

Lignin-based Biochar/graphene Oxide Composites as Supercapacitor Electrode Materials

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Abstract. The lignin-based biochar/graphene composites were effectively obtained via an easy and rapid co-precipitation method. The chemical structure, microstructure, electrochemical properties of lignin/graphene oxide composites before and after carbonization were investigated by Fourier transformation infrared spectrum (FTIR), Scanning electron microscope (SEM), x-ray diffraction (XRD) and cyclic voltammetry (CV). FTIR results confirmed that the oxygen-containing groups of lignin, GO and their composites were partly removed after 800 °C carbonization and GO had a positive impact on the formation of graphitic structure for lignin. XRD results showed that lignin could completely block the restacking of GO sheets. The electrochemical test presented that lignin/graphene oxide composites exhibited a typical CV curve and the specific capacitance reached ~103F/g at a scan rate of 20mv/s.

1. Introduction

Recently, graphene has attracted many attentions in such application area as energy storage, gas molecular sensors, fuel battery, etc., due to its superb characteristics of chemical stability, high electrical conductivity ($\sim 10^6$ S/m), and large specific surface area (~ 2630 m²/g). More importantly, its theoretical capacitance is up to 550 F/g, showing a huge potential in supercapacitors as electrode materials.[1] However, it is extremely difficult to realize such high capacitance because single-layer graphene is prone to restacking with each other via strong Van der Waals interactions. Currently, an effective way to improve the capacitance is building 3D carbon-based structure via the combination of 2D graphene with 0D or 1D carbon materials to prevent its self-aggregation.[2] This can maintain high specific surface area and porous constructions, thereby providing more high-speed electronic and ionic channel of transmission for capacitors. It has been reported that the incorporation of carbon-based materials such as carbon nanotube (CNT), carbon black, biomass-derived carbon materials, into graphene can easily form a stable three-dimensional network and effectively increase the interlayer spacing of graphene. Among these carbonaceous materials, biochar from the carbonization of biomass resources exhibits more advantages in cost, environmental protection and renewability. Therefore, biochar/graphene composites have received many interests from researchers.[3] Lignin, as the second most renewable resource after cellulose and by-products of pulping and paper industry, is regarded as one of the most promising biopolymers. But the complex chemical and physical structure of lignin seriously hinders its progress of industrial applications. Lignin is natural polyphenolic material which contains a high content of carbon elements (40-60 wt %). Hence, many efforts have been focused to convert lignin into a high value carbonaceous material such as carbon fiber, carbon black and active carbon.[4] It is noted that lignin can be mixed with graphene oxide (GO) at any ratio in alkaline



solution, and stabilize reduced GO via π - π interactions.[5] This makes it possible to prevent GO from restacking during co-precipitation and carbonization process. In return, GO may render lignin a special morphology and electro chemical properties. There is no doubt that lignin is a low-cost, non-toxic and high efficiency modifier for graphene as supercapacitor electrode materials.

2. Materials and methods

2.1. Preparation of lignin/graphene oxide (Lignin-GO) composites

80 g alkaline lignin was dispersed into 320 ml deionized water. Then a small amount of NaOH was added into the lignin solution to adjust pH to 12.5. After that, 80 ml GO solution with GO concentration of ~ 5 mg/ml was mixed in aforesaid solution and stirred under room temperature for 1h, followed by ultrasonic treatment for 20 min. The pH of mixture solution was adjusted to 2.7 by 5wt % H_2SO_4 , and then the mixture solution was heated to 90°C for 1 h of flocculation. Finally the hot mixture solution was filtered and washed by deionized water for five times, followed by drying in an oven at 40°C for 48 h.

2.2. Carbonation

Lignin, dried GO powder and Lignin-GO composites were placed into a chamber furnace and heated to 800°C with the protection of nitrogen at heating rate of $10^\circ\text{C}/\text{min}$. Those carbonized samples are named as C-Lignin for lignin, C-GO for GO and C-Lignin-GO for lignin-GO composites, respectively.

2.3. Methods

FTIR spectra of the samples were analysed using a Nicolet-6000 spectrometer (America). XRD analysis was carried out on a Bruker-D8 ADVANCE and DAVINCI DESIGN diffractometer (Germany). SEM images were determined on a Philips-FEI sirion 200 microscope (Netherlands). Electrochemical measurements were tested on a CHI900C electrochemical working station (Shanghai).

3. Results and Discussion

Figure 1 shows the FTIR spectra of graphite, GO, C-GO, lignin, C-Lignin, Lignin-GO composites and C-Lignin-GO. As shown in Figure 1B, graphite showed no absorption peaks in all observed range. However, after oxidation of graphite, a series of oxygen-containing absorption peaks appeared in the sample of GO, such as $-\text{OH}$ ($\sim 3400\text{ cm}^{-1}$), $\text{C}=\text{O}$ (1720 cm^{-1}) and $\text{C}-\text{O}$ (1176 cm^{-1} , 1070 cm^{-1} and 1010 cm^{-1}). After carbonization of GO, an obvious decrease in the peak intensity of oxygen-containing groups was observed in the sample of C-GO. This indicated the loss of oxygen-containing groups after 800°C carbonization. But, the absorption peaks of $-\text{OH}$ and $\text{C}-\text{O}$ groups were existed in C-GO, suggesting the incomplete reduction of GO. Lignin showed abundant absorption peaks of various groups, such as $\text{C}=\text{O}$ of carboxylic and carbonyl groups (1710 cm^{-1}), $\text{C}=\text{C}$ of benzene ring skeleton (1604 cm^{-1}) and $\text{C}-\text{O}$ of aromatic and aliphatic ether (1218 cm^{-1} , 1117 cm^{-1}), as shown in Figure 1B. Similarly, after 800°C carbonization, the absorption peak of $\text{C}=\text{O}$ almost disappeared, and an overlapped absorption band of $\text{C}-\text{O}$ bonds at $1000\text{--}1250\text{ cm}^{-1}$ was observed in C-lignin. Regarding Lignin-GO composites, the FTIR spectra showed a very similar profile as pure lignin, due to the high lignin content in Lignin-GO composites. It is interesting that C-Lignin-GO exhibited different spectra from C-lignin and C-GO. Especially, the vibration of benzene ring skeleton for C-Lignin-GO composites located at 1556 cm^{-1} , while it was 1623 cm^{-1} for C-Lignin and 1564 cm^{-1} for C-GO. This suggested that GO facilitated the carbonization of lignin to form more $\text{sp}^2\text{ C}$ atoms.

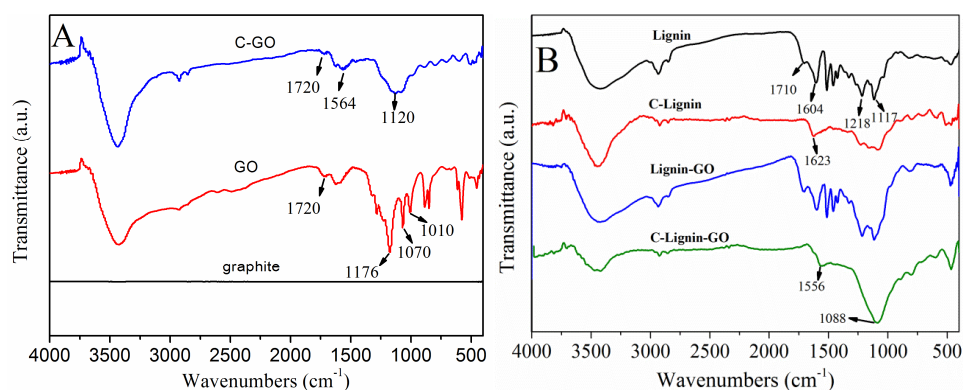


Figure 1. FTIR spectra of graphite powder, GO and C-GO (A); FTIR spectra of lignin and lignin-GO composites before and after carbonization (B).

Figure 2 shows SEM images and corresponding digital photos of lignin and Lignin-GO composites before and after carbonization. As shown in Figure 2 A1, lignin exhibited a blurry and irregular morphology due to its amorphous characteristic of chemical structure. After carbonization (Figure 2 A2), a bigger micro-meter sized carbon particle with numerous porous structures was found. In fact, these carbon particles were fused with each other to form a free standing bulk with high bonding strength (Figure 2 A3), due to the condensation reaction of lignin during carbonization process. As for Lignin-GO composites, the profile became more clear and some layered structures were observed because of the addition of GO. It was obvious that many lamellar structures appeared in C-Lignin-GO (Figure 2 B2) after carbonization, which very differed from the morphology of C-Lignin. This indicated that GO affected the carbonization behaviour of lignin. Furthermore, the carbon particles of C-Lignin-GO composites were loosely accumulated together, as shown in Figure 2 B3.

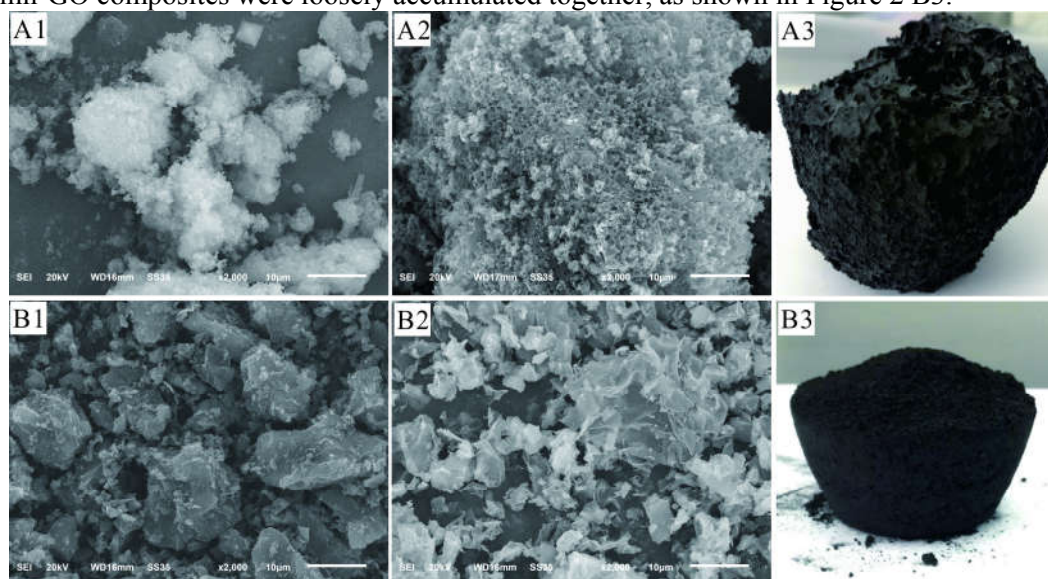


Figure 2. SEM images of lignin before (A1) and after carbonization (A2), Lignin-GO composites before (B1) and after (B2) carbonization, and the corresponding digital photos of C-Lignin (A3) and C-Lignin-GO (B3) composites.

Figure 3 presents the XRD patterns of graphite, C-Lignin and C-Lignin-GO. Graphite showed a sharp diffraction peak at $2\theta = 26.5^\circ$, corresponding to the interlayer spacing of 0.336 nm. This was well consistent with the theoretical interlayer spacing of graphite with perfect graphitic structure. The XRD pattern of C-Lignin showed two wide diffraction peaks at $2\theta = 26^\circ$ and 44° . They were assigned to the diffractions from the (002) plane and (100/101) plane of graphited carbon structure, respectively. This indicated that lignin could form a small amount of graphitic framework to enhance its conductivity. Interestingly, C-Lignin-GO showed an almost duplicated XRD pattern as C-Lignin did.

Furthermore, no intense diffraction peaks were found in the profile. This sufficiently confirmed that lignin could prevent GO from restacking during co-precipitation and carbonization process.

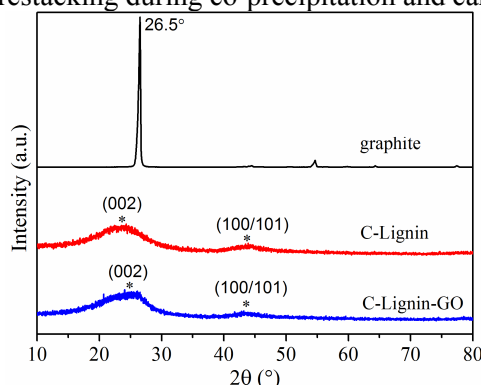


Figure 3. XRD patterns of graphite, C-Lignin and C-Lignin-GO.

Figure 4 shows the CV curves of C-Lignin and C-Lignin-GO at scan rates of 5 mV/s, 10 mV/s, 20 mV/s, 50 mV/s, 100 mV/s, 150 mV/s, 200 mV/s. The almost rectangular CV curves can be observed, revealing a typical electrical behaviour of double layer capacitor. With the increase of scan rate, the shape of CV curves become less rectangular, which may be owing to the complete infiltration of electrolyte ions into porous structures at low scan rate. As the incorporation of GO, the integral area of CV curve become bigger due to the high specific surface area and excellent electrical conductivity. The specific capacitance of C-Lignin-GO was calculated to be 103 F/g at a scan rate of 20 mV/s.

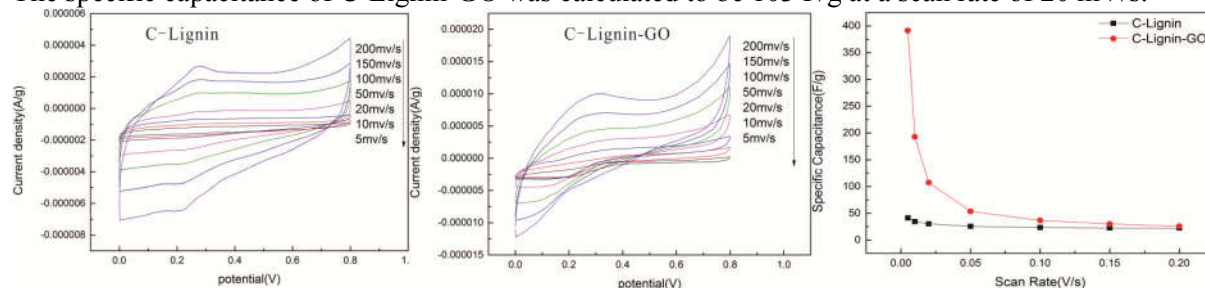


Figure 4. CV curves of C-Lignin and C-Lignin-GO and specific capacitance at different scan rate.

4. Conclusions

Lignin-GO composites were successfully prepared by a simple co-precipitation method. The Carbonized lignin-GO composites showed a high specific capacitance as electrode materials, due to the strong lignin-GO interactions to prevent GO from restacking.

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