



Carbon quantum dots anchoring MnO₂/graphene aerogel exhibits excellent performance as electrode materials for supercapacitor



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HIGHLIGHTS

- CQDs as the mediation connect MnO₂ and graphene in the composite aerogel.
- The composite aerogel is formed with the 3D net structure.
- MnO₂/CQDs/GA presents an improved electrochemical performance.
- The CQDs and 3D structure are the key factors of its enhanced property.

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ABSTRACT

Manganese oxides/graphene composite material has become regarded as a highly promising electrode material for high-performance supercapacitors. However, some shortages such as low bonding strength and poor stability are faced to solve. In this work, carbon quantum dots serve as the bridge for connecting MnO₂ and graphene, which contribute to synthesize the stable MnO₂/carbon quantum dots/graphene composite aerogel. Due to the connection function of CQDs the stable combinations are formed between MnO₂ nanoparticles and graphene nanosheets. Subsequently, the composite aerogel as-fabricated has the three-dimensional net structure, indicating a large specific surface area and abundant electron transport pathways. The MnO₂/CQDs/GA electrode exhibits excellent electrochemical performance as compared to those of MnO₂/GA and MnO₂/G that are synthesized without the addition of CQDs. This composite electrode displays high specific capacitance of 721 F g⁻¹ at 1 A g⁻¹, good rate capability of 89.2% capacitance retention at 20 A g⁻¹ and remarkable cycle stability of 92.3% capacitance retention after 10,000 at 10 A g⁻¹. Moreover, the MnO₂/CQDs/GA is quite stable and has pre-eminent electrochemical performance, which demonstrates the great potential for the development of high-performance supercapacitors.

1. Introduction

Supercapacitors as one of the emerging energy storage devices have gradually become the research focus in recent years [1–4]. However, present supercapacitors are still unable to completely meet the growing demands for efficient energy storage, which means that it is urgent to design the supercapacitors with high energy density, power density and stability. Manganese oxides (MnO₂) is a promising electrode material for high-performance supercapacitors because of high theoretical specific capacitance (1370 F g⁻¹), wide potential window, abundance and

environmentally benign nature [5–8]. But some drawbacks of MnO₂ such as poor electron conductivity and instability restrict the practical application for these supercapacitors. In order to overcome these shortcomings, enormous efforts have been made in the past decades. Multifarious crystal structure, morphology and composites have been fabricated to improve the electrochemical performance of MnO₂ electrodes [9–13].

Among these designs of MnO₂ electrode materials, carbon materials as the optimal material were used to composite with MnO₂, which have been widely reported in the current study [14–19]. Because of the

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characteristics such as large specific surface area and high conductivity, carbon materials can improve the shortcomings of MnO_2 effectively. In particular, graphene as a one-atom-thick two-dimensional carbon material has attracted intensive attention. It is widely applied in electrode materials of supercapacitors due to its high surface area, mechanical strength, electrical conductivity, stability and low density. In fact, compared to the pristine MnO_2 , it has already been clearly demonstrated that various MnO_2 composites formed with graphene exhibit high specific capacitance and good cycle stability in previous investigations [20–27]. Yao et al. [28] successfully synthesized mesoporous MnO_2 nanosphere/graphene composite displayed excellent electrochemical performance as compared to the pure MnO_2 and graphene. The composite electrode exhibits superior specific capacitance of 466.7 F g^{-1} , remarkable cycle stability of 92% capacitance retention after 2000 at 1 A g^{-1} .

However, it is noticeable that graphene nanosheets are apt to reunite in aqueous solution, which results that the actual specific surface area is much less than the theoretical specific surface area. What's worse, it also leads to less active layer and higher internal resistance. In order to avoid the re-stacking of graphene nanosheets, the three-dimensional net structure graphene aerogel has been assembled. Porous structure of the graphene aerogel is conducive to enlarge the active areas of electrode materials contacted with electrolyte and reduce the internal resistance. Net structure can prevent the nanosheets aggregating effectively. Therefore, the three-dimensional net structure graphene aerogel as supporting material in composite can provide large surface area to load other materials, multiple channels to transport the electrolyte ions and interlaced conductive network [29–35]. However, the weak bonding strength between the rigid inorganic metal oxide, such as MnO_2 , and the graphene leads to less improvements of conductivity and stability. Hence, it is highly desirable to add a stable and firm link between MnO_2 and graphene to fabricate a stable and high-performance MnO_2 /graphene composite material.

Carbon quantum dots (CQDs) as one of the emerging carbon materials attract much attention because of their small size (below 10 nm), various functional groups and photoluminescence properties. CQDs can be well combined with inorganic and organic materials, which are contributed to the enhancing of bonding strength between multiple materials. Current studies indicated that CQDs can be used as the connection of the composite material that presents the excellent and stable electrochemical property [36–42]. Zhang et al. [43] used CQDs to link GO film and polypyrrole, which accelerated the electron transportation and increased the dielectric constant. The synthesized ternary composite exhibited high specific capacitance and cycle stability. All these studies show that CQDs as the link in the composite materials can not only improve the bonding strength among each component of the composites, but can also reduce the internal resistance and charge transfer resistance.

In this work, we synthesized the MnO_2 /carbon quantum dots/graphene composite aerogel (MnO_2 /CQDs/GA) by employing CQDs to connect MnO_2 and graphene. Compared to MnO_2 /graphene composite aerogel (MnO_2 /GA) and MnO_2 /graphene (MnO_2 /G) synthesized in the same conditions just without CQDs, the MnO_2 /CQDs/GA exhibited outstanding electrochemical performance, which indicated that CQDs and the three-dimensional net structure can efficiently improve the conductivity and stability of the composite. The formed three-dimensional net structure can enlarge the contact area with electrolyte and increased the ion diffusion channels. In addition, the added CQDs not only contribute to enhance the bonding strength between MnO_2 and graphene, but also improve the specific capacitance and cycle stability. These advantages can lead to the significant improvement of the capacitive performances of the MnO_2 /CQDs/GA that are constructed with CQDs and 3D net structure.

2. Experimental

2.1. Preparations

The citric acid was used as carbon source to prepare the CQDs by a hydrothermal treatment at 200°C for 4 h, which has been reported in our previous work [44]. The obtained CQDs were well dispersed in 40 mL deionised water under sonication, which the concentration was $125 \mu\text{g mL}^{-1}$.

The CQDs/GA was synthesized by one-step hydrothermal method. Firstly, graphene oxide (GO) was prepared from conductive squama graphite by the modified Hummers' method [45]. Secondly, the homogenous GO aqueous dispersion was formed by dispersing the as-synthesized GO in the as-prepared CQDs solution with ultrasonication for 2 h. Thirdly, the dispersion was transferred into an autoclave and heated at 160°C for 6 h. The hydrothermal reaction products were centrifuged and washed with deionised water for several times. Finally, the CQDs/GA was obtained by freeze-drying for 24 h.

The obtained CQDs/GA were cut into some pieces and added into the deionised water and fully dispersed with stirring. Subsequently, the dispersion was mixed with 5 mM KMnO_4 and heated at 80°C for 4 h. After the reaction finished, the as-synthesized MnO_2 /CQDs/GA was collected via vacuum filtration, washed with deionised water, and freeze-dried. In order to investigate the significant roles played by the CQDs in the composite material, the MnO_2 /GA without CQDs was synthesized with the same conditions and similar procedures. Besides, to investigate the effect of the aerogel structure, the MnO_2 /G was prepared by using the same amount of graphene reacted with KMnO_4 . The graphene was reduced by hydrazine hydrate without the three-dimensional aerogel net structure.

2.2. Characterizations

The X-ray diffraction patterns of the as-prepared MnO_2 /CQDs/GA, MnO_2 /GA and MnO_2 /G were collected by utilizing a Bruker D8 Advance spectrometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The field-emission scanning electron microscopy (FESEM, Zeiss Supra 55) was used to characterize the morphology of the samples. To further investigate the microstructure, the samples were examined by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The specific surface area and the pore size distribution were calculated by using the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method, respectively. To investigate the defects of different samples, a LabRAM HR furnished with 532 nm laser was employed to record Raman spectra.

2.3. Electrochemical measurements

The MnO_2 /CQDs/GA, MnO_2 /GA and MnO_2 /G were used to fabricate the working electrodes. The three samples were pressed to form films by the roller machine, and then the square ($1 \times 1 \text{ cm}^2$) cut from the films was directly pressed on the pre-treated nickel foam. The working electrodes were obtained after drying at 60°C for 12 h in a vacuum oven. The active material loadings were determined by weighing the Ni foam substrate before and after applying the active material, which calculated that about 1.0–2.0 mg of the active materials on the Ni foam was loaded.

A three-electrode system was fabricated with the as-prepared working electrode, counter electrode (Pt foil) and reference electrode (Ag/AgCl). The electrochemistry tests including cyclic voltammetry (CV) and galvanostatic current charge-discharge (GCD) were measured in 1 M Na_2SO_4 aqueous solution.

The symmetrical supercapacitor device was assembled with the two as-prepared electrodes that have the same quality MnO_2 /CQDs/GA (about 1 mg). The MnO_2 /CQDs/GA/ MnO_2 /CQDs/GA symmetrical capacitor was also tested by CV and GCD in a two-electrode system to

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