Synthesis of rGO via UV-assisted photocatalytic reduction of graphene oxide

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Abstract

We perform a novel strategy for the synthesis of reduced graphene oxide (rGO) with an 18 W UV-assisted photocatalytic reduction method. The surface morphology and internal structure of the obtained rGO were identified by Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). The rGO electrode materials have 2-6 layers graphene layers with a thickness of 1.1 nm to 2.2 nm after the photocatalytic reduction for 10 h. The rGO shows a superb capacitance of 250.41 Fg^{-1} with obvious triangles in the electrochemical charge-discharge analysis, which indicates good reversibility between the graphene oxide and reduced graphene oxide. This research may provide new insights that contribute to resolving the capacity issues of lithium batteries. Copyright © 2018 VBRI Press.

Keywords:

Introduction

Graphene has drawn significant attention due to its two-dimensional single crystal carbon atom layer composed of hybridized sp^2 orbitals. Graphene exhibits excellent electrical properties, good chemical stability and a high specific surface area[1]. Graphene's unique structure allows it to be an excellent material candidate for ultracapacitor electrode[2,3]. Recently, various methods to prepare reduced graphene oxide have been studied, such as the chemical reduction method[4], the high temperature reduction method[5], the solvothermal reduction route[6], and the electrochemical reduction method[7]. However, graphene has an incomplete reduction due to defects and agglomerations using these synthetic methods. To overcome these disadvantages, many efforts have been undertaken to develop proper synthetic methods[8,9]. Several works have used the photocatalytic reduction method to synthesize reduced graphene oxide. The photocatalytic reduction method is environmental friendly, has a high efficiency, low cost and tunable reduction degree[10,11]. The photocatalytic methodology can avoid the re-aggregation of graphene to a certain extent, while producing a porous structure to obtain a high surface area and high energy density[12].

In this work, we use the photocatalytic reduction method to synthesize the rGO electrode material. The microstructure of the samples is investigated by Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). Furthermore, the electrochemical performance of the rGO electrode material, which shows a superb capacitance, is also investigated. Therefore, this study applied the photocatalytic reduction method for preparing graphene materials and explored its ultra-capacitance applications in lithium batteries.

Experimental

GO was synthesized by the improved Hummer's method[13]. Firstly, sulfuric acid and phosphoric acid in a volume ratio of 9:1 were mixed and 3 g of graphite was added to the mixture and stirred for 1 h. Secondly, 12 g of potassium permanganate ($KMnO_4$) was added with a stirring rate of 600 rpm for 2 h at 35^0C. Thirdly, the reaction temperature was increased to 50^0C with agitation for 12 h. Lastly, H_2O_2 was added to obtain a golden-colored solution. After centrifugation, acid washing, and water washing to neutral, the brownish-yellow GO was prepared with vacuum drying at 50^0C for 24 h.

The synthesized GO was added into absolute ethyl alcohol. The solution was ultrasonicated for 30 min under a nitrogen atmosphere and then irradiated with UV-light (254 nm, 18 W, Philips) for different selected times. The temperature was controlled at 40℃ and the suspended rGO black solution was washed with water and protected from light sources.

The as-prepared rGO was analyzed by TEM (JEOL, TEM-3010) at an acceleration voltage of 80 kV and by AFM (BRUKER, Dimension Icon).

The rGO, polytetrafluoroethylene as a binder, and a black carbon as a conductive additive at a weight ratio of 8:1:1 were dispersed in 2-propanol. The homogeneous mixture was obtained by stirring for 12 h. The slurry was coated onto graphite paper as a current collector, as previously reported[9].

The electrochemical properties were investigated with a three electrode cell system in a 1 M H_2SO_4 electrolyte by a cyclic voltammetry (CH Instruments, Model 400) method at scan rates of 10 and 75 mVs^{-1} within the voltage range of -0.5 to 0.5 V.

Results and discussion

Fig. 1(a) shows the AFM images of the rGO electrode material after photocatalytic reduction for 10 h. In theory, the single layer thickness of graphene is approximately 0.35 nm. However, the actual thickness is higher than the theoretical thickness due to existence adsorbates on the surface. **Fig 1(a)** shows that the surface morphology of the as-prepared rGO has irregular flakes and distinct wrinkles. Moreover, disordered stacks occur on the surface of the samples during the reduction process.

The thickness of the rGO electrode material is between 1.3 nm and 2.0 nm, as shown in **Fig. 1(b)**. Therefore, we can estimate that obtained rGO electrode material contains approximately 2-6 layers.

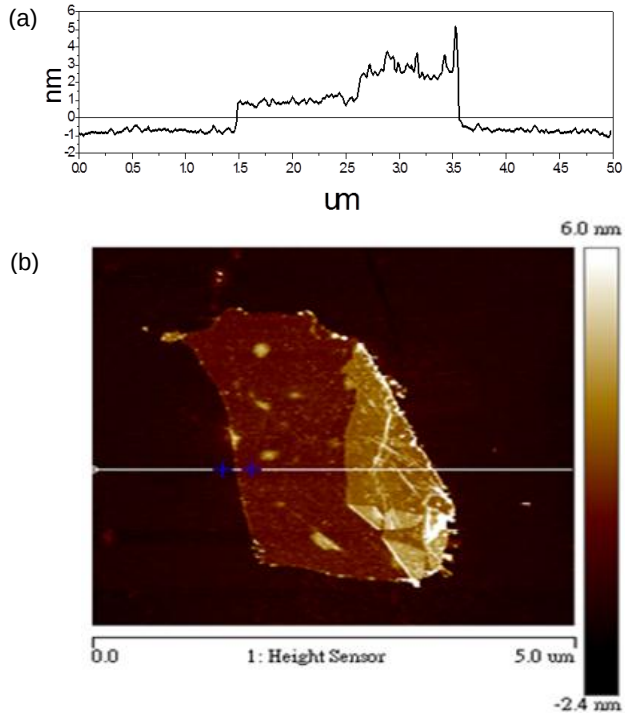

Fig. 1. AFM images (a) and thickness (b) of rGO electrode material after photocatalytic reduction for 10 h.

Fig. 2 shows TEM images of the as-prepared rGO electrode material after photocatalytic reduction for 10 h. As seen in **Fig. 2 (a),** the phenomena are likely to cause the graphene to gather and curl to produce folding. The electron diffraction pattern was used to observe the crystal structure and to determine the number of graphene layers. **Fig. 2 (b)** shows the electron diffraction patterns of the as-obtained rGO electrode material after photocatalytic reduction for 10 h. The spots from the hexagonal ring electron diffraction were observed in the electron diffraction maps of the rGO. However, with careful observation it is found that the tail of the light spots was missing. Upon further analysis, the intensity of the (1100) is stronger than the intensity of the (2110), which reveals that the spots are strong for the monolayer hexagonal structure.

We can observe an obvious halo around the electron diffraction patterns, which may be considered a result of the as-prepared rGO with several layers, and not a single layer. The results agree with the analysis of the AFM.

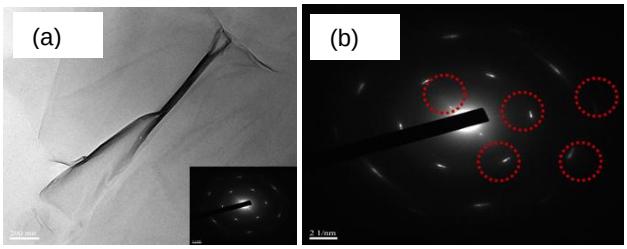

Fig. 2. TEM images (a) and electron diffraction patters (b) of rGO electrode material after photocatalytic reduction for 10h.

From the electron diffraction patterns, we can see an obvious halo around it. It may be considered as the as-prepared rGO with several layers, not a single layer. The results agree with the analysis of the AFM.

The capacitance (C_s) values of rGO electrode materials can be calculated from the *C-V* curves according to the following the equation[14]:

$$c_s = \frac{\int Idv}{vm\,\Delta v}$$

where *m* is the mass of the rGO electrode material (mg), *v* is the scan rate (Vs^{-1}), Δv is the potential window (V) and the integrated area under the *C-V* curve, and *I* is the current (A).

Fig. 3 shows the *C-V* curves of the GO and rGO electrode materials obtained for various photocatalytic reduction times. The results show that *C-V* curves are not a rectangle shape for the GO, where the electric double layer has no obvious redox peaks. However, the GO has a high specific surface area, and the surface and edge of the GO contain several oxygen groups. Therefore, the conductivity of the GO has fallen dramatically, where the capacitance value is only 74.69 Fg^{-1}. When the photocatalytic reduction time is 1 h, the overall capacitance value rises to 22.21 Fg^{-1} as calculated from equation (1) and shown **Table 1**. It can be deduced that the surface of the GO contains in-part, activated oxygen functional groups. When the photocatalytic reduction time is 5 h, the capacitance value decreases, indicating that the oxygen functional groups are eliminated. Moreover, the graphene layers stack again in the reduction process. With increasing the photocatalytic reduction time to 10 h, the reduction reaction becomes more complete, and the rectangular features are observed in the *C-V* curves.

Table 1. C-V capacitance of the rGO under various photocatalytic reduction times.

Scan rate ($0.01v\ s^{-1}$)	Capacitance (Fg^{-1})			
	GO	1 h	5 h	10 h
	74.69	221.21	189.26	250.41

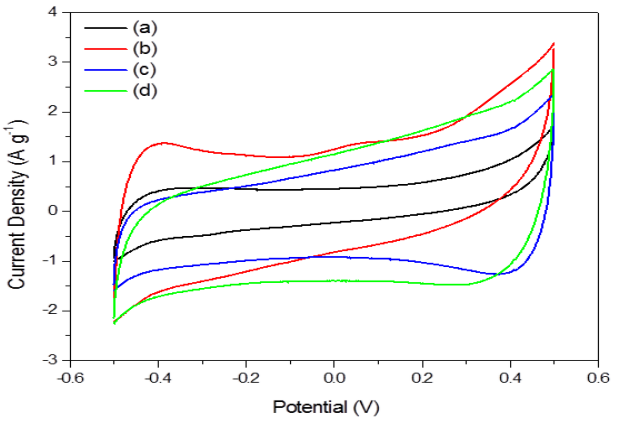

Fig. 3. The *C-V* curves of GO and rGO material electrode obtained from various times of photocatalytic reduction: (a) GO (b) 1 h (c) 5 h (d) 10 h .

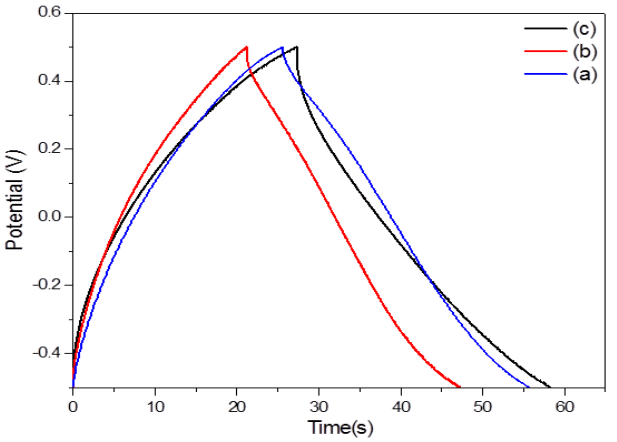

Fig. 4. The charge and discharge electrochemical analysis of rGO material electrode obtained from various times of photocatalytic reduction: (a) 1 h, (b), (c) 10 h .

Fig. 4 shows the charge and discharge of the electrochemical analysis for different photocatalytic reduction times of the rGO. All of the curves are approximately trianglular in shape, indicating good redox reversibility between the graphene and rGO.

Moreover, an excellent capacitance value was obtained from a certain time of photocatalytic reduction reaction. Therefore, the rGO has great value in research and applications. Through these experimental analyses, we find that the photocatalytic reduction is an efficient approach for the synthesis of rGO, where the method requires reduced cost and time.

Conclusions

In summary, rGO electrode materials have been synthesized by a photocatalytic reduction method. The surface morphology and internal structure were analyzed by TEM and AFM. A more complete reduction reaction was obtained by an increase in the photocatalytic reduction time, which is due to the removal of the oxygen functional groups at the surfaces and edges of the GO. Moreover, increasing the photocatalytic reduction time also increased the degree reduction of the graphene oxide for rGO, resulting in a higher capacitance value. The electron diffraction patterns of the rGO electrode material also revealed that the rGO electrode materials have between 2 and 6 layers of rGO and a thickness of between 1.3 nm and 2.0 nm.

Acknowledgments

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