Producing “Symbiotic” Reduced Graphene Oxide/Mn₃O₄ Nanocomposites Directly from Converting Graphite for High-Performance Supercapacitor Electrodes

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ABSTRACT: Almost all existing methods for preparing reduced graphene oxide/Mn₃O₄ (RGO/Mn₃O₄) composites are based on the synthetized graphene or graphene oxides (GO), which make them complicated and high-cost processes. Here, we reported a new method, which is able to convert graphite directly to RGO/Mn₃O₄ composites. Thus, it is simpler, more economical, and productive. The structure of RGO/Mn₃O₄ inheriting intermediate product GO/MnO₂ composites that are formed by the present method is a novel three-dimensional “multilayer steamed bread” nanostructure, which constitutes mutually beneficial “symbiosis”. The nano-Mn₃O₄ supports the space between RGO layers and further to the combination of RGO to self-assemble into large-sized (>40 μm) nanocomposites. Meanwhile, the formed Mn₃O₄ particles were small (60 × 10 nm²) in diameter and distributed homogeneously without the use of any template and surfactant. Because the structure and nanosize of composite cause the excellent electrochemical properties, RGO/Mn₃O₄ electrodes deliver an enhanced specific capacitance of 438.7 F/g at 0.3 A/g and outstanding cyclic stability (77.5% of its initial capacitance is retained after 1000 cycles).

1. INTRODUCTION

In recent years, transition-metal oxide pseudocapacitors have attracted wide attention owing to their high capacitance, high energy, and low pollution to the environment. Among them, Mn₃O₄ has been studied as a potential electrochemical material because of its excellent physical and chemical properties in ordinary conditions, including abundance, nontoxicity, and low price. However, on the other hand, its poor electrical conductivity and dense morphology have impeded its application. As a result, some researchers have suggested to combine Mn₃O₄ with graphene to overcome its shortages to be used for chemical absorption, sensors, supercapacitors, and so forth. Unfortunately, the existing method to produce the uniform composite of Mn₃O₄ nanoparticles and graphene or graphene oxide (GO) is a very complicated and costly process.

GO, an embellished monomolecular graphene with numerous oxygen-containing functional groups, has attracted much attention of potential usages in various fields in the past decade, including electronics, electrochemistry, sensors, films, and so forth. Meanwhile, GO can also serve as the precursors in the preparation of reduced GO (RGO), and high-quality GO is vital in controlling the structure, property, and application potential of RGO. A chemical method is commonly used to prepare GO at the present, owing to the advantage of high processing ability, ease of mass production by low-cost graphite, and good physical and chemical properties after reduction.

The earliest work about the chemical synthesis of GO was reported by Brodie in 1859, which took more than 4 days. Later in 1958, Hummers and Offeman developed their widely used classical method (the Hummers method). With the contributions of many other researchers, the mechanism of Hummers method has been extensively explored since then. Specifically, potassium permanganate (KMnO₄) and concentrated sulfuric acid (H₂SO₄) react to form the main oxidants, manganese heptoxide (Mn₂O₇) and permanganyl cation (MnO₃⁺), which diffuse between the graphene layers and react with nearby carbon atoms. The oxidants would attack the graphene layers, and the oxidized areas spread randomly over the flakes. Unlike sulfur, manganese does not

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form any functionality and has a long lifetime on the GO basal planes.28 It was also proved that the products of oxidants were divalent manganese ions (Mn$^{2+}$) because deionized water was added into the reaction system, and further oxidation of MnO$_4$$^{-}$ with high oxidizing potential occurs.

RGO/Mn$_3$O$_4$ composites were studied widely in supercapacitors and achieved outstanding achievements. The specific research results of RGO/Mn$_3$O$_4$ and its similar composites for supercapacitors are shown in Table 1.34

In this article, a new method was introduced, which is able to produce high-grade GO along with in situ formed MnO$_2$ nanoparticles in one-step. Based on the synthesis of “multilayer steamed bread” GO/MnO$_2$ composites, we obtain the same nanostructure of RGO/Mn$_3$O$_4$ composites that are a highly effective type of ultracapacitor materials only by thermal reduction. The properties of the nanocomposites with different mass ratios were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Finally, the possible mechanism of the new method was described as well. The composite electrode achieves an excellent specific capacitance of 438.7 F/g at 0.3 A/g and extraordinary cycling stability with a significant 77.5% capacity retention after 1000 cycles.

2. RESULTS AND DISCUSSION

2.1. Structures and Compositions of GMH$_{0.5}$, GMH$_{1.3}$, and GMH$_{2.6}$. According to the adding amount of H$_2$O$_2$, we named the three samples GMH$_{0.5}$, GMH$_{1.3}$, and GMH$_{2.6}$ which are shown in Figure 1. The crystal structure and composition of MnO$_2$/GO samples with different mass ratios were analyzed using XRD and Raman spectrometry. Broad XRD peaks of GMH$_{0.5}$ were observed indicating that samples’ crystallization is incomplete, and the α-MnO$_2$ (JCPDS 44-0141) particle size is small.41,42 It was also observed that the XRD peaks of α-MnO$_2$ decreased from GMH$_{0.5}$ to GMH$_{2.6}$ and totally disappeared at GMH$_{2.6}$. In contrast, the XRD peaks of pure GO show the opposite trend (Figure 2b). However, the Raman spectra clearly show that both GMH$_{0.5}$ and GMH$_{1.3}$ contain α-MnO$_2$ and GO (Figure 2a). This is because the peak at about 640 cm$^{-1}$, labeled A, corresponds to the Mn–O vibration perpendicular to the MnO$_6$ octahedral double chains of MnO, and I$_G$/I$_D$ is typical of GO.43 Furthermore, the A/(D + G) peak area ratio can be used to estimate the proportions of GO and MnO$_2$ in the composites. The contents of carbon and manganese elements in GMH$_{0.5}$ and GMH$_{1.3}$ measured using the infrared sulfur–carbon analyzer and flame atomic absorption spectrometer and shown in Figure 2c can also prove that all samples containing lots of GO, GMH$_{0.5}$, and GMH$_{1.3}$ contain MnO$_2$ (Figure 2c). It should be noticed that the observed XRD patterns disagreed with the Raman spectra. In the Raman spectrum, the G band (1590 cm$^{-1}$) represented the in-plane bond-stretching motion of the pairs of C sp$^2$ atoms (the E$_2g$ phonons), and the D band (1350 cm$^{-1}$) corresponded to the breathing modes of rings or K-point phonons of A$_{1g}$ symmetry. However, the XRD peaks were only

| materials          | capacitor type      | specific capacity | cycling stability | refs  |
|--------------------|---------------------|-------------------|-------------------|-------|
| RGO/Mn$_3$O$_4$     | symmetric supercapacitor | 243 F/g at 0.5 A/g | 82.3% after 1000 cycles | 29    |
| RGO/Mn$_3$O$_4$     | symmetric supercapacitor | 310 F/g at 1 A/g  | 100% after 30,000 cycles | 30    |
| graphene/Mn$_3$O$_4$ | symmetric supercapacitor | 312 F/g at 0.5 A/g | 76% after 1000 cycles | 27    |
| graphene/Mn$_3$O$_4$ | symmetric supercapacitor | 270 F/g at 0.2 A/g | 91% after 1500 cycles | 31    |
| RGO/Mn$_3$O$_4$     | symmetric supercapacitor | 228 F/g at 5 A/g  | 95% after 5000 cycles | 32    |
| RGO/Mn$_3$O$_4$     | symmetric supercapacitor | 311 F/cm$^2$ at 300 mA/cm$^2$ | 33    |
| graphene/Mn$_3$O$_4$ | symmetric supercapacitor | 317 F/g at 10 mV/s | 100% after 4000 cycles | 8     |
| graphene/polyaniline/Mn$_3$O$_4$ | symmetric supercapacitor | 500 F/g at 5 mV/s  | 97% after 3000 cycles | 35    |
| graphene/Mn$_3$O$_4$ | symmetric supercapacitor | 326 F/g          | 94.6% after 1000 cycles | 36    |
| graphene/Mn$_3$O$_4$ | symmetric supercapacitor | 457 F/g at 1.0 A/g | 91.6% after 5000 cycles | 37    |
| N-dope graphene/Mn$_3$O$_4$/Mn$_3$O$_2$ | symmetric supercapacitor | 739 F/g at 0.5 A/g | 93.4% after 10,000 cycles | 38    |
| RGO/Mn$_3$O$_4$     | symmetric supercapacitor | 221.6 F/g at 50 mA/g | 97.1% after 1000 cycles | 39    |
| RGO/Mn$_3$O$_4$     | symmetric supercapacitor | 351 F/g at 0.5 A/g | 80.1% after 10,000 cycles | 40    |
| graphene/CeO$_2$/Mn$_3$O$_4$ | symmetric supercapacitor | 310 F/g at 2 A/g  | 92.4% after 1000 cycles | 7     |
| RGO/Mn$_3$O$_4$     | symmetric supercapacitor | 438.7 F/g at 0.3 A/g | 77.5% after 1000 cycles | this work |
affected by the distance between crystal spacing. Therefore, we deduced that the α-MnO2 and GO of the compounds formed a symbiosis, which leads to the much larger interlamellar spacing of GO in the samples than pure GO. This explains why the XRD peaks of the pure GO phase disappeared in GMH0. This observation was also supported by the subsequent morphological analyses of SEM and TEM described in the following paragraphs. When the mass percentage of α-MnO2 in the composites decreases, the peak of pure GO (2θ = 10.2) emerged in GMH1.3, which is lower than in GMH2.6. Because of the smaller number of MnO2 particles, a part of graphene basic planes in GMH1.3 collapsed to regular spacing. The XRD and Raman spectrum both identified that GMH2.6 contained no or very little manganese particles. It could be concluded that the composites made in the present study were GO and α-MnO2 composites, and the ratio of GO to α-MnO2 could be adjusted by H2O2 addition.

The chemical structure of GO/MnO2 was further investigated by X-ray photoelectron spectroscopy (XPS), as shown in Figure 3. The XPS survey spectrum of GMH0 showed clearly C, Mn, and O elements. The separation of peak energy between the Mn 2p1/2 and Mn 2p3/2 is 11.7 eV, which agrees with classical XPS peaks of MnO2. The C 1s spectrum was deconvoluted into five peaks assigned to C–C, C–OH, C–O–C, C–OH, and HO–C=O. The C–OH, C–O–C, C–OH, and HO–C=O peaks attribute to the oxygen-containing group of GO. Also, the C=C is the chemistry state of GO base sheets. The chemical interaction of MnO2 nanoparticles and GO gives rise to the Mn–O–C peaks in the XPS O 1S spectrum.

Figure 2. (a) Raman spectra of GMH0, GMH1.3, and GMH2.6. (b) XRD patterns of GMH0, GMH1.3, and GMH2.6. (c) C and Mn contents measured for different samples using the infrared sulfur–carbon analyzer and flame atomic absorption spectrometer.

Figure 3. XPS spectra of the GMH0 composite. (a) Survey spectrum, (b) Mn 2p, (c) C 1s, and (d) O 1s.
The microstructures of the composites are analyzed by the image of SEM. First, we analyze GMH₀ treating without ultrasonication. We could see that many MnO₂ nanoparticles joined with GO together. Upon closer inspection, we found that the combination of GO and MnO₂ shows three kinds of location relation. The area in which nanoparticles MnO₂ generate on the surface of GO is labeled letter A, as shown in Figure 4a. In area B, we could observe that very thin GO covers on the MnO₂. Finally, we label the rest of area by letter C, where smooth and occasionally undulating graphene appeared but no nanoparticles were found. We can infer that most nanoparticles exist between GO layers compared with MnO₂ on the surface.

To further analyze the structural relationship between MnO₂ and GO, we ultrasonically treated GMH₀ for 2 h. It was found that agglomerated nanoparticles of the surface fell out under the action of ultrasonication, and the GO surface with full of pleats fell out entirely (Figure 4b), which were similar to areas C, as shown in Figure 4a. Except for GO, we found vaguely that densely packed nanoparticles were underneath GO (Figure 4b,c). Together with XRD, Raman spectra (Figure 2a,b), SEM images (Figure 4c,f), and TEM (Figure 4d), we conclude second that small-size nanorob MnO₂ (60 × 10 nm²) is homogeneously generated in the GO layers. In addition, the formation of MnO₂ not only further “exfoliated” GO but also acted with the GO layers to self-assemble into the large size (>40 μm) but nanostructured composites. Meanwhile, after the action of ultrasonication for 2 h, the nanostructure remains intact under the force of MnO₂ joint. It can also be seen that this nanostructure is very stable.

2.2. Thermal Reduction and the Formation of Mn₃O₄

The thermal-reduced samples were named RGMH₀, RGMH₁.₃, and RGMH₂.₆. The XRD patterns of the samples manifest that α-MnO₂ was transformed to Mn₃O₄, and GO was reduced to RGO (Figure 5a). The changing rules on the XRD patterns of RGMH₀, RGMH₁.₃, and RGMH₂.₆ are similar to those of GO/MnO₂ (Figure 2b). Hence, we infer that the nanostructure of RGO/Mn₃O₄ inherits the GO/MnO₂ and the macro size of composites did not change after low-temperature heating (Figure 5b). Moreover, we found that the abundant nano-Mn₃O₄ prevents the graphene to come in contact with each other, as observed from XRD (Figure 5a). The theories of secondary electron image and back-scattered electron image are different. The former only presents the details on the surface because the low-energy incident electron is almost impenetrable. In comparison, the latter has a larger average atomic number of Z and brighter image, and the high-energy incident electron promotes the penetration ability to the micron level. In this study, the back-scattered electron contrast images (Figure 5d,f,h) show the Mn₃O₄ plane projection of three-dimensional distribution of each sample in the absence of MnO₂ particles on the surface (Figure 5c,e,g). In other words, MnO₂ homogeneously remains in the RGO layers. Next, we conclude third that GO/MnO₂ turns to RGO/Mn₃O₄ during the heat treatment. Moreover, the macrostructure and microstructure of the composites are unchanged. Figure 5i directly shows that the shape and size of Mn₃O₄ are the same to MnO₂ of the intermediate products. The atomic ratio of element Mn and C (0.81) is very close to Mn₃O₄ (0.75) (Figure 5j).

Chemical bonding detail states of RGO/Mn₃O₄ nanocomposites are further investigated by XPS spectrometry, which are shown in Figure 6. The survey spectrum of RGMH₀ identifies that Mn, C, and O elements exist in nanocomposites. Energy separation between two peaks of Mn 2p₁/₂ and Mn 2p₃/₂ locating at 653.10 and 641.50 eV, respectively, is computing to be about 11.60 eV, which attributes to Mn₃O₄. The weak peaks of M 2p spectrum at 642.90 eV correspond to Mn³⁺ ions in Mn₃O₄. The peak of the C 1s spectrum (Figure 6b) located at 284.3, 286.40, and 288.50 eV represents C–C bond, C=OH, and O–C=O, respectively.

2.3. Mn(VII) Converts to Mn(II) in the Oxidation Process

The origin stage of our experiment only contains K⁺, H⁺, MnO₄²⁻, and SO₄²⁻ ions. According to the color of the wastewater (Figure 7b), the MnO₄²⁻ ion does not exist in the wastewater. The XRD patterns of sediment and graphite show that the sediment contains no other insoluble substances, except the partially oxidized graphite (Figure 7a). Hence, we guess that MnO₄²⁻, the main oxidizing agent, was fully reduced to another colorless soluble ion. During the experiment
(measurement of Mn²⁺ ions in wastewater), the color of wastewater turned purple (Figure 7c). From the above analysis, we conclude that MnO₄⁻ converts to Mn²⁺. The equation is as follows

\[
2\text{Mn}^5\text{S} \text{O}_8\text{H}_2\text{O} + 16\text{H}_2\text{O} \rightarrow \text{Mn}^2\text{O}_4^- + 10\text{SO}_4^{2-} + \text{H}^+ + \text{H}^+ + \text{H}_2\text{O}
\] (1)

2.4. Formation Mechanism of RGO/Mn₃O₄. Based on the above results and other relevant studies, we propose a reaction mechanism to interpret the formation process of the special nanostructures composed of RGO and Mn₃O₄. We divide the method of converting bulk graphite to RGO/Mn₃O₄ into four steps. In the first step of preoxidation, sulfuric acid reacts with graphite to form a sulfuric acid graphite intercalation compound (stage-1 GIC-H₂SO₄). In the second step of oxidation, the graphite oxide is synthesized when KMnO₄ is added slowly. The third step begins when the mixture of water and H₂O₂ acts with the reaction system, which converts graphite oxide into GO. Meanwhile, MnO₂ is synthesized between the GO layers, which is called the synthesis stage. The last step is converting GO/MnO₂ to RGO/Mn₃O₄.

In addition, another oxidation process also occurs in this step. In the first step, the graphite blended with concentrated sulfuric acid is initially jet-black but it slowly turns deep blue as the reaction occurs. During the color variation, sulfuric acid is inserted into the layers of graphite to form stage-1 GIC-H₂SO₄. The theoretical chemical reaction rate of stage-1 GIC-H₂SO₄ depends on the electrochemical potential of the concentrated sulfuric acid in the reaction (Figure 8). In the experimental condition of modified Hummers’ method, stage-1 GIC-H₂SO₄ is formed within 3–5 min.

As reported, the oxidation process consists of two sequential steps, which can be partitioned by the liquid media in each step.

Oxidation-1 step

\[
\text{KMnO}_4 + 2\text{H}_2\text{SO}_4 \rightarrow \text{Mn}_3\text{O}_7 + 2\text{H}_2\text{O} + \text{KHSO}_4
\] (2)
\[
\text{MnO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{MnO}_3^+ + 2\text{HSO}_4^- + \text{H}_2\text{O}
\]  
\text{(3)}

Oxidation-2 step

\[
\text{Mn}_2\text{O}_7 + 3\text{H}_2\text{O} \rightarrow 2\text{MnO}_4^- + 2\text{H}_2\text{O}^+
\]  
\text{(4)}

\[
\text{MnO}_3^+ + 3\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + 2\text{H}_2\text{O}^+
\]  
\text{(5)}

The chemical reaction mechanism of the second step is more complicated. The KMnO₄ is dissolved slowly into the mixture and transformed to manganese heptoxide (Mn₂O₇) and manganese trioxide ion (MnO₃⁺) in the medium of concentrated sulfuric acid. Because of the high wettability of graphite with MnO₃⁺ in sulfuric acid and the larger interval distance of stage-1 GIC-H₂SO₄, the two types of manganic acids act as the oxidizing agents to intercalate relatively easily into the gallery of stage-1 GIC-H₂SO₄. The manganese of manganic acids is reduced to Mn²⁺. At this stage, the positively charged Mn²⁺ and MnO₃⁺ favorably bind, via an electrostatic force, with the O atoms of the negatively charged oxygen-containing functional groups on the GO sheets, which is the basis for the homogeneous generation of nano-MnO₂ in the GO layers. In the oxidation-1, the stage-1 GIC is converted into oxidized graphite (Figure 9), which is defined as pristine graphite oxide (PGO). Certainly, in the nearly 100% H₂SO₄ solvent, the above-mentioned compounds exist predominantly in their nonionized forms while water was added into acid, ionization takes place.

When the reaction circumstance is changed by the deionized water, the third step starts. MnO₄⁻, the main oxidant of oxidation-2, is formed in an acidic aqueous medium, which can be easily seen from the solvent color. In the stage of oxidation-2, the oxidant agent selectively oxidizes the edge and atomistic defects of PGO. Furthermore, the epoxide groups introduced in oxidation-1 are hydrolyzed in the aqueous acidic media to form additional hydroxyl groups. Because our experiments were conducted at room temperature, the oxidation of MnO₄⁻ with GO proceeds very slowly. In contrast, the formation of MnO₂ shows more activity. Along with the addition of water, MnO₃⁺ and Mn₂O₇ are immediately

Figure 6. XPS spectra of the RGMH₀ composite. (a) Survey spectrum, (b) C 1s, (c) Mn 2p, and (d) O 1s.

Figure 7. (a) XRD patterns of partially oxidized graphite. (b) Wastewater was collected during the GO filtration from the reaction system. (c) Pictures of color test of Mn²⁺ ions.
converted to $\text{MnO}_4^-$ (eqs 4, 5). Next, dissociative $\text{MnO}_4^-$ reacts with $\text{Mn}^{2+}$ (eq 6) to form abundant nuclei within short time. These nuclei act as anchor sites for the crystal growth. In addition, the space of graphene layers restricts the size growth of $\text{MnO}_2$ particles (Figure 10). Because of the above reasons, $\text{MnO}_2$ nanoparticles are uniformly generated in the graphite oxide layers. According to classical Hummers’ method, the graphite oxides exposed to water are exfoliated to GO through a series of chemical transformations.\(^4^6\) In our experiment, the generation of $\text{MnO}_2$ nanoparticles enlarges the graphite oxide layer spacing to dozens of nanometers, which is far larger than the lamellar spacing formed in classical Hummers’ method and is thus called further “exfoliation”. Moreover, the “exfoliated” GO layers, which are not randomly dispersed to water in our experiment, bond with $\text{MnO}_2$ to form a novel three-dimensional “multilayer steamed bread” nanostructure. Because GO/$\text{MnO}_2$ was heated, the oxygen-containing chemical bonds on the surface of GO in GO/$\text{MnO}_2$ are broken, causing small molecules of water and carbon dioxide to escape.

In the last step, because GO/$\text{MnO}_2$ was heated, the oxygen-containing chemical bonds on the surface of GO are broken, causing small molecules of water and carbon dioxide to escape. Meanwhile, nanosize $\text{MnO}_2$ thermally converted to nanosize $\text{Mn}_3\text{O}_4$. The intermediate product GO/$\text{MnO}_2$ transforms into the final product RGO/$\text{Mn}_3\text{O}_4$. In addition, the structure and property of composites remain unchanged.

In the condition of acidic solution

$$3\text{Mn}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$$ (6)

At last, we discuss the effect of $\text{H}_2\text{O}_2$ in deionized water on the $\text{MnO}_2$ formation. After the second step reaction with deionized water containing $\text{H}_2\text{O}_2$, the $\text{MnO}_4^-$ and $\text{Mn}_2\text{O}_7$ react with deionized water to form $\text{MnO}_4^-$ (eqs 4, 5). Next, $\text{MnO}_4^-$ reacts with $\text{H}_2\text{O}_2$ in the acidic solution to form $\text{Mn}^{2+}$ (eq 7).

Hence, we can control the $\text{MnO}_4^-$ concentration in the acidic aqueous solution by adjusting the dosage of $\text{H}_2\text{O}_2$. According
to eq 6, the molar quantity of MnO$_4^-$ decides the production of MnO$_2$. After the reaction, the redundant Mn$^{2+}$ and H$_2$O$_2$ can be completely removed by centrifugal washing. The ratio of GO and MnO$_2$ in GO/MnO$_2$ finally decided the content of Mn$_3$O$_4$ in RGO/Mn$_3$O$_4$.

\[5\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}\]  

(7)

3. ELECTROCHEMICAL EXPERIMENTS

The main features of the "multilayer steamed bread" architecture are as follow: first, RGO supported by Mn$_3$O$_4$ nanoparticles has high specific surface areas, open porosity, and highly conducting, which satisfy double-layer capacitance requirements. Furthermore, its highly conductive nature is able to provide fast charge exchange with nickel foam (current collector). Second, the process of the faradaic redox pseudocapacitance includes the surface adsorption, and the electrolyte ions react with active substance of the electrode. The space of RGO layers enables the intercalation of the electrolyte, the ions of which directly contact with nanoparticle Mn$_3$O$_4$. Nanosize Mn$_3$O$_4$ and RGO enhance its electronic conductivity and increase the number of redox points. The approach has the advantage of dual mechanisms, which lead to high performance of the electrochemical supercapacitor.

\[C_{sp} = \frac{Q}{\Delta V} = \frac{1}{\text{mv}(V_f - V_i)} \int_{V_i}^{V_f} I(V) \, dv\]  

(8)

For exploring the potential applications of in situ nanocomposites, supercapacitor electrodes were characterized by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD). The tests were performed in 6 M KOH electrolyte and used a classical three-electrode system, under a potential window of 1.6 V (−0.8 to +0.8 V). First, in order to comparison purposes, nano-MnO$_2$, GMH$_0$, and RGMH$_0$ were

Figure 10. Schematics of the third step from PGO into the GO + MnO$_2$/oxidant-2 step.

Figure 11. (a) CV curves of RGMH$_0$, GMH$_0$, and nano-MnO$_2$ at scan rate of 10 mV/s. (b) GCD curves of RGMH$_0$, GMH$_0$, and nano-MnO$_2$ at 0.3 A/g. (c) EIS of RGMH$_0$, GMH$_0$, and nano-MnO$_2$ at 0.3 A/g.

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fabricated as electrodes to test (Figure 11). Because the electrical conductivity of RGO is much higher than GO and manganite, the electrical conductivity of RGMH$_0$ is highest in the three samples (Figure 11c). The CV curves and GCD curves (Figure 12a,b) clearly show that the capacitance of RGMH$_0$ is higher than nano-MnO$_2$ and GMH$_0$. The capacitance of GMH$_{2.6}$ is higher than nano-MnO$_2$, which can be attributed to pseudocapacitive contribution of GO and nanostructure of nanocomposites. Second, the results shown in figure indicate that the capacitance of the supercapacitor increases with the ratio of Mn$_3$O$_4$/RGO. According to the area of the CV curve (Figure 12a) and eq 8, we could infer that RGMH$_0$ is the largest capacitance, followed by RGMH$_{1.3}$ and RGMH$_{2.6}$. The capacitance of composites (RGMH$_0$ and RGMH$_{1.3}$) combines double layer and pseudocapacitive contribution, which is different from the ideal rectangular shape of double-layer capacitors. Two sharp peaks come from the process of the pseudocapacitive material, which are easily distinguished. The redox peaks are the reason that there are the redox transitions of Mn between (Mn$^{2+}$/Mn$^{3+}$) and (Mn$^{3+}$/Mn$^{4+}$) in an alkaline medium (eq 9). This behavior like the electrode that porous Mn$_3$O$_4$ nanocrystal graphene electrodes.

Another key factor is that the space between RGO, without being supported by enough Mn$_3$O$_4$ nanoparticles, collapse, reduces the specific surface area of RGO and wraps Mn$_3$O$_4$. The Mn$_3$O$_4$ wrapped by RGO slowly reacts with electrolyte. Especially, RGMH$_{2.6}$ hardly ever include Mn$_3$O$_4$, which only belongs to double-layer capacitance. Moreover, during the process of GO being thermally reduced to RGO, parts of the GO could convert back to graphite without nanoparticles in our experiment. This is the main reason that electrochemical performance of RGMH$_{2.6}$ is well below the theoretical value of graphene. The maximum values of capacitance for RGMH$_0$ are 517.4 F/g at 10 mV/s, which are greater than RGMH$_{1.3}$ (283.3 F/g) and RGMH$_{2.6}$ (114.3 F/g) at the same scan speed. The electrochemical performance of RGMH$_0$ nanocomposite could be ascribed to the interaction of the nanostructure of nano-Mn$_3$O$_4$ and RGO, where open-layered and well-dispersed Mn$_3$O$_4$ nanowire can provide sufficient ions to the Mn$_3$O$_4$. Finally, from the above analysis, we can know that the total capacitance of RGMH$_0$ and RGMH$_{1.3}$ is contributed by the double layer and pseudocapacitator, and the capacitance of RGMH$_{2.6}$ only contain double-layer capacitance. Because the condition of chemical test and the electrode preparation of three samples is identical, we could consider that the value of double-layer capacitance of three samples is same. The value of pseudocapacitor of
RGMH₀ is the difference value of RGMH₀ and RGMH₂, which is 403.1 F/g. Similarly, the pseudocapacitor of RGMH₁.₃ is 169 F/g.

\[
\text{Mn}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow 3\text{MnOOH} + e^- \quad (9)
\]

To get more information about the potential RGO and \(\text{Mn}_3\text{O}_4\) nanocomposite supercapacitors, we carried out GCD measurements in the 6 M KOH at selected current density between 0.3 and 2 A/g and in the potential window range of −0.8 to +0.8 V. During the C/D steps, the charge curve of RGMH₀ is almost symmetric to its discharge curve with a slight curvature (Figure 12d), which indicates the pseudocapacitive contribution along with the double-layer contribution. It is corresponding with the CV curve (Figure 12a). The curve (Figure 12c) manifests double layer and pseudocapacitance of RGMH₁.₃ and RGMH₀. \(C_s\) is calculated as \(C_s = I \times \Delta t/(\Delta V \times m)\) from the discharge curves, where \(I\) is the constant discharge current, \(\Delta t\) is the discharge time, and \(\Delta V\) is the potential drop during discharge. The maximum value calculated from the curve is 438.7 F/g (based on the total mass of RGO and \(\text{Mn}_3\text{O}_4\)), which corresponds to the current density of 0.3 A/g. However, we found that tendency of the RGMH₀ capacitance decreases with the scan rate or current density increasing. The possible reason for the capacitance decreasing is the electrolyte penetration in pores and defects of the structure, thus the number of ions is less available near the surface of the electrode. Then, during the annealing process of GO and \(\text{Mn}_2\text{O}_3\) composite, the oxygen-containing chemical bonds on the surface of GO transform to small molecules of water and carbon dioxide to escape and the volume change of \(\text{Mn}_2\text{O}_3\) converting to \(\text{Mn}_3\text{O}_4\). It causes to weaken the nanostructure, which also affects its electronic conductivity. Moreover, the deformation of nano-\(\text{Mn}_3\text{O}_4\) during the oxidation process may have caused the increasing number of defects formed in the connection point of \(\text{Mn}_2\text{O}_4\) and RGO. The produced connecting defects could cause decreasing of the electronic and ionic conductivity, thus having great influence on the rate capability both of pseudocapacitive and the double-layer response. Furthermore, the capacitance stability of the RGMH₀ composite evaluated is 77.5% after 1000 cycles at 100 mV/s (Figure 12f), which is ascribed to its structure that is further damaged.

### 4. CONCLUSIONS

RGO/\(\text{Mn}_3\text{O}_4\) nanocomposites were prepared from natural graphite via modified Hummers’ method at room temperature without the use of templates or surfactants and simple thermal reduction at 190 °C. The method is a facile, low-cost, and industry-oriented technique. The integration of RGO and the needle-like \(\text{Mn}_3\text{O}_4\) crystals endowed such composites with excellent electrochemical behaviors that are useful as electrode materials for supercapacitors. The electrochemical results show high performance including excellent specific capacitance and remarkable capacitance stability. The electric double-layer capacitance of RGO and the pseudocapacitance of nano-\(\text{Mn}_3\text{O}_4\) between RGO layers has been achieved simultaneously in the “multilayer steamed bread”-like nanostructure. Moreover, the RGO and \(\text{Mn}_3\text{O}_4\) of the nanostructure are beneficial for each other.

### 5. EXPERIMENTAL SECTION

#### 5.1. Chemicals

Graphite powder (1000 mesh, 98%, Jinan) was purchased from NORMIC Co., Ltd. Analytically pure sulfuric acid (\(\text{H}_2\text{SO}_4\), 98%), potassium permanganate (KMnO₄), hydrogen peroxide (\(\text{H}_2\text{O}_2\)), concentrated phosphoric acid (\(\text{H}_3\text{PO}_4\), 85%), sodium phosphate dibasic dihydrate (\(\text{Na}_2\text{HPO}_4\cdot2\text{H}_2\text{O}\)), ammonium persulfate [(\(\text{NH}_4\)₂\text{S}_2\text{O}_8\)], and silver nitrate (\(\text{AgNO}_3\)) were all obtained from Aladdin Industrial Corporation. All materials were used without further purification.

#### 5.2. Synthesis of RGO/\(\text{Mn}_3\text{O}_4\)

The new process was developed in the current work for synthesis of RGO/\(\text{Mn}_3\text{O}_4\), and the details of which are graphically shown in Figure 1. It can be seen that graphite powder (0.1 g) was slowly added to concentrated \(\text{H}_2\text{SO}_4\) (10 mL) at room temperature while being continuously stirred. After 30 min, KMnO₄ (0.45 g) was slowly added to the mixture under stirring while the mixture was cooled to 5 °C in an ice bath. Afterward, the mixture was heated back to 35 °C stirred for 3 h, and during the period, the color of the mixture was changed from black to green. The mixture was then dropwise added into deionized water (100 mL) containing 3% \(\text{H}_2\text{O}_2\) under intense stirring at temperatures between 35 and 55 °C. The sediments were obtained and were centrifugally washed (4000 rpm) with deionized water until pH 7 was achieved in order to remove \(\text{SO}_4^{2-}\) ions and extra metal ions. The solutions were sonicated for 2 h and then centrifuged at 4000 rpm for 40 min. The obtained sediments were dehydrated by using a freeze dryer, and one-tenth of the bottom sediments was taken out to remove agglomerated \(\text{MnO}_2\) (the agglomerated \(\text{MnO}_2\) of the GO surface fell off and deposited on the bottom in the function of centrifugaf force). The dried samples of the GO/\(\text{MnO}_2\) powders were thermally treated at 190 °C in argon flow for 10 h and then cooled to room temperature. The final composites were called RGO/\(\text{Mn}_3\text{O}_4\).

#### 5.3. Fabrication the Electrochemical Measurement of RGO/\(\text{Mn}_3\text{O}_4\)

The RGO/\(\text{Mn}_3\text{O}_4\) or GO/\(\text{MnO}_2\) and \(\text{MnO}_2\) mixed with polyvinylene fluoride at a mass ratio of 95:5. Appropriate amount of N-methyl-2-pyrroldione was added into the mixture under stirring to form a homogeneous and high-fluidity suspension liquid. Nickel foam that was used as current collectors (1.0 × 1.0 cm²) was soaked overnight in the suspension liquid until its color was turned black. After taking it out from the liquid, the nickel foam was dried at 80 °C for 10 h in a vacuum furnace and then cooled in vacuum to room temperature. The formed electrodes were then immersed into 6 M KOH solution for further tests.

The electrochemical properties of the electrodes prepared in this work were tested at room temperature by using a classical three-electrode system consisting of a platinum foil, a saturated calomel electrode, and a 6 M KOH solution as the counter electrode, the reference electrode, and the electrolyte, respectively. The CVs were measured using an Alalis CHI660B electrochemical workstation (Shanghai Alalis Instrument Company, China), and GCD was detected using a CHI1140C electrochemical workstation (Shanghai CH Instrument Company, China).

#### 5.4. Measurement of Mn²⁺ Ions in Wastewater

Except for decreasing the additive amount of KMnO₄ and removing the \(\text{H}_2\text{O}_2\) the new experiment was basically identical to the above described (Section 5.2). Briefly, graphite powder (0.1 g) was slowly added to concentrated \(\text{H}_2\text{SO}_4\) (10 mL) at room temperature stirring. After 30 min, KMnO₄ (0.01 g) was slowly added to the mixture. After the reaction was completed, wastewater was collected during the GO filtration from the reaction system. The sediments were centrifugally washed
(4000 rpm) with deionized water and dehydrated by a freeze dryer. Then, 6 mL of the wastewater was diluted to 294 mL and stirred at 50 °C for 10 min. The diluted wastewater was then added with 15 mL of concentrated H₃PO₄, 5 g of Na₂HPO₄·2H₂O, 3.5 g of (NH₄)₂S₂O₈, and 3 mL of 2% AgNO₃ solution under stirring. The resulting mixture was boiled for 1 min.

5.5. Characterization. The crystallographic structures of GO/MnO₂ and RGO/MnO₄ samples were analyzed by powder XRD measurements (X’PertPro, PANalytical B.V Company, Netherlands) with Cu Kα radiation (λ ≈ 1.54 Å). Their metallography and particle distribution were observed using SEM equipped with an SSX-550 field-emission SEM meter (Zeiss Microscopy Company, Germany) and TEM equipped with a G20 TEM meter (FEI Company, the USA). Their Raman spectra were measured using an HR800 Raman spectrometer at 633 nm (Horiba Jobin Yvon LabRAM). Chemical compositions were analyzed by using an SC-144DR infrared sulfur−carbon analyzer (LECO, The USA) and a Z-2300 flame atomic absorption spectrometer (Hitachi, Japan). The components of composites are identified XPS (ESCALAB 250, Thermo VG Company, the USA).

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Notes

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■ REFERENCES

(1) Augustyn, V.; Simon, P.; Dunn, B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. Energy Environ. Sci. 2014, 7, 1597.
(2) Xu, H. Y.; Xu, S. L.; Li, X. D.; Wang, H.; Yan, H. Chemical bath deposition of haussmanite MnO₂ thin films. Appl. Surf. Sci. 2006, 252, 4091–4096.
(3) Lokhande, C. D.; Dubal, D. P.; Joo, O.-S. Metal oxide thin film based supercapacitors. Curr. Appl. Phys. 2011, 11, 255–270.
(4) Belkheder, M. R.; Ubale, A. U. Physical properties of Fe doped MnO₂ thin films synthesized by SILAR method and their antibacterial performance against E. coli. J. Saudi Chem. Soc. 2016, 20, 553–560.
(5) Yang, S.; Li, G.; Wang, G.; Zhao, J.; Gao, X.; Qu, L. Synthesis of MnO₄ nanoparticles/nitrogen-doped graphene hybrid composite for nonenzymatic glucose sensor. Sens. Actuators, B 2015, 221, 172–178.
(6) Li, Y.; Qu, J.; Gao, F.; Lv, S.; Shi, L.; He, C.; Sun, J. In situ fabrication of MnO₂ decorated graphene oxide as a synergistic catalyst for degradation of methylene blue. Appl. Catal., B 2015, 162, 268–274.
(7) Qian, J.; Wang, Y.; Chen, Z.; Liu, C.; Zhou, Y.; Yang, Y.; Song, Y.; Kong, B. Three dimensional MnO₂-CeO₂/holey-graphene hierarchical architectures from stem for high-performance asymmetric supercapacitors. Inorg. Chem. Commun. 2019, 104, 8–13.
(8) Tian, Y.; Li, D.; Liu, J.; Wang, H.; Zhang, J.; Zheng, Y.; Liu, T.; Hou, S. Facile Synthesis of MnO₂ Nanoplates-Anchored Graphene Microspheres and Their Applications for Supercapacitors. Electrochem. Acta 2017, 257, 155–164.
(9) Yao, J.; Yao, S.; Gao, F.; Duan, L.; Niu, M.; Liu, J. Reduced graphene oxide/MnO₂ nanohybrid for high-rate pseudocapacitive electrodes. J. Colloid Interface Sci. 2018, 511, 434–439.
(10) Yang, X.; He, Y.; Bai, Y.; Zhang, J.; Kang, L.; Xu, H.; Shi, F.; Lei, Z.; Liu, Z.-H. MnO₂ nanocrystalline/graphene hybrid electrode with high capacitance. Electrochem. Acta 2016, 188, 398–405.
(11) Yang, J.; Wang, L.; Ma, Z.; Wei, M. In situ synthesis of MnO₂ on Ni foam/graphene substrate as a newly self-supported electrode for high supercapacitive performance. J. Colloid Interface Sci. 2019, 534, 665–671.
(12) Rathour, R. K. S.; Bhattacharya, J. A green approach for single-pot synthesis of graphene oxide and its composite with MnO₂. Appl. Surf. Sci. 2018, 437, 41–50.
(13) Kang, J. H.; Kim, T.; Choi, J.; Park, J.; Kim, Y. S.; Chang, M. S.; Jung, H.; Park, K. T.; Yang, S. J.; Park, C. R. Hidden Second Oxidation Step of Hummers Method. Chem. Mater. 2016, 28, 756–764.
(14) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon 2007, 45, 1558–1565.
(15) Stankovich, S.; Piner, R. D.; Chen, X.; Wu, N.; Nguyen, S. T.; Ruoff, R. S. Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate). J. Mater. Chem. 2006, 16, 155–158.
(16) Park, S.; Ruoff, R. S. Chemical methods for the production of graphenes. Nat. Nanotechnol. 2009, 4, 217–224.
(17) Bagri, A.; Mattevi, C.; Acik, M.; Chabal, Y. J.; Chhowalla, M.; Shenoy, V. B. Structural evolution during the reduction of chemically derived graphene oxide. Nat. Chem. 2010, 2, 581–587.
(18) Lee, S.; Park, W. K.; Yoon, Y.; Baek, B.; Yoo, J. S.; Kwon, S. B.; Kim, D. H.; Hong, Y. J.; Kang, B. K.; Yoon, D. H.; et al. Quality improvement of fast-synthesized graphene films by rapid thermal chemical vapor deposition for mass production. Mater. Sci. Eng., B 2019, 242, 63–68.
(19) Smith, A. T.; LaChance, A. M.; Zeng, S.; Liu, B.; Sun, L. Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites. Nano Mater. Sci. 2019, 1, 31–47.
(20) Chen, D.; Feng, H.; Li, J. Graphene oxide: preparation, functionalization, and electrochemical applications. Chem. Rev. 2012, 112, 6027–6053.
(21) Wu, Z.-S.; Ren, W.; Gao, L.; Liu, B.; Jiang, C.; Cheng, H.-M. Synthesis of high-quality graphene with a pre-determined number of layers. Carbon 2009, 47, 493–499.
(22) Zhang, L.; Liang, J.; Huang, Y.; Ma, Y.; Wang, Y.; Chen, Y. Size-controlled synthesis of graphene oxide sheets on a large scale using chemical exfoliation. Carbon 2009, 47, 3365–3368.
(23) Zhang, L.; Li, X.; Huang, Y.; Ma, Y.; Wan, X.; Chen, Y. Controlled synthesis of few-layered graphene sheets on a large scale using chemical exfoliation. Carbon 2010, 48, 2367–2371.
(24) Parvez, K.; Yang, S.; Feng, X.; Müller, K. Exfoliation of graphene via wet chemical routes. Synth. Met. 2015, 210, 123–132.
(25) Brodie, B. C. On the atomic weight of graphite. Philos. Trans. R. Soc. London 1859, 189, 249–259.
(26) Hummers, W. S.; Offeman, R. E. Preparation of graphitic oxide. J. Am. Chem. Soc. 1958, 80, 1339.
(27) Raj, B. G. S.; Ramprasad, R. N. R.; Asiri, A. M.; Wu, J. J.; Anandan, S. Ultrasound assisted synthesis of MnO₂ nanoparticles anchored graphene nanosheets for supercapacitor applications. Electrochem. Acta 2015, 156, 127–137.
(28) Dimiev, A. M.; Tour, J. M. Mechanism of graphene oxide formation. ACS Nano 2014, 8, 3060–3068.
(29) Wu, H.; He, D.; Wang, Y. Facile one-step process synthesized reduced graphene oxide/MnO₂ nanocomposite for a symmetric supercapacitor. Mater. Lett. 2020, 268, 127613.
(30) Jia, P. K.; Kashyap, V.; Gupta, K.; Kumar, V.; Debnath, A. K.; Roy, D.; Rana, S.; Kurungot, S.; Ballav, N. In-situ generated MnO3O4 reduced graphene oxide nanocomposite for oxygen reduction reaction and isolated reduced graphene oxide for supercapacitor applications. Carbon 2019, 154, 285–291.
(31) Jin, G.; Xiao, X.; Li, S.; Zhao, K.; Wu, Y.; Sun, D.; Wang, F. Strongly coupled graphene/Mn₃O₄ composite with enhanced electrochemical performance for supercapacitor electrode. Electrochim. Acta 2015, 178, 689–698.
(32) Anilkumar, K. M.; Manoj, M.; Jinisha, B.; Pradeep, V. S.; Jayalekshmi, S. MnO₂ reduced graphene oxide nanocomposites with tailored morphology for high power supercapacitor applications. Electrochim. Acta 2017, 236, 424–433.
(33) Chen, S.; Wang, L.; Huang, M.; Kang, L.; Lei, Z.; Xu, H.; Shi, F.; Liu, Z.-H. Reduced graphene oxide/Mn 3 O 4 nanocrystals hybrid fiber for flexible all-solid-state supercapacitor with excellent volumetric energy density. Electrochim. Acta 2017, 242, 10–18.
(34) Haldar, P.; Biswas, S.; Sharma, V.; Chowdhury, A.; Chandra, A. MnO₂ polyaniline-graphene as distinctive composite for use in high-performance supercapacitors. Appl. Surf. Sci. 2019, 491, 171–179.
(35) Zhang, N.; Qi, P.; Ding, Y.-H.; Huang, C.-J.; Zhang, J.-Y.; Fang, Y.-Z. A novel reduction synthesis of the graphene/MnO₃O₄ nanocomposite for supercapacitors. J. Solid State Chem. 2016, 237, 378–384.
(36) Shah, H. U.; Wang, F.; Javed, M. S.; Shaheen, N.; Saleem, M.; Li, Y. Hydrothermal synthesis of reduced graphene oxide-MnO₃O₄ nanocomposite as an efficient electrode material for supercapacitors. Ceram. Int. 2018, 44, 3580–3584.
(37) Cui, M.; Tang, S.; Ma, Y.; Shi, X.; Syed, J. A.; Meng, X. Monolayer standing MnO₂-Nanosheet covered MnO₂ octahedrons anchored in 3D N-Doped graphene networks as supercapacitor electrodes with remarkable cycling stability. J. Power Sources 2018, 396, 483–490.
(38) Xu, J.; Fan, X.; Xia, Q.; Shao, Z.; Pei, B.; Yang, Z.; Chen, Z.; Zhang, W. A highly atom-efficient strategy to synthesis reduced graphene oxide-MnO₃O₄ nanoparticles composites for supercapacitors. J. Alloys Compd. 2016, 685, 949–956.
(39) Huang, Z.; Li, S.; Li, Z.; Li, J.; Zhang, G.; Cao, L.; Liu, H. MnO₃O₄ nanoflakes/rGO composites with moderate pore size and O=JC-O-Mn bond for enhanced supercapacitor performance. J. Alloys Compd. 2020, 830, 154637.
(40) Xu, C.; Li, B.; Du, H.; Kang, F.; Zeng, Y. Supercapacitive studies on amorphous MnO₂ in mild solvents. J. Power Sources 2008, 184, 691–694.
(41) Yan, J.; Fan, Z.; Wei, T.; Qian, W.; Zhang, M.; Wei, F. Fast and reversible surface redox reaction of graphene–MnO₂ composites as supercapacitor electrodes. Carbon 2010, 48, 3825–3833.
(42) Kudin, K. N.; Ozbas, B.; Schnepp, H. C.; Prud’homme, R. K.; Aksay, I. A.; Car, R. Raman spectra of graphite oxide and functionalized graphene sheets. Nano Lett. 2008, 8, 36–41.
(43) Stobinski, L.; Lesiak, B.; Malolepszy, A.; Mazurkiewicz, M.; Mierzw, B.; Zemek, J.; Jiricek, P.; Bieloshapka, I. Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods. J. Electron Spectrosc. Relat. Phenom. 2014, 195, 145–154.
(44) Dimiev, A. M.; Bachilo, S. M.; Saito, R.; Tour, J. M. Reversible formation of ammonium persulfate/sulfuric acid graphite intercalation compounds and their peculiar Raman spectra. ACS Nano 2012, 6, 7842–7849.
(45) Mei, J.; Zhang, L. Facile and economic synthesis of nitrogen doped graphene/manganese dioxide composites in aqueous solution for energy storage devices. Mater. Lett. 2015, 143, 163–166.
(46) Dimiev, A.; Kosynkin, D. V.; Alemany, L. B.; Chugaev, P.; Tour, J. M. Pristine graphite oxide. J. Am. Chem. Soc. 2012, 134, 2815–2822.
(47) Dimiev, A. M.; Alemany, L. B.; Tour, J. M. Graphene oxide. Origin of acidity, its instability in water, and a new dynamic structural model. ACS Nano 2013, 7, 576–588.
(48) Shaik, D. P.; Pitcheri, R.; Qiu, Y.; Hussain, O. M. Hydrothermally synthesized porous MnO₂ nanoparticles with enhanced electrochemical performance for supercapacitors. Ceram. Int. 2019, 45, 2226–2233.
(49) Zhang, J.; Chu, R.; Chen, Y.; Zeng, Y.; Zhang, Y.; Guo, H. Porous carbon encapsulated MnO₂ for stable lithium storage and its ex-situ XPS study. Electrochim. Acta 2019, 319, 518–526.
(50) Wang, K.; Zhu, M.; Ma, S.; Li, X.; Zhang, M.; Gao, E. Three water soluble coordination polymers: Synthesis, crystal structure and luminescent sensing for Cr(VI) and MnO₄ ions in the aqueous phase. Polyhedron 2019, 166, 60–64.
(51) Huang, B.; Wang, M.; Yang, X.; Xu, G.; Gu, Y. Enhanced electrochemical performance of the layered nickel-rich oxide cathode by KMnO₄ treatment precursor. J. Alloys Compd. 2019, 808, 151683.
(52) Zhang, C.; Li, R.; Liu, J.; Chen, G.; Guo, S.; Xu, R.; Li, X.; Xiao, S.; Shen, Z. Effect of KMnO₄ on chemical, crystal and microscopic structure of polycyacrylonitrile fibers. Ceram. Int. 2019, 45, 17669–17674.
(53) Arison, S.; Frishberg, C.; Frankl, G. Thermodynamic properties of the graphite-bisulphate lamellar compounds. Carbon 1971, 9, 715–723.
(54) Park, J.; Cho, Y. S.; Sung, S. J.; Byeon, M.; Yang, S. J.; Park, C. R. Characteristics of graphene oxide-based graphene to various end-uses. Energy Storage Mater. 2018, 14, 8–21.
(55) Dimiev, A. M.; Ceriotti, G.; Behabtu, N.; Zakhidov, D.; Pasquali, M.; Saito, R.; Tour, J. M. Direct real-time monitoring of stage transitions in graphite intercalation compounds. ACS Nano 2013, 7, 2773–2780.
(56) Park, J.; Kim, Y. S.; Sung, S. J.; Kim, T.; Park, C. R. Highly dispersible edge-selectively oxidized graphene with improved electrical performance. Nanoscale 2017, 9, 1699–1708.
(57) Simon, P.; Gogotsi, Y. Materials for electrochemical capacitors. In Nanoscience and Technology: A Collection of Reviews from Nature Journals; Rodgers, P., Ed.; World Scientific Publishing Group: Singapore, London, 2010; pp 320–329.
(58) Wang, D.; Li, Y.; Wang, Q.; Wang, T. Facile Synthesis of Porous MnO₂ Nano-crystal-Graphene Nanocomposites for Electrochemical Supercapacitors. Eur. J. Inorg. Chem. 2012, 628–635.