365 nm, the intensity is 250 mW/cm^2, and the band speed is 5 m/min with a projection time of 1.2 seconds. The duration of the UV radiation measurements was 1.2, 3.6, and 6.0 seconds. UV irradiation is used to reduce GO into rGO and polymerize AA into PAA. The obtained rGO/PAA electrode is washed with distilled water multiple times to remove any excess reactants and kept for drying in the air.

Electrochemical measurements

The electrochemical properties of prepared electrodes were studied by cyclic voltammetric (CV) method in 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ redox solution, scanning potential from -0.4 V to +1.0 V, scan rate of 50 mV/s, 10 cycles.

The capacitance properties of the electrode are investigated by CV and galvanostatic charge/discharge curves (GCD) in H_2SO_4 1 M solution. The specific capacitance C_s (F/g) is calculated from cyclic voltammetry, according to the following equation [1]:

$$C_s = \frac{\int_{V1}^{V2} I(V)dV}{\nu(\mathrm{V2}-\mathrm{V1})\mathrm{m}} \quad (1)$$

where *v* is the scan rate (mV/s), *m* is the mass of the active materials (g), and *(V2-V1)* is the potential window. The integral part in the numerator gives the area under the CV curve.

The specific capacitance is also calculated from the GCD curve using the following equation [1]:

$$C_s = \frac{I.\Delta t}{m.\Delta V} \quad (2)$$

where *I* (A) is the discharge current, Δt (s) is discharge time, ΔV (V) is the potential window, and *m* (g) is the mass of the active materials.

Capacity retention is evaluated after 5000 continuous charge-discharge cycles at a current of 5 A/g.

3. RESULTS AND DISCUSSION

3.1. Effect of time UV irradiation

The production of the GO/AA composite film involves the utilization of DIW technology, followed by exposure to UV irradiation at varying time intervals of 1.2, 3.6, and 6.0 seconds. When exposed to UV light, GO undergoes reduction to form rGO, while AA polymerization to form PAA. The performance of this procedure was evaluated indirectly through the measurement of the cyclic voltammetry (CV) method in a redox reversible solution containing 5 mM $K_3[Fe(CN)_6]/K_4[Fe/(CN)_6]$, with a scan rate of 50 mV/s. This is a common method for evaluating the electrochemical properties of material electrodes. CV results of the GO/AA composite film at various UV exposure times are shown in figure 2.

It can be seen from figure 2 that the GO/AA film exhibits a low redox intensity and lacks clarity in the absence of UV irradiation (line a). Following UV projection, GO undergoes a reduction process, resulting in improved electrical conductivity. The redox

pairs of peaks exhibit a distinct sharpness, and the current intensity increases as the projection duration progresses raise. Nevertheless, when exposed to UV irradiation for 6.0 seconds (line d), the current intensity is less than the case of the 3.6 seconds (line c). The composite film blistered and peeled off the substrate due to excessive exposure to UV light. In addition, figure 3 shows that the composite film remains flat and adherent after exposure to UV for 3.6 seconds, but in the case of 6.0 seconds, it has undergone a peeling process. On the other hand, after 3.6 seconds of irradiation, GO film was expelled and detached from the substrate. Therefore, the combination of GO with AA and benzophenone has resulted in the formation of PAA, which enhances the adherence to rGO with substrate. From these results, a UV exposure time of 3.6 seconds was chosen to create the film.

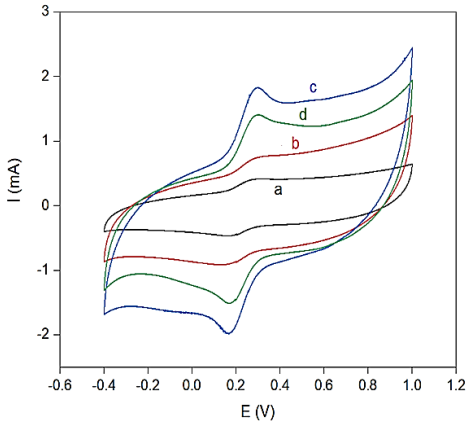

Figure 2. *CV results of GO/AA composite film in $K_3[Fe(CN)_6]/K_4[Fe/(CN)_6]$ 5 mM solution with the time UV irradiation of 0 (a); 1.2 (b); 3.6 (c) and 6.0 seconds (d).*

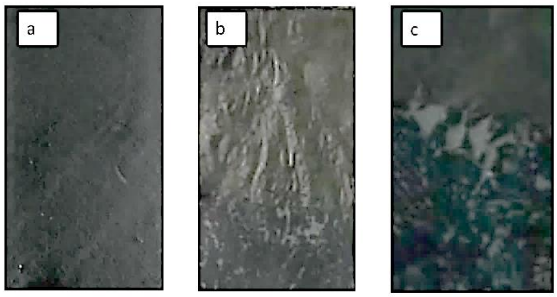

Figure 3. *Image of GO/AA composite film after UV irradiation of 3.6 (a), 6.0 seconds (b), and GO film after UV irradiation of 3.6 seconds.*

3.2. Characterization of rGO/PAA composite film

FT-IR spectra

The chemical structure of printed composite films before (GO/AA) and after UV irradiation (rGO/PAA) were characterized by FT-IR spectroscopy and presented in figure 4. The film of pristine GO, AA has also been printed and analyzed for comparison.

It can be seen that on the FT-IR spectrum of the GO/AA composite printed film appears the absorption peak characteristic of AA structure, at 1702 cm^{-1}, 1614 cm^{-1}, and 1408 cm^{-1}, which are respectively assigned to the C=O, C=C, and C-C stretching vibrations. The peak at 1299 cm^{-1} and 1056 cm^{-1} corresponds to the O-H bending out of the plane and the peaks at 1188 cm^{-1} are attributed to the C-C bending vibration. Moreover, the peaks at 977 cm^{-1} and 807 cm^{-1} are attributed to the $=CH_2$ and C-H bending vibration, respectively. On the other hand, we also found two characteristic absorption bands of GO structure, at 1023 cm^{-1} and 1614 cm^{-1}, which are respectively assigned to the C=O and C=C stretching vibrations. FT-IR spectrum of rGO/PAA film represents the characteristic absorption bands of PAA: the peak at 1614 cm^{-1} is now shifted to 1616 cm^{-1}, related to the C=C bond and the intensity has decreased considerably; the peak at 1188 cm^{-1} attributed to the C-C bond has also increased strongly. These results show that AA underwent successful polymerization to form PAA according to the diagram shown in figure 5.

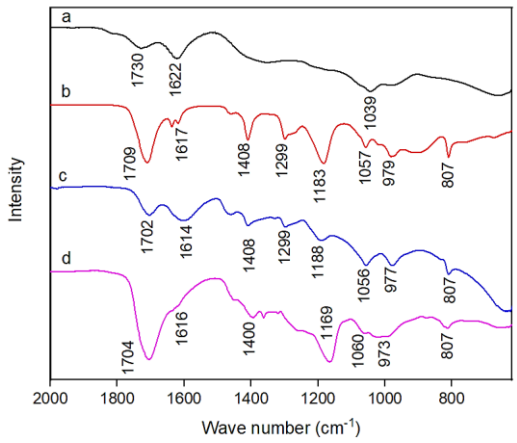

Figure 4. *FT-IR spectra of GO (a), AA (b), GO/AA composite (c), and rGO/PAA composite (d).*

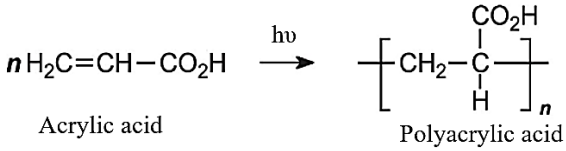

Figure 5. *The diagram polymerization of PAA .*

EDX spectra

The components of GO/AA and rGO/PAA composite film have also been analyzed using the X-ray energy spectroscopy (EDX) method, the results as shown in figure 6.

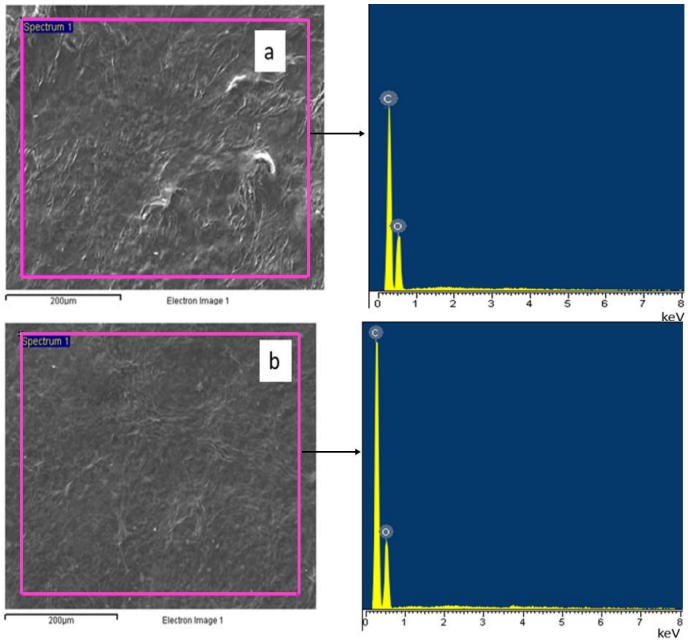

Figure 6. *EDX spectra of GO/AA composite (a) and rGO/PAA composite (b).*

The EDX spectrum indicates the presence of C and O, with peaks appearing at 0.27 and 0.52 keV, respectively. The mass and atomic percentages of the elements are also averaged from five different points and presented in table 1.

Table 1. *EDX elemental analysis of material.*

Sample	Element	% Atomic	% Weight
GO/AA	C	54,23	58,14
	O	45,77	41,86
rGO/PAA	C	65,25	69,83
	O	34,75	30,17

The results in table 1 show that after UV irradiation, the ratio of element O decreased from 41.86% to 30.1%, demonstrating the success of the GO reduction process. The surface of the GO contains oxygen function groups such as hydroxyl (OH) and epoxy (C_2O) that can be removed by UV radiation [7]:

$$(COH)_x + h\nu \rightarrow C_x + x\ OH\cdot$$
$$2\ OH\cdot \rightarrow H_2O + O\cdot$$
$$C_xC_2O + h\nu \rightarrow C_{x+1} + CO$$
$$C_x\,(COOH)_4\ h\nu \rightarrow C_{x+2} + 2CO + 2H_2O$$

3.3. Electrochemical properties

The electroactivity of the rGO/PAA film has been evaluated by the CV method in 1 M H_2SO_4 solution, between –0.4 and +1.0 V (*vs.* SCE) with a scan rate from 5 to 150 mV/s, the results are presented in figure 7A and figure 7B.

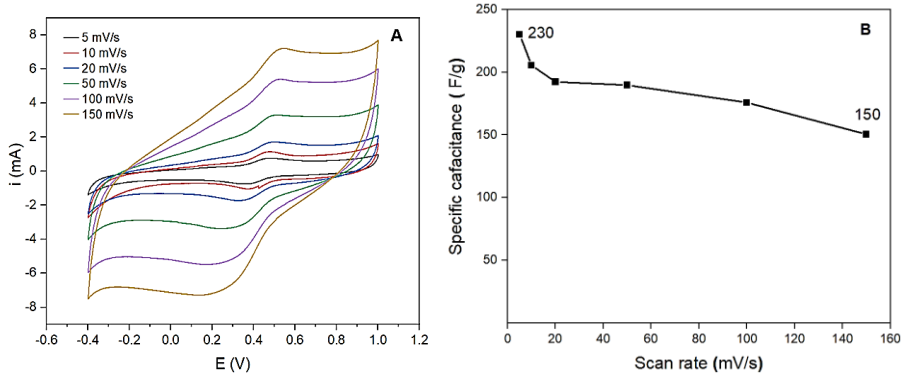

Figure 7. *CV curves in 1 M H_2SO_4 solution of rGO/PAA at different scan rates (A) and specific capacitance depend on the scan rate (B).*

It can be observed from figure 7A that the obtained CV curves are characteristic of both electric double-layer capacitors and pseudo-capacitors. The CV line also remains rectangular at a high scan rate, which is characteristic of a double-layer graphene capacitor. At the start of the negative scan from +1,0 V to -0,4 V, the H^+ ion moves to the surface of the electrode, where it undergoes absorption and subsequent diffusion into the internal pores of the material, forming a double layer of electricity. When scanned in reverse direction, from -0.4 V to +1.0 V, the H^+ ion is desorbed and diffused out of the pores. On the CV, we observed that the redox peaks appeared around +0,5V/+0,3V, which is characteristic of the carboxylic reaction in the composition of PAA [8]. The specific capacitance of the material is determined from the CV line and shown in figure 7B. The results show that the capacity of the composite rGO/PAA decreases as the scan rate increases. At a scanning rate of 5 mV/s, the C_s reach 230 F/g and drop to 150 F/g at a scan rate of 150 mV. The decrease of C_s is explained by the limitation of the diffusion of ions in

the electrolyte solution. At a low scanning rate, the ions of the electrolyte disperse and insert into most of the holes, and electronics exchange occurs at many locations. When the scan rate increases, this process decreases efficiency, resulting in a decrease in the capacity.

Figure 8A and figure 8B present the results of measuring GCD curves for rGO/PAA composite with varying current densities from 1 to 5 A/g. Results indicate that GCD curves exhibit characteristics of combined double-layer capacitance and pseudo-capacitance. A linear is characteristic of a double-layer capacitor, and a non-linear is an attribute of a pseudo-capacitor. Figure 8B displays the calculated specific capacitance obtained from the GCD measurements. At a low current density of 1 A/g, the C_s reaches 321 F/g and decrease to 175 F/g at a current density of 5 A/g. As the current density increases, the specific capacity also decreases because the ions only have time to diffuse into a thin surface layer outside the electrode, not enough time to diffuse inside the material. The high current density also prevents the ions from dispersing out of the material, which can cause blockage inside the material structure.

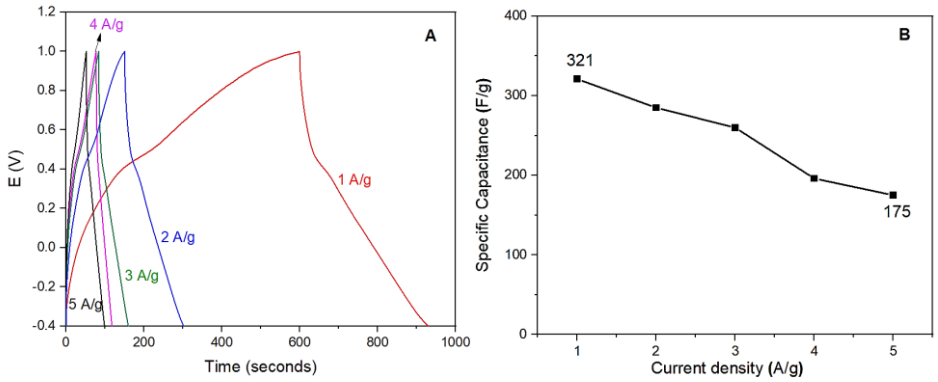

Figure 8. *GCD curves of the rGO/PAA electrode at various current densities (A). The plot of specific capacities vs. current densities (B).*

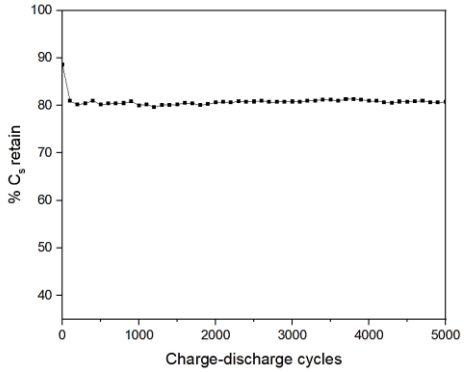

Figure 9. *Cyclic stability of the rGO/PAA electrode tested for continuous 5000 charge-discharge cycles at a current density of 5 A/g.*

The durability of the composite electrode was evaluated by examining the decrease in specific capacitance over multiple charge-discharge cycles at a current density of 5 A/g. Results shown in figure 9 demonstrate that the rGO/PAA electrode retained 82% of its specific capacitance initial value after 5,000 cycles. This finding indicates that rGO/PAA synthetic compound film by 3D printing combined with UV irradiation has the potential application for supercapacitors.

4. CONCLUSIONS

The rGO/PAA composite film is synthesized utilizing a 3D printing technique with GO/AA ink and a combination of UV irradiation. The FT-IR and EDX, spectral analysis results, demonstrate that GO was reduced to rGO following UV exposure, and AA was polymerized to PAA. CV measurements in $K_3[Fe(CN)_6]/K_4[Fe/(CN)_6]$ solution indicated that the UV radiation time of 3.6 seconds is most suitable for creating composite film. The composite film is applied as an electrode for a supercapacitor with a specific capacitance value of 321 F/g at 1 A/g density, and the C_s value is 82% after 5000 charge-discharge cycles at 5 A/g density.

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TÓM TẮT

Chế tạo điện cực rGO/polyacyrlic acid sử dụng kỹ thuật in 3D vẽ mực trực tiếp kết hợp với bức xạ UV

Bài báo nêu kết quả tổng hợp màng composite rGO/PAA bằng kỹ thuật in 3D vẽ mực trực tiếp sử dụng mực in từ hỗn hợp GO/AA và bức xạ UV. Kết quả cho thấy sau thời gian chiếu UV 3,6 giây GO được khử thành rGO và AA được trùng hợp quang hóa thành PAA. Vật liệu sau tổng hợp được đặc trưng tính chất bằng phổ hồng ngoại (FT-IR), tán xạ năng lượng tia X (EDX) và kỹ thuật quét thế vòng đa chu kỳ (CV), phương pháp nạp-phóng dòng tĩnh (GCD). Màng composite được khảo sát khả năng ứng dụng làm điện cực cho siêu tụ điện. Ở mật độ dòng 1 A/g, điện cực có điện dung riêng đạt 321 F/g và và duy trì được 82% giá trị điện dung ban đầu sau 5000 chu kỳ nạp-phóng ở mật độ dòng 5 A/g.

Từ khoá: Composite; Graphen oxit; Polyacyrlic axit; Siêu tụ điện.