Self-Assembly Synthesis of Graphene Oxide Double-Shell Hollow-Spheres Decorated with Mn_3O_4 for Electrochemical Supercapacitors

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Abstract

Novel graphene oxide double-shell hollow-spheres decorated with Mn_3O_4 nanocrystals were synthesized via a facile solvothermal self-assembly method. They had the uniform outer diameter in *ca.* 100 nm and the thickness of each shell in *ca.* 5 nm. The electrochemical supercapacitive properties of the prepared double-shell hollow-sphere composites showed the capacitance of $225 \text{ F}\cdot\text{g}^{-1}$ at the scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$, high electrochemical stability that retained about 99.5 % capacitance after cycling 6000 times, and the energy density as high as $34.1 \text{ Wh}\cdot\text{kg}^{-1}$ at the power density of $251 \text{ W}\cdot\text{kg}^{-1}$. These performances were superior to those of most reported planar graphene- Mn_3O_4 nanocomposites as well as pure Mn_3O_4 nanocrystals.

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1.Introduction

Graphene, a two-dimensional (2D) carbon nanostructure consisting of single-layer of sp^2 carbon atoms, have drawn tremendous research attention because of its unique properties such as high surface area, excellent electronic conductivity, and strong mechanical strength.[1-10] Recently, great attentions have been focused on the possibility of assembly of 2D graphene sheets into hollow spheres due to their wide applications including catalyst support, drug-delivery, electrode materials for energy storage devices and substrate for developing core/shell structure composites.[11-19] For example, Song's group has fabricated hollow graphene oxide spheres from graphene oxide nanosheets utilizing a water-in-oil (W/O) emulsion technique without surfactant.[20] Jang's group synthesized hollow graphene capsules by capillary molding of graphene oxide (GO) sheets against a polystyrene bead template. [21] Kim's group prepared hollow graphene capsules through assembly of the stable reduced GO nanosheets with opposite charges onto a sacrificial polystyrene (PS) colloidal particle.[18] However, to the best of our knowledge, there are no reports on the preparation of double-shell of graphene hollow-spheres.

Nowadays, supercapacitors have been deemed to be promising devices for energy storage due to their high power density and long cycling life.[22, 23] As one of the best supercapacitor materials, manganese oxides (such as MnO_2 and Mn_3O_4) are considered to be very encouraging, because of its low-cost, large potential window (0 to 1.0 V), non-toxicity and long cycling life.[24-26] However, low electronic

conductivity and low ion diffusion constant have hindered development of this material for use in supercapacitors. To address these issues, one popular approach is to combine manganese oxide materials with the high conductivity materials such as conducting graphene and graphene derivatives.[27-31] To date, great effort has been devoted to developing manganese oxide and graphene composite nanomaterials for energy storage applications in supercapacitors[32-35], Li ions batteries[36-38] and electrochemical catalysis[39, 40]. For example, Choi's group has reported on a MnO_2 /graphene oxide composite for use in an electrode with superior lithium storage capability.[36] Wu's group prepared MnO_2 hollow spheres and reduced graphene oxide composite nanostructures for high-performance electrochemical capacitors.[41] Qiao and coworkers reported mesoporous Mn_3O_4 and graphene hybrids material with notable oxygen reducing reaction (ORR) activity.[42] Kim and co-workers found that the ORR pathway of these composites is tunable by adjusting the amount of Mn_3O_4 supported on graphene sheets.[43] However, all of these studies are concerned with various manganese oxide nanostructures on planar graphene sheets. Graphene hollow-spheres supported manganese oxide nanocrystals have not been reported for energy storage applications up to now.

Herein, we first reported the synthesis of double-shell of hollow GO spheres decorated with Mn_3O_4 nanoparticles (Mn_3O_4 -GO) via a facile solvothermal self-assembly method. The double-shell composite structure was supposed to be formed via the vesicles of octylamine molecules self-assembly in ethanol

solvent, followed by oriented aggregation of GO sheets and Mn_3O_4 nanoparticles at the inner and outer surfaces of octylamine vesicles (as shown in **Fig. 1**). Performing as electrode materials, the prepared Mn_3O_4 -GO composite exhibited a distinctly enhanced capacitance of $225 \text{ F}\cdot\text{g}^{-1}$ at the scan rates of $5 \text{ mV}\cdot\text{s}^{-1}$ and high stability of 99.5 % after cycling 6000 times, superior to that of pure Mn_3O_4 nanocrystals as well as most reported planar graphene- Mn_3O_4 nanocomposites.[44-50]

Fig. 1 Illustration of the process and mechanism for preparing composite double-shell hollow-spheres

2. Experimental section

2.1 Chemicals

n-octylamine (99% mass fraction) was purchased from J&K Scientific Ltd., KMnO_4 (99% mass fraction) was obtained from Guang Zhou Chemical Industry Co. Ltd, H_2O_2 (AR reagent grade 30%) was provided by Beijing chemical works and ethanol (AR reagent grade, 99.7%) was purchased from Sinopharm Chemical Reagent Co. Ltd, Graphene oxide nanosheets (GO) were prepared through the modified Hammer's method. Detailed preparation procedure can be found in previous report[51].

2.2 Synthesis of double-shell of Mn_3O_4 -GO hollow spheres and the pure Mn_3O_4 nanoparticles

In a typical procedure to prepare Mn_3O_4 -GO double-shell hollow-spheres, potassium permanganate (0.0064 g, 0.04 mmol) and graphene oxide (0.0008 g, 0.067 mmol) were dissolved into 12 mL absolute ethanol and 1 mL n-octylamine under agitation for 30 min at room temperature. After the formation of a brown slurry in a Teflon autoclave of 20 mL, 2 mL hydrogen peroxide and 1 mL n-octylamine were dropped to the solution in turn, then the obtained precursor solution was stirred for 25 minutes. The Teflon autoclave was sealed in a stainless autoclave and maintained at 150 °C for 3 hour in a preheated oven. After the reaction, the Teflon autoclave was taken out and cooled down to the room temperature. The black precipitate at the bottom was separated by centrifugation

with a speed of 5500 rpm. The products were washed repeatedly with absolute ethanol and purified water for several times, then dried in oven.

Mn₃O₄(2-fold)-GO and Mn₃O₄(3-fold)-GO were prepared via the same process as Mn₃O₄-GO, where the amounts of the KMnO₄ were changed into 0.0128g and 0.0192g, respectively.

The pure Mn₃O₄ nanoparticles were prepared via the same process as Mn₃O₄-GO only without GO adding.

2.3 Materials characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max 2200 PC diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a graphite monochromator from 10 to 70° with a scanning rate of 5.0° per min. Unit cell dimensions were determined using the JADE 5 program for X-ray-diffraction pattern processing, identification, and quantification. The size and morphology of the obtained Mn₃O₄-GO samples were characterized on a transmission electron microscope (TEM, JEM100-CXII) equipped with a selected area electron diffractometric (SAED). The structure and lattice fringes of nanocrystals were observed by using a high resolution TEM (HRTEM, FEI Tecnai G2 F30) equipped with a scanning transmission electron microscope (STEM). X-ray photoelectron spectroscopy (XPS) analyses were performed to characterize the components and surface of the nanocrystals. The XPS spectra were recorded on a PHI-5300 ESCA spectrometer (Perkin-Elmer) with its energy analyzer working in

the pass energy mode at 35.75 eV, and the Al K α line was used as the excitation source. After subtraction of X-ray satellites and inelastic background (Shirley-type), peak deconvolution was carried out. To gain a better understanding of the elemental distribution throughout these nanocrystals, the prepared samples were characterized using high angle annular dark field-scanning transmission electron microscope (HAADF-STEM) imaging in conjunction. Raman spectra were recorded using multi-wavelength micro-Raman spectroscopy (Renishaw inVia) utilizing 514.5 nm incident radiation.

2.4 Fabrication of electrodes for supercapacitors and Electrochemical Measurements.

Typically, the tapping density of the Mn₃O₄-GO composite after the pulverization is around 0.95 g cm⁻³. After compressing the powders into a cylindrical shape under 6 Mpa, the density of the composite without binder/carbon black is about 1.24 g cm⁻³. The electrochemical properties of as-obtained products were investigated under a three-electrode cell configuration at room temperature. The working electrodes were fabricated by mixing the prepared powders with 15wt% acetylene black and 5wt % polytetrafluorene-ethylene (PTFE) binder. A small amount of absolute ethanol was added to the mixture to produce a homogeneous paste. The mixture was pressed onto 3.0 ×1.0 cm nickel foam current-collectors within 1.0×1.0 cm by physical pressing(8 MPa). The mass of the active material was in a range of 1.5-2.5 mg. The electrochemical characterizations were carried

out in a conventional three-electrode system with the 0.5 M Na₂SO₄ aqueous solution as the electrolyte. Platinum foil and Ag/AgCl were used as the counter and reference electrodes, respectively. Additionally, to investigate the electrochemical behaviors of as-synthesized samples in 0.5 M Na₂SO₄. CV measurements were conducted on a CHI 660D electrochemical workstation (Beijing CH Instrument Company, China).

3. Result and discussion

The detailed morphologies and microstructures of Mn₃O₄-GO product were investigated by transmission electron microscope (TEM). As can be seen from Fig. 2a, the sample was composed of double-shell hollow-spheres with a uniform outer diameter in *ca.* 100 nm and the thickness of each shell in each sphere was *ca.* 5 nm. The distance between the outer shell and the inner shell was approximately 5-10 nm. The inset of Fig. 2a is the magnified image of one Mn₃O₄-GO hollow-spheres, which confirms the double-shell structure of a hollow sphere. It also indicates that small curl flakes are present as graphene sheets composing the double-shell of hollow spheres. Fig. 2b shows the selected area electron diffraction (SAED) pattern of the Mn₃O₄-GO sample. The regular circular diffraction rings indicate that these hollow spheres were crystalline in nature with the component of graphene and Mn₃O₄. Fig. 2c is the high-resolution TEM (HRTEM) image of Mn₃O₄-GO shells. The areas marked in Fig. 2c are enlarged as shown in Fig. 2d and 2e. Fig. 2d indicates that the lattice spacing was measured to be 0.232 nm and the other is 0.248 nm,

corresponding to (004) and (211) planes in tetragonal Mn_3O_4 . These two sets of planes crossed an angle of approximately 73° , which coincided with the angle between (004) and (211) planes. Fig. 2e shows a lattice spacing of 0.214 nm, which is consistent with the (100) planes of graphite. Fig. 2f shows high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image, confirming the double-shell structure of hollow spheres. To gain a better understanding of the elemental distribution of Mn, O and C in the Mn_3O_4 -GO product, the corresponding elemental mappings were recorded in Fig. 2g-2i. These mappings illustrate that the signals of C, O and Mn elements are mainly detected in the shell region and seldom in the core region.

Fig. 2 TEM image (a), SAED pattern (b), HRTEM images (c, d and e) and HAADF-STEM image (f) of the Mn_3O_4 -GO double-shell hollow-spheres. (g-i) are elemental mappings of C, O and Mn elements acquired from the Mn_3O_4 -GO, respectively. The inset of (a) is magnified image of one double-shells hollow spheres.

The phase and crystal structure of the prepared samples were examined by using X-ray diffraction (XRD). As shown in Fig. 3a, the XRD peaks of the product can be indexed to two phases of Mn_3O_4 (JCPDS Card 01-1127) and C (JCPDS Card 41-1487). The weak diffraction peaks located at 18.0, 36.2, 38.1,

44.6 and 60.0 degrees correspond to the (101), (211), (004), (220) and (224) planes of tetragonal Mn_3O_4 ($a = b = 0.575$ nm, and $c = 0.942$ nm, $\alpha = \beta = \gamma = 90^\circ$). While the peaks appearing at 26.1 and 44 degrees represent the (002) and (100) lattice planes in hexagonal graphite ($a = b = 0.246$ nm $c = 0.674$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$). The low intensity and broad width of the diffraction peaks of the obtained Mn_3O_4 -GO hollow spheres in the XRD patterns should be related to weak crystalline Mn_3O_4 .

To investigate the lattice vibrational properties, Raman scattering measurements were conducted on the GO and the prepared Mn_3O_4 -GO. As seen in Fig. 3b, the D band observed at 1329 cm^{-1} can be assigned to defects in the GO lattice including sp^3 hybridized carbon and the G band at 1577 cm^{-1} originated from the vibrations of the sp^2 hybridized framework while the 2D band (the second order of the D peak) at 2649 cm^{-1} resulted from the double resonant Raman scattering with two-phonon emissions.[4] The intensity ratio (I_D/I_G) for GO was 1.39 indicating surface defects due to the abundant presence of surface functional groups like $-\text{CH}$, $-\text{OH}$, $\text{C}-\text{OOH}$ etc.[34] For the Mn_3O_4 -GO double-shell spheres, the I_D/I_G ratio was 1.12, indicating a decrease in the number of surface defects since these oxygen containing functional groups of GO were involved in the reaction with H_2O_2 in the formation of Mn_3O_4 -GO.[52] Another peak appearing at 642 cm^{-1} in Mn_3O_4 -GO hollow-spheres is the characteristic peak for the Mn_3O_4 lattice.[35] The stronger intensity of the D band, G band 2D band for the Mn_3O_4 -GO hollow spheres in the Raman patterns was attributed to electrical effect of Mn_3O_4 particle on the GO.[53]

We further characterized samples by X-ray photoelectron spectroscopy (XPS) to investigate the chemical composition and chemical bonding state of Mn_3O_4 -GO double-shell hollow-spheres. From Fig. 3c, the C 1s spectrum of Mn_3O_4 -GO reveals four types of carbon bonds: C=C/C-C (284.6 eV), C-O (hydroxyl and epoxy, 286.2 eV), C=O (carbonyl, 287.5 eV) and O-C=O (carboxyl, 288.7 eV), matching well with those of GO reported previously.[35, 54] Fig. 3d is the XPS spectrum of elemental Mn. The peaks located at 642.0 eV and 653.6 eV can be attributed to Mn 2p_{3/2} and Mn 2p_{1/2} levels, respectively. Both the bonding energy peaks agreed well with those of Mn_3O_4 in literature, indicating the correct Mn oxidation state in Mn_3O_4 . [55]

Fig. 3 (a) XRD pattern of Mn_3O_4 -GO samples, (b) Raman spectra of GO and Mn_3O_4 -GO samples; (c) C 1s XPS spectrum and (d) Mn 2p XPS spectrum of Mn_3O_4 -GO samples

The as-synthesized Mn_3O_4 -GO double-shell hollow-spheres were further investigated as electrode materials for use in a supercapacitor and, as such, were characterized using cyclic voltammetry (CVs) and galvanostatic charge/discharge (GCD) measurement in a three-electrode system with $0.5 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_4$ as the aqueous electrolyte (as shown in Fig. 4). As a control, pure Mn_3O_4 nanoparticles were also subjected to the same electrochemical conditions detailed above. The CV response of as-synthesized samples carried out at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$ in the potential range of 0-1 V in $0.5 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_4$ aqueous electrolyte is shown in Fig. 5a. The CV results show that the Mn_3O_4 -GO double-shell hollow-spheres had larger area with the higher symmetry of the quasi-rectangular CV curves than did the pure Mn_3O_4 nanoparticle. This indicated that the Mn_3O_4 -GO double-shells hollow spheres electrode had better reversibility and an ideal pseudocapacitive nature. Fig. 5b is the relationship between the specific capacitance and scan rate for the Mn_3O_4 -GO products and the pure Mn_3O_4 nanoparticles. The specific capacitance and volumetric capacitance was calculated from the CV results (Fig. 4a and 4b) according to the following equation (eq.):

$$C_s = \int_{V_a}^{V_c} I(V) dV / [2mv(V_c - V_a)] \quad (1)$$

$$C_v = \rho \times C_s \quad (2)$$

where C_s is the specific capacitance ($\text{F}\cdot\text{g}^{-1}$), m is the mass of the active material in the working electrode (g), v is the scan rate of CV curves ($\text{V}\cdot\text{s}^{-1}$), and $(V_c - V_a)$ represents the potential window (V), C_v ($\text{F}\cdot\text{cm}^{-3}$) is the volumetric capacitance of the single electrode, ρ ($\text{g}\cdot\text{cm}^{-3}$) is the density of the compressed electrode material. Fig. 4a reveals that the Mn_3O_4 -GO electrode exhibited high C_s values (according to eq.1) of

225 F·g⁻¹ and 97 F·g⁻¹ at scan rates of 5 mV·s⁻¹ and 100 mV·s⁻¹, respectively. Converted to volumetric capacitances, which are important for the miniaturization of devices[56-60], the values were calculated as high as 279 F·cm⁻³ and 120 F·cm⁻³ at the scan rates of 5 mV·s⁻¹ and 100 mV·s⁻¹ (according to eq.2), respectively. By comparison (Fig. 4b), the pure Mn₃O₄ electrodes exhibited low Cs values of 98 and 23 F·g⁻¹ at scan rates of 5 mV·s⁻¹ and 100 mV·s⁻¹. The higher specific capacitance of the prepared Mn₃O₄-GO double-shell hollow-spheres compared with the pure Mn₃O₄ nanoparticles sample resulted from the higher specific area and the synergistic effect between the favorably conductive GO and Mn₃O₄. In the Mn₃O₄-GO double-shell hollow-spheres, the Mn₃O₄ was mainly responsible for pseudocapacitance, and the favorably conductive GO contributed to higher the double-layer capacitance of GO as well as reduced the interface resistance of Mn₃O₄ nanocrystals to improve charge transfer.[61]

Fig. 4 (a) the CV curves of Mn₃O₄-GO double-shell hollow-spheres at the scan rates of 5, 10, 20, 50 and 100 mVs⁻¹ (b) the CV curves of the pure Mn₃O₄ particles at the scan rates of 5, 10, 20, 50 and 100mV/s (c) the GCD curves of Mn₃O₄-GO double-shell hollow-spheres at the current density of 0.5, 1, 5, and 10 A/g (d) the GCD curves of Mn₃O₄-GO double-shell hollow-spheres at current density of 0.5, 1 and 5 A/g.

Fig. 5 (a) CV curves of $\text{Mn}_3\text{O}_4\text{-GO}$ double-shell hollow-spheres and the pure Mn_3O_4 nanoparticles at scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$ (b) The plot of the relationship between the specific capacitance and current density (c) The galvanostatic charge-discharge curves at current density of $1 \text{ A}\cdot\text{g}^{-1}$ (d) The plot of the relationship between the specific capacitance and current density

To obtain more information about the potential of $\text{Mn}_3\text{O}_4\text{-GO}$ double-shell hollow-spheres as electrode materials for supercapacitors, galvanostatic charge/discharge measurements were conducted in $0.5 \text{ M Na}_2\text{SO}_4$ between $0\text{-}1.0 \text{ V}$ at a current density $1 \text{ A}\cdot\text{g}^{-1}$ using pure Mn_3O_4 nanoparticles as a control. Fig. 5c is the galvanostatic charge-discharge curves at current density $1 \text{ A}\cdot\text{g}^{-1}$ of the $\text{Mn}_3\text{O}_4\text{-GO}$ sample and pure Mn_3O_4 nanoparticles. These results show that the charging curve of $\text{Mn}_3\text{O}_4\text{-GO}$ double-shell hollow-spheres is almost symmetric with its corresponding discharge counterpart with a slight curvature. The charge and discharge time were

both longer than the pure Mn_3O_4 nanoparticles. These results indicated the Mn_3O_4 -GO double-shell hollow spheres possessed high current efficiency, reversible electrochemical performance and higher capacitance at $1 \text{ A}\cdot\text{g}^{-1}$. The C_s values of the Mn_3O_4 -GO double-shell hollow spheres and pure Mn_3O_4 nanoparticles electrodes (Fig. 5d) were also calculated from the galvanostatic charge-discharge curve results (Fig. 4c and 4d) according to the following equation:

$$C_s = I\Delta t/m\Delta V \quad (3)$$

where I is the constant discharging current ($\text{A}\cdot\text{g}^{-1}$) and Δt is the discharging time (s), ΔV is the potential drop at a constant discharge current (V), and m is the mass of the electrode material (g) excluding the binder and conductive carbon black. The calculated C_s values of Mn_3O_4 -GO double-shell hollow spheres at 0.5, 1, 5, and 10 $\text{A}\cdot\text{g}^{-1}$ was 216.0, 197.2, 141.5, and 111.1 $\text{F}\cdot\text{g}^{-1}$, while the C_s of Mn_3O_4 pure Mn_3O_4 nanoparticles calculated at 0.5, 1 and 5 $\text{A}\cdot\text{g}^{-1}$ was 98, 63 and 47 $\text{F}\cdot\text{g}^{-1}$, respectively (Fig. 5d). Approximately 51.4% of C_s of Mn_3O_4 -GO was retained when the current density was increased from 0.5 to 10 $\text{A}\cdot\text{g}^{-1}$. We attribute this to the discrepant insertion/deinsertion behavior of alkali ions (Na^+) from the electrolyte to Mn_3O_4 -GO double-shell hollow-spheres. At a low current density (0.5 $\text{A}\cdot\text{g}^{-1}$), the diffusion of ions from the electrolyte can access to almost all available pores of the electrode, leading to a complete insertion reaction. However, with the increment of current density, the effective interaction between the ions and the electrode is greatly reduced, resulting in a reduction in capacitance.[34, 62]

On the basis of the galvanostatic charge/discharge results (Fig. 4c and 4d), the energy

density (E) and power density (P) of the Mn_3O_4 electrode can be calculated from the following equations:

$$E = \frac{1}{2} C_s \Delta V^2 \quad (4)$$

$$P = E/t \quad (5)$$

where C_s is the specific capacitance ($\text{F}\cdot\text{g}^{-1}$), V the potential drop (V), and the discharge time(s). Ragone plots of the device describing the relation between energy density and power density were obtained and are shown in Fig. 6a. These results reveal that the asymmetrical supercapacitor can deliver an energy density as high as $34.1 \text{ Wh}\cdot\text{kg}^{-1}$ at the power density of $251 \text{ W}\cdot\text{kg}^{-1}$ and maintain $13.5 \text{ Wh}\cdot\text{kg}^{-1}$ at a high power density of $4844 \text{ W}\cdot\text{kg}^{-1}$. Furthermore, the long-term cycling stability of the Mn_3O_4 -GO double-shell hollow spheres was also determined by CV measurement at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ for 6000 cycles, as depicted in Fig. 6b. After cycling 1000 cycles, the capacitance retained 96.7%, and then retained about 99.5 % after cycling 6000 times. This stable behaviour is similar to that of reported materials[63]. The result indicates that Mn_3O_4 -GO can be considered as a very promising material for energy storage systems. The detailed comparisons of the current work with others in capacitance and stability were revealed in Table 1.

In order to investigate the resistance of Mn_3O_4 -GO, we carried electrochemical impedance spectroscopy (EIS) in the range of 100kHz - 0.01 Hz for the Mn_3O_4 -GO sample, as shown in Fig. 6c. The spectrum is composed of a typical semicircle in the high frequency region and a straight line at low frequency. The diameter of the semicircle indicated the low charge-transfer resistance

(Rct) of the Mn_3O_4 -GO electrode to be approximately 2.5Ω , which meant the fast charge transfer during electrochemical reactions.

Fig. 6 (a) The Ragone plot of the relation between energy density and power density; (b) CV curves at a scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$ for 6000 cycles; (c) EIS in the range of 100kHz to 0.01 Hz.

Table 1 Specific capacitances (C_s) of Mn_3O_4 and GO composites.

Sample description	Specific capacitance (F g^{-1})	Cycle retention rate	Ref
Mn_3O_4 -nanorods/graphene	121 (0.5 A g^{-1})	100% (10000 cycles)	[35]
Mn_3O_4 - nanoparticles/graphene	256 (5 mVs^{-1})	None	[46]
Mn_3O_4 /graphene composites	161.0 (1 A g^{-1})	230 F g^{-1} (1000 cycles)	[64]
Mn_3O_4 /graphene hybrid	30.8 (50 mA g^{-1})	little decay (250 cycles)	[65]
Mn_3O_4 -nanoparticles/graphene	171 (0.1 A g^{-1})	159.4 F g^{-1} (50 cycles)	[66]
graphene/ Mn_3O_4 nanocomposites	147 (0.1 A g^{-1})	95% (500 cycles)	[45]
Mn_3O_4 /graphene-nanosheets	271.5 (0.1 A g^{-1})	100% (20000 cycles)	[67]
Mn_3O_4 -nanoparticles/graphene	312 (0.5 mAcm^{-2})	76% (1000 cycles)	[68]
graphene/ Mn_3O_4 composites	270.6 (0.2 A g^{-1})	91% (1500 cycles)	[44]
Mn_3O_4 /reduced-graphene-oxide	193 (25 mVs^{-1})	81% ($25\text{-}1000 \text{ mV s}^{-1}$)	[49]
graphene/ Mn_3O_4 composites	193 (50 mA g^{-1})	92% (800 cycles)	[47]
Mn_3O_4 -GO	225 (5 mVs^{-1})	99.5% (6000 cycles)	This work

Fig. 7 (a) CV curves ($50 \text{ mV}\cdot\text{s}^{-1}$) and (b) GCD curves ($1 \text{ A}\cdot\text{g}^{-1}$) of the obtained Mn_3O_4 -GO, $\text{Mn}_3\text{O}_4(2\text{-fold})$ -GO and $\text{Mn}_3\text{O}_4(3\text{-fold})$ -GO samples

In addition, we loaded Mn_3O_4 component with different content in the Mn_3O_4 -GO composite via varying the contents of KMnO_4 and H_2O_2 in the reaction solution. When the Mn_3O_4 contents in the prepared composites were increased to 2-fold and 3-fold, for which the samples were defined as $\text{Mn}_3\text{O}_4(2\text{-fold})$ -GO and $\text{Mn}_3\text{O}_4(3\text{-fold})$ -GO, the CVs at the scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$ exhibited the C_s values of 210.8 and $154 \text{ F}\cdot\text{g}^{-1}$, respectively, as shown in Fig. 7a. Fig. 7b is the GCD curves at the current density of $1 \text{ A}\cdot\text{g}^{-1}$, which reveals the C_s values of the $\text{Mn}_3\text{O}_4(2\text{-fold})$ -GO and $\text{Mn}_3\text{O}_4(3\text{-fold})$ -GO reached 170 and $152 \text{ F}\cdot\text{g}^{-1}$, respectively. Compared to the Mn_3O_4 -GO sample, the results show a little change of the C_s for the $\text{Mn}_3\text{O}_4(2\text{-fold})$ -GO but an obvious decrease for the $\text{Mn}_3\text{O}_4(3\text{-fold})$ -GO.

4. Conclusions

In summary, a novel Mn_3O_4 -GO composite double-shell of hollow GO spheres was synthesized via a facile one-step solvothermal method. The double-shell composite hollow spheres were originated from the self-assembly of octylamine molecules, and had the uniform diameter of ca. 100 nm. When used as the electrode materials of electrochemical supercapacitor, the prepared Mn_3O_4 -GO composite exhibited the capacitance of $225 \text{ F}\cdot\text{g}^{-1}$ at the scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ and retained about 99.5% capacitance after 6000 charge/discharge cycles. These performances exceeded those of most of reported planar Mn_3O_4 -GO composites as well as pure Mn_3O_4 nanocrystals. The different content of Mn_3O_4 have an impact on capacitance properties of the Mn_3O_4 -GO samples.

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