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MnO_2/reduced graphene oxide composite as high-performance electrode for flexible supercapacitors

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ABSTRACT

In this paper, we reported a facile method to prepare MnO_2/reduced graphene oxide (RGO) composites and examined their applications as electrodes in flexible solid-state supercapacitors. The as-fabricated solid-state device based on these MnO_2/RGO composite electrodes exhibit a good electrochemical performance with an area capacitance of 14 F cm^{-2} at 2 mV s^{-1} and excellent stability.

Flexible solid-state supercapacitors have attracted great attention as promising energy storage device due to increasing energy demands for the portable and wearable electronics [1–3]. Compared with conventional supercapacitors, they have significant advantages such as light-weight, ease of handing, excellent reliability and wider range of operation temperature, which make them very promising for laptops, roll-up displays, cell phones, etc. [4]. Among various electrode materials, MnO_2 have been intensively investigated as electrode materials for supercapacitors because of its ultrahigh theoretical capacitance (1370 F g^{-1}), low cost, abundance and environmentally friendly. Unfortunately, owing to its poor conductivity (10^{-5}–10^{-6} S cm^{-1}), the reported capacitance for MnO_2 is still far away from its theoretical capacitance, especially at high mass loading (>0.1 mg/cm^2). Generally, there are two major strategies to improve the capacitance of MnO_2 electrodes. The first one is to develop the MnO_2 nanostructures with rational morphology and large surface area [5]. A large number of MnO_2 nanostructures including nanorods, nanotubes, nanowires and nanoflowers have been reported for supercapacitors. The other one is to develop MnO_2-based composites by incorporating with high conductive materials. Recently, various composites such as MnO_2/graphene [6], MnO_2/TiO_2 [7,8], MnO_2/Ni(OH)$_2$ [9], and Zn_2SnO_4/MnO_2 [10], have been widely studied as electrode materials for supercapacitors and exhibited enhanced electrochemical performances. Despite these achievements, it is still important but challenging to rationally design and prepare high-performance MnO_2-based composites for supercapacitors.

Recently, graphene has drawn considerable interest for its fascinating properties and wide applications. As a two-dimensional (2D) structure of sp^2-bonded carbon materials, graphene has an ultrahigh surface area of up to 2630 m^2 g^{-1}, and excellent conductivity [11,12]. Up to now, composites of graphene and MnO_2 have been used to improve their capacitance, and remarkable advances have been achieved [13,14]. However, most of the previous studies are mainly focused on single electrodes or aqueous electrolyte supercapacitors. In this paper, we reported the facile synthesis of MnO_2/reduced graphene oxide (RGO) composites and their implementation as high-performance electrode for flexible solid-state supercapacitors. Carbon fabric was here chosen as the substrate mainly due to its cost-effectiveness, high conductivity, and excellent chemical stability. On the other hand, the flexible nature of carbon fabric is also preferable for designing a flexible device.

MnO_2/RGO composites were grown on carbon cloth by one-step electrochemical deposition (Experimental section, ESI). Fig. 1a shows the typical scanning electron microscopy (SEM) image of MnO_2/RGO composites. Obviously, the surface of carbon cloth was covered uniformly by a film of MnO_2/RGO composites. To study the microstructure of the MnO_2/RGO composites, transmission electron microscopy (TEM) was performed. Fig. 2b shows the typical TEM image of the MnO_2/RGO composites, which reveals that these composites are nanosheet-like nanostructures. High resolution TEM (HRTEM) image (Fig. 1c) further confirms that the MnO_2 are decorated homogeneously on the RGO sheets and also indicates that the MnO_2 is amorphous. Energy dispersive X-ray spectroscopy (EDS) analysis was also conducted for the MnO_2/RGO composites. As shown in Fig. S1, besides the Cu signals coming from the TEM grid, Mn, O, and C were detected from the MnO_2/RGO composites, suggesting that the composite is made up of MnO_2 and RGO.

In order to further investigate the chemical compositions of as-prepared MnO_2/RGO composites, X-ray photoelectron spectroscopy

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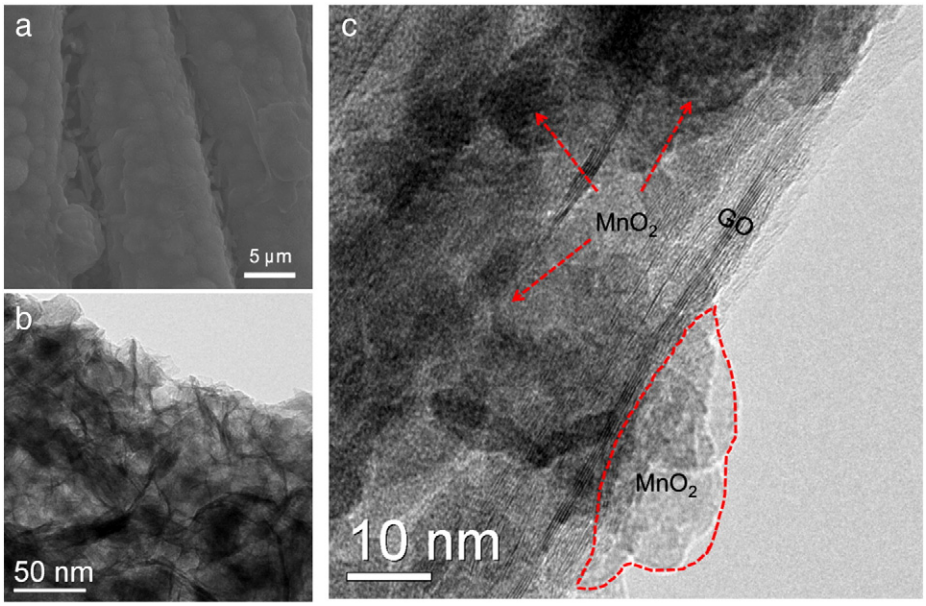

Fig. 1. (a) SEM, (b) TEM and (c) HRTEM images of the MnO_2/RGO composites.

(XPS) analysis was also carried out. Fig. 2a displays the XPS survey spectrum of MnO_2/RGO composites, which confirms the presence of C, O, and Mn in the composite. This result is in agreement with EDS result. Core level Mn 2p spectrum is shown in Fig. 2b. Two peaks at 654.0 and 642.3 eV that correspond to the Mn $2p_{1/2}$ and Mn $2p_{3/2}$ binding energies were observed, which indicates that the Mn ions is +4 [5]. Fig. 1c is the core level C 1s spectrum, which reveals that there are three components of carbon bond, namely C–C (284.9 eV), C–O (258.9 eV) and C═O (287.6 eV) are presented in the composites [13]. Fig. 2d is the core level O 1s spectrum of MnO_2/RGO composites, suggesting the presence of O^{2-} and OH bond [15]. Based on the analyses above, the composites are made up of MnO_2 and RGO.

To evaluate the electrochemical property of the MnO_2/RGO composites, electrochemical measurements were performed in a conventional three-electrode electrochemical cell with a carbon rod (4 cm^2) as counter electrode and a saturated calomel electrode (SEC) as reference electrode in 0.5 M Na_2SO_4 solution. To the better comparison, pristine MnO_2 and MnO_2/RGO mixture (denoted as MnO_2/RGO-binder) electrodes were also tested in the same conditions. Fig. 3a shows the voltammogram (CV) curves of pristine MnO_2, MnO_2/RGO-binder, and

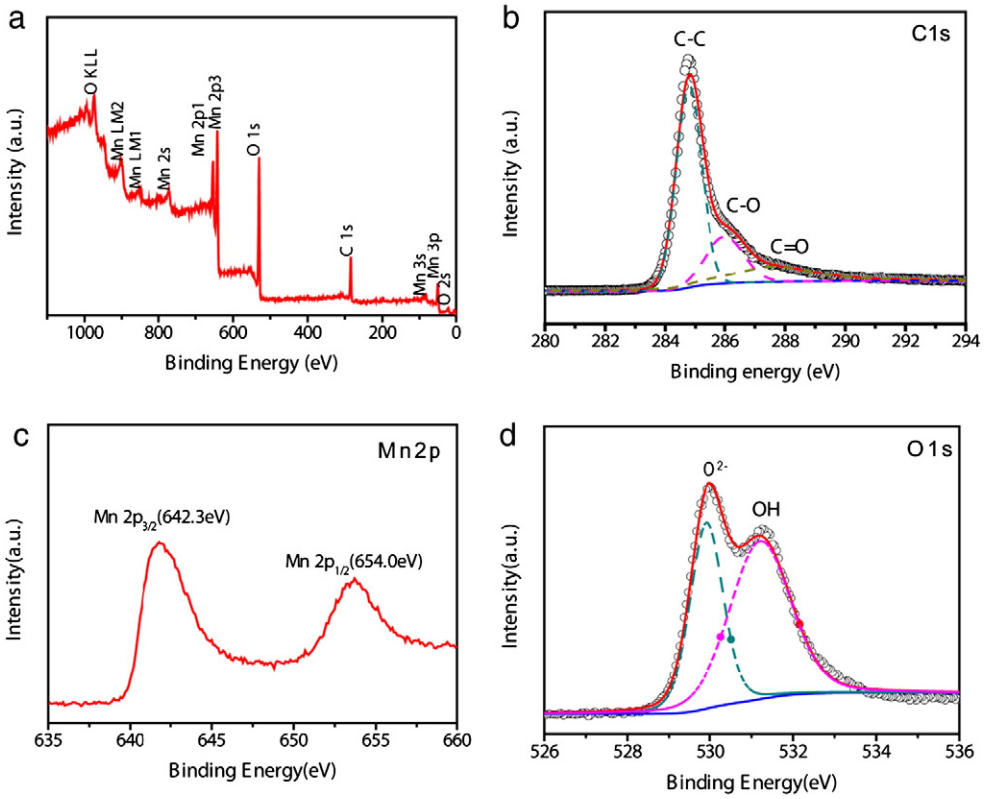

Fig. 2. (a) XPS survey spectrum, Core level (b) C1s, (c) Mn2p and (d) O1s spectra of the MnO_2/RGO composites.