Synthesis and characterization of MnO2/Eggplant carbon composite for enhanced supercapacitors

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ARTICLE INFO

Keywords:
MnO2
Eggplant carbon
Hydrothermal
Supercapacitor

ABSTRACT

In this paper, the eggplant carbon (EC) was derived from eggplant skin by one-step carbonization method. Subsequently, the MnO2/eggplant carbon (MnO2/EC) composite was prepared via in-situ hydrothermal method. The morphology and structure as well as electrochemical performance were investigated through a series of characterization and tests. The results showed that the urchin shaped structures of MnO2 was successfully loaded on the surface of EC. The electrochemical studies indicated that the specific capacitance of the MnO2/EC composite could reach 652.5 F/g at 0.5 A/g in 1 M Na2SO4 aqueous electrolyte. In addition, the MnO2/EC composite exhibits excellent cyclic stability after 10000 cycles, which might be ascribed to the synergistic effect of MnO2 and EC for the improvement of electrochemical performance. Taken together, this work demonstrated that MnO2/EC composite can be used in the aspect of energy storage for high-performance supercapacitors.

1. Introduction

Over the past decades, in face of the excessive consumption of fossil energy and increasingly severe energy supply as well as environment pollution problem, developing sustainable and ecofriendly energy have become very urgent [1, 2, 3]. As the next-generation energy storage device, supercapacitors have much higher energy storage capacity and power density than traditional physical capacitors [4, 5, 6]. As is well known, the pseudo capacitor store charges via the redox process, which can provide a higher energy density in the faster charge-discharge than electrical double-layer capacitor (EDLC) [7, 8, 9].

The electrode materials of supercapacitors play an important role in the energy storage [10, 11]. At present, high performance electrode materials include carbon-based materials [12], transition metal oxides [13] and conductive polymers [14]. Among the various transition metal oxides, MnO2 is an ideal charge storage material for electrochemical supercapacitors [15], because it has the advantages of high theoretical ratio (up to 1370 F/g), low cost, low toxicity and environmental friendliness [16, 17]. However, its electrical conductivity, stability and proton diffusion ability is poor, which can not meet the high-performance requirement of the supercapacitor [18, 19, 20]. In order to improve this situation, the carbon material has been used to prepare the MnO2-based composites, which effectively improves its electrochemical performance [21, 22]. At present, carbon materials such as activated carbon, graphene and carbon nanotubes are widely used in MnO2-based composites due to their high specific surface area, excellent electrical conductivity, unique internal structure and well thermal stability. Fu [23] reported the symmetrical supercapacitors, yielding specific capacitances of 616.3 and 481.4 F/g at 1 and 10 A/g, respectively. However, the preparation process of these carbon materials is complex and the cost is relatively high [24, 25]. Therefore, several biomass carbon materials have been developed and exhibited excellent electrochemical performance [26]. In addition, biomass carbon materials have the advantages of renewable, low cost and environmental protection [27]. Various biomass resources such as peanut shell [28], bamboo bagasse [29], sugarcane bagasse [30], egg white [31], corn silk [32], rice husk [33], pomelo peel [34] and onion [35] have been reported as the carbon precursors for supercapacitor applications. Meanwhile, the combination of biomass carbon and manganese dioxide to improve the electrochemical properties of materials has been widely studied. WU [21] obtained a two-dimensional carbon sheet composed of a large number of mesoporous and microporous structures through acid treatment and pyrolysis carbonization of cucurbit-based biomass. The specific surface area was as high as 1 308 m2/g, and the ideal pore volume was 0.84 cm3/g. When the current density was 1 A/g, the specific capacitance was 273 F/g. When the current density gradually increases from 1 A/g to 50

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https://doi.org/10.1016/j.heliyon.2022.e10631
Received 16 March 2022; Received in revised form 1 June 2022; Accepted 8 September 2022
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indicating this new material can be utilized in the field of energy storage.

In this work, we select the eggplant skin as carbon precursor, which can be facilely converted into carbon nanosheets via simple carbonization. Then, designed a simple synthetic route for synthesis of MnO2/EC composite utilized as the electrode material for supercapacitors. More-dried eggplant skin was calcined at 500°C in a glovebox. Finally, the MnO2/EC composite was synthesized by a hydrothermal method. 3.1. Preparation of eggplant carbon

The fresh eggplant skin was firstly cut into small pieces. Next, the eggplant skin pieces were dried by a freeze-drying technique. Finally, the dried eggplant skin was calcined at 500°C for 2 h in N2 flow to obtain carbonized eggplant carbon.

2.2. Preparation of MnO2/EC composite

The MnO2/EC composite was synthesized by a hydrothermal method. In a typical preparation: 3.95 g KMnO4, 0.25 g eggplant carbon, 4mL H2SO4 and 75 mL distilled water were mixed to form a homogeneous solution under magnetic stirring. The mixture was transferred into a Teflon-lined stainless steel autoclave and maintained at 120°C (see Scheme 1). Pure MnO2 was also prepared in the absence of EC. After the EC and MnO2 being composited, the MnO2/EC composite shows another two broad diffraction peak near 28°, which corresponds to the carbon peak. The results confirm that the composition of EC and MnO2 under hydrothermal condition.

3. Results and discussion

3.1. Characterization of phase structure

3.1.1. XRD analysis

The XRD patterns of the MnO2 and MnO2/EC composite are shown in Figure 1(a). According to the pure MnO2 pattern, there are three major diffraction peaks appearing at 12°, 37° and 65°, which can be indexed to (001), (111) and (020) crystal face of birnessite-type MnO2 (JCPDF No. 42-1317), respectively [38]. For the MnO2/EC composite, the peaks appear at 12°, 37° and 65° confirming the crystal face of MnO2 is not changed with addition of EC. Moreover, the XRD patterns of the MnO2/EC composite shows another two broad diffraction peak near 28° and 42°, which corresponds to the carbon peak. The results confirm that the composition of EC and MnO2 under hydrothermal condition.

3.1.2. Raman analysis

The specific structure nature of the EC, MnO2 and MnO2/EC was investigated by the Raman spectroscopy, as shown in Figure 1(b). Typically, both EC and MnO2/EC composite exhibit two dominant Raman peaks at 1347 cm⁻¹ and 1589 cm⁻¹, which can be assigned to the D band (corresponding to the disordered carbon) and G band (corresponding to the graphitic carbon), respectively. Besides, compared with the EC sample, we can see that MnO2 has an obvious characteristic peaks centered at 646 cm⁻¹, which can be assigned to the Mn-O lattice vibration. After the EC and MnO2 being composited, the peak belonging to Mn-O vibrations is still observed at 646 cm⁻¹ and the peaks belonging to EC are not changed.
3.2. Spectroscopy analysis

Fourier transform infrared analysis was utilized to investigate the surface functional groups of MnO₂ and MnO₂/EC composite. As shown in Figure 1(c), the characteristic absorption peaks of MnO₂ appear at 523 cm⁻¹, which can be attributed to the Mn-O vibrations, and two prominent absorption peaks at 1392 cm⁻¹ and 1626 cm⁻¹ correspond to the stretching vibration of O-H on Mn atom. The broad absorption bands at 3432 cm⁻¹ can be assigned to the O-H stretching vibration [33]. In comparison with MnO₂, the absorption peak at 1098 cm⁻¹ in the MnO₂/EC spectrum corresponds to the C-O stretching vibration. Similar vibration absorption peaks at 1626 cm⁻¹ and 523 cm⁻¹ are caused by the O-H stretching vibration and Mn-O bond vibration, respectively. Combined with XRD, SEM, Raman spectral and FTIR analysis, the results indicated that the MnO₂ has been successfully incorporated with EC backbone.

3.3. The surface morphology

The morphology and surface structure of the as prepared materials were characterized in terms of SEM as shown in Figure 2(a) and (b), the corrugated paper-like morphology of EC was clearly observed, which is ideal for loading the metal oxide [37]. As shown in Figure 2(c) and (d), interconnected nanorods are self-assembled to form the urchin-like architecture of MnO₂. For the MnO₂/EC composite, the urchin-like architecture of MnO₂ is well coated on EC sheets as shown in Figure 2(e) and (f). It could be expected that such an intimate interfacial contact for the MnO₂/EC would favor the electronic transport, thus leading to the improvement of the supercapacitor performance.

The TEM image of MnO₂/EC nanomaterials is shown in Figure 3(a), which further confirms the morphology of nanorods. Figure 3(b) further reveals the TEM image of MnO₂/EC at high resolution, and show that the lattice spacing of 0.357 nm for MnO₂ (002) face according to JCPDF data.

3.4. Thermal stability

The thermal stability of MnO₂ and MnO₂/EC composites were studied by TGA as shown in Figure 4. The initial weight loss of MnO₂ is 8 %, which due to the dehydration of the sample before 200 °C. A little weight loss in the range of 500–550 °C can be ascribed to the loss of oxygen in the lattice, which leads to phase transformation from MnO₂ to Mn₂O₃ [39]. TGA diagram of MnO₂/EC composite shows a slight weight loss.
about 2\% when the temperature rises to 200 °C, which can be contributed to the removal of adsorbed water or crystalline hydrate \[23\]. In addition, the weight loss observed in the range of 200–500 °C is the combustion of carbon catalyzed by MnO₂, and with the temperature increase, residual carbon underwent combustion and the crystalline transformation of MnO₂ will occur. The results show that the stability of MnO₂/EC composite is higher than that of MnO₂.

3.5. Electrochemical properties

Figure 5 shows the electrochemical properties of the composites in a three-electrode system. The curves of CV and GCD were measured under the potential windows of -0.2–0.8 V in 1M Na₂SO₄ electrolyte. The CV curves of EC, MnO₂ and MnO₂/EC composites exhibit rectangular-like shape at a scan rate of 25 mV/s as presented in Figure 5(a). And the curves closure area of MnO₂/EC composite is much larger than pure EC and MnO₂, indicating the superior electrochemical performance of MnO₂/EC composite. This is due to the synergistic effect between EC and MnO₂ in the composite, which to some extent promotes the electrochemical performance. At the same time, the charge-discharge time of MnO₂/EC composite is longer than pure EC and MnO₂, indicating the superior electrochemical performance of MnO₂/EC composite. This is due to the synergistic effect between EC and MnO₂ in the composite, which to some extent promotes the electrochemical performance. At the same time, the charge-discharge time of MnO₂/EC composite is longer than pure EC and MnO₂, as shown in Figure 5(b). According to Eq. (1), the \( C_i \) of the EC, MnO₂ and MnO₂/EC composite are 134.2 F/g, 400.5 F/g and 652.5 F/g at current density of 0.5 A/g, respectively. The specific capacitance of MnO₂/EC composite is nearly five times as much as that of carbon material. This means that the composites have excellent capacitance rate and high coulombic efficiency. Figure 5(c) presents the CV curves of the MnO₂/EC composites at different scan rates. With the increase of scanning rate, the shape of the curves shows some distortions from the rectangle, which may be due to the polarization of the increase of ion transport and contact resistance between electrolyte and MnO₂ \[40\]. Additionally, the oxidation-reduction peaks in the CV curves of the composites are not obvious, which may be due to the enhancement of the electrical conductivity of the materials after the addition of EC, and the rapid reversible conversion of manganese ions between different valence states. As shown in Figure 5(d), the GCD curves of MnO₂/EC composite at different current densities are almost symmetric with slight deformation, which illustrated the pseudocapacitive along with the electric double-layer contribution. The relationship between specific capacitance and current density are presented in Figure 5(e). The specific capacitance for all samples decreases with the increasing of current density. Significantly, the specific capacitance of MnO₂/EC composite remained 229 F/g even at a high current density of 10 A/g, this value is still larger than that of the EC and MnO₂. This result suggests that the MnO₂/EC composite possesses a high rate of capacitance, which is recognized as one of the most essential electrochemical properties for supercapacitor application.

3.5.1. Long-term cyclic stability

The electrochemical properties of the EC, MnO₂ and MnO₂/EC composite were further studied by EIS as shown in Figure 5(f). The linear curve slope in the low frequency region represents the diffusion resistance of the electrolyte in the electrode surface, while the compressed semicircle in the high frequency region and the intermediate frequency region indicates the charge transfer resistance. It is obvious that in the low frequency region, the EC is an approximate vertical straight line along the virtual coordinates, which indicates its ideal double layer capacitive behavior. The semicircle diameter of MnO₂/EC is smaller than that of pure MnO₂, which indicates that the charge transfer resistance of MnO₂/EC composite is smaller than that of pure MnO₂, and the EC component of MnO₂/EC composite is favorable for electron transport. In addition, in the low frequency region, it can be seen that the slope of the composite electrode MnO₂/EC is much larger than that of pure MnO₂, which means that the MnO₂/EC has a lower diffusion resistance and a faster ion transport speed due to the introduction of the carbon material.

Figure 3. TEM images of MnO₂/EC (a, b).

Figure 4. TGA plots of the MnO₂ and MnO₂/EC.
4. Conclusion

In this paper, we successfully prepared MnO₂/EC composite via in-situ hydrothermal method. The structure and morphology analysis show that the urchin shape MnO₂ was successfully loaded on the fold of the EC surface. The results of electrochemical measurement show that the specific capacitance of MnO₂/EC composite remain 652.5 F/g at 0.5 A/g with a higher cycling stability of 79.2 % after 10000 charge and discharge cycles. This is due to the synergistic effect of MnO₂ and EC, in which MnO₂ provides a higher pseudo-capacitance and EC enhances the overall conductivity of the material, so that the composite has excellent capacitance performance. It is believed that biomass carbon as electrode material has a broad application prospect in new carbon-based composite supercapacitors.

Declarations

Author contribution statement

Xin Wang: Conceived and designed the experiments; Wrote the paper.
Jia Chu: Performed the experiments.
Huijun Yan: Analyzed and interpreted the data.
Hongkun Zhang: Contributed reagents, materials, analysis tools or data.

Funding statement

This work was supported by the Joint Guidance Project of Heilongjiang Provincial Natural Science Fund.

Data availability statement

Data included in article/supplementary material/referenced in article.
Declaration of interests statement
The authors declare no conflict of interest.

Additional information
No additional information is available for this paper.

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