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Taking full advantage of $KMnO_4$ in simplified Hummers method: A green and one pot process for the fabrication of alpha MnO_2 nanorods on graphene oxide

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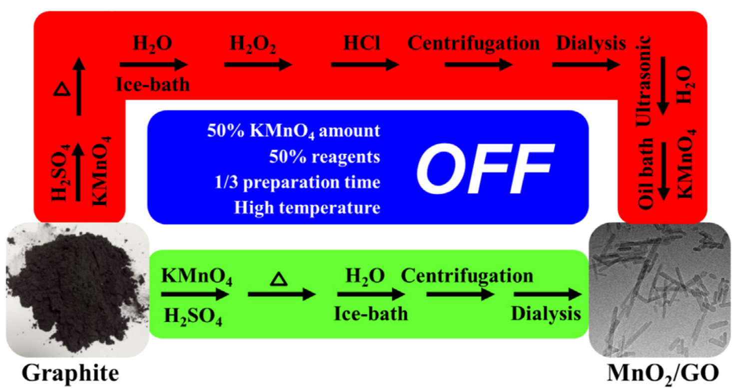
HIGHLIGHTS

- A simplified Hummers method was developed to fabricate MnO_2/GO composite.
- Exceed 50% of $KMnO_4$ amount, 50% of reagents and 1/3 of preparation time were cut.
- High reaction temperature was avoid.
- The method is green, low cost, eco-friendly, time and energy saving, easy to scale up.

GRAPHICAL ABSTRACT



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ABSTRACT

In the work, we demonstrated the possibility of directly using the existing $KMnO_4$ as Mn precursor and graphite as the carbon precursor in Hummers method to decorate MnO_2 nanomaterials over graphene oxide (GO). Nanorod-like α-MnO_2 in the form of single crystal were found closely decorated over GO. The MnO_2 content could be easily adjusted from 45% to 18% by decrease the amount of $KMnO_4$ from 15.0 g to 7.5 g. Compared with the reported work, the developed simplified Hummers method in this work could better utilize $KMnO_4$ by cutting exceed 50% of $KMnO_4$ amount, cut the reagents especially some hazardous reagents from 6–8 items to 3 items, cut 1/3 of the preparation time, avoid high temperature reaction. All those advantages make the simplified Hummers method green, low cost, eco-friendly, time and energy saving, which are beneficial to the industrialization of the MnO_2/GO composite. The MnO_2/GO composite showed good performance in the degradation of methylene blue with the assistance of H_2O_2.

1. Introduction

In the past decade, graphene oxide (GO) has been attracting tremendous attention in the applications of catalysts, electronics, polymer composites, energy-related materials, sensors, etc. owing to its remarkable electrical, mechanical and thermal properties (Georgakilas et al., 2016; Li et al., 2016; Lin et al., 2016; Shen et al., 2016; Xu et al., 2016; Zhou et al., 2017). The performances of GO in different applications could be further promoted through decorating different metal oxides onto the surface of GO (H. Ma et al., 2016; Z. Ma et al., 2016; Moussa et al., 2016; Zhu and

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Deng, 2016). Among them, the composite of MnO_2/GO has been used as an effective material in supercapacitors, lithium batteries, sensors and catalysts by combining the unique properties of MnO_2 in abundance, low cost, environmental friendliness and excellent catalytic performance (Huang et al., 2015, 2017; Wang et al., 2016; Zhao et al., 2015). MnO_2 in the different forms of nanoparticles, nanorods, nanosheets has been reported to optimize the properties of MnO_2/GO composite (Hu et al., 2016; Li et al., 2015; Liu et al., 2018; Tanggarnjanavalukul et al., 2017; L. Wang et al., 2015; Y. Wang et al., 2015; Zhu and He, 2012). For example, the combination of MnO_2 nanorods and GO showed good electrochemical behaviors for supercapacitors and high-performance lithium-ion batteries (Chae et al., 2016; Chen et al., 2010; Yang et al., 2015). Different approaches have been development to fabricate MnO_2/GO, such as, chemical precipitation method, hydrothermal treatment, thermal decomposition routes, electrodeposition and microwave method (Cheng et al., 2011; Dong et al., 2012; Ma and Zhao, 2016; Sun et al., 2016; Yan et al., 2010). In those methods, GO obtained through different methods (e.g. Hummers method) was used as the support. MnO_2 was decorated on GO through the redox reaction between $KMnO_4$ as reductant and Mn^{2+} as oxidant according to the following equation (Portehault et al., 2007; Qu et al., 2014):

$$2MnO_4^{-} + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^{+} \quad (1)$$

In this process, high temperature and pressure, organic solvent even some hazardous reagents are usually required to obtain high quality MnO_2/GO (Chen et al., 2012; Fan et al., 2011; Feng et al., 2013; Huang and Wang, 2011; Lee et al., 2011; J.X. Li et al., 2012; Y. Li et al., 2012; Mao et al., 2012; Wu et al., 2010; Xu et al., 2017; Yu et al., 2011a, 2011b; Zhao et al., 2012). For example, Wu et al. reported a MnO_2 nanowire/graphene composite as high-energy electrochemical capacitor by a heating method. About 26 h for heating and different agents like $NH_4S_2O_8$, K_xMnO_2, and tetrabutylammonium are required (Wu et al., 2010). It is thus urgent to develop a simple, low cost, green and scalable approach to fabricate a hybrid of MnO_2/graphene with high quality from the application consideration.

Hummers method is a well-known method for the fabrication of GO since it was developed by Hummers and Offeman in 1958 due to the important advantages including time saving, safety and less toxicity compared with previous techniques (Hummers and Offeman, 1958). In this process, the oxidation of graphite into graphite oxide within a few hours was achieved by harsh treatment of graphite powders in a concentrated H_2SO_4 solution containing both $KMnO_4$ and $NaNO_3$ (Chen et al., 2013, 2015). In the past 20 years, a few number of modified Hummers methods were further developed to promote the yields and avoid the generation of toxic gases (e.g. NO_2, N_2O_4) and residual nitrate through removing $NaNO_3$. However, other reagent H_3PO_4 or more $KMnO_4$ were needed. In those processes, excessive $KMnO_4$ are required for the oxidation of graphite, leaving a large amount wastewater containing Mn ions. Oppositely, the residual Mn species on the surface of GO were further removed to purify the obtained GO. Obviously, this process is absolutely not atom economy while causing water pollution. Is it possible to fully or partially use those Mn species as Mn precursor for preparing MnO_2 nanomaterials over GO started from the precursor of graphite?

From this respect, in this work, we simplified the Hummers method to prepare MnO_2 over GO directly use the existing $KMnO_4$ as Mn precursor and graphite as the carbon precursor as demonstrated in Fig. 1. Firstly, the approach with red background illustrated a reported process for the fabrication of MnO_2/GO started from graphite. Two major steps, namely the formation of GO through modified Hummers method and the followed deposition of MnO_2 nanostructure (e.g. hydrothermal process) were involved. Obviously, this process is tedious and time consuming. In the former step (modified Hummers method), graphite was first oxidized to GO and the produced impurities (acids, manganese salts, etc.) were followed removed by the addition of H_2O_2 and HCl and the dialysis process. The later step was the redox reaction between $KMnO_4$ and Mn^{2+} species to produce MnO_2 over GO. Here, we proposed to preserve the Mn species without adding H_2O_2 and HCl in the former step (green background). Only the dialysis was reserved to purify the samples. Amazingly, the reserved Mn species were found in the form of MnO_2 single crystal nanorods which means that the steps for the decorating of MnO_2 are no longer needed. Obviously, in this process, the $KMnO_4$ was better utilized, both H_2O_2 and HCl are avoid, the preparation duration was reduced from 32 h to 21 h. All those properties indicate that the developed approach for MnO_2/GO preparation is green, eco-friendly, low cost, time-saving and scalable.

2. Experimental section

2.1. Materials

Potassium permanganate ($KMnO_4$), Sulphuric acid (H_2SO_4), Graphite powder, Citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) were purchased from Sinopharm Chemical Reagent Company (Shanghai,

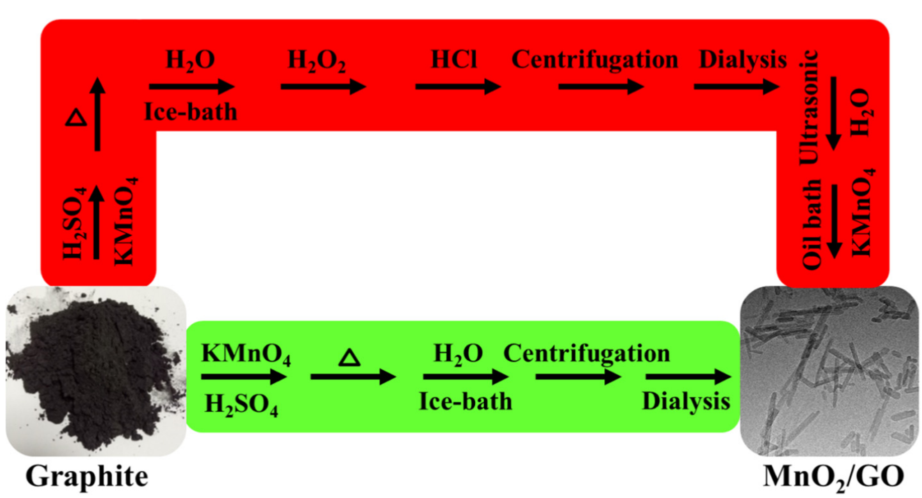

Fig. 1. Schematic illustration of the simple and complex synthesis processes of MnO_2/GO.