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Fabrication of stable aqueous dispersions of graphene using gellan gum as a reducing and stabilizing agent and its nanohybrids

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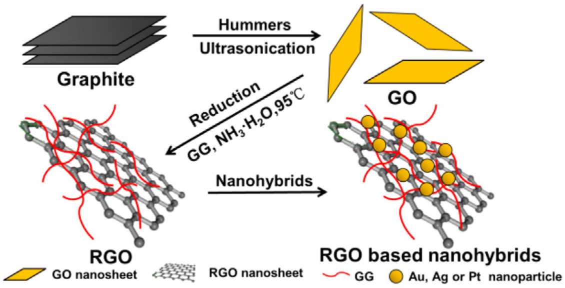
HIGHLIGHTS

- A green method for preparation of reduced graphene oxide (RGO) was developed.
- Gellan gum (GG) was used as both a reducing and a stabilizing agent.
- RGO nanosheets can be dispersed stably in aqueous medium by adsorption of GG.
- RGO containing GG can be used as a template to prepare noble metal nanohybrids.
- These obtained nanohybrids exhibit good electrochemical activities.

GRAPHICAL ABSTRACT



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ABSTRACT

An environment-friendly method for the reduction of graphene oxide (GO) was developed by utilizing the acid polysaccharide of gellan gum (GG) as both a reducing and a stabilizing agent. The reduction process of GO was monitored by UV–Vis spectroscopy and the factors that affect the reduction of GO, such as the molecular weight of GG, the weight ratio of GG/GO, pH and reaction temperature, were studied. A mechanism for reduction of GO with GG and the optimum reaction condition were proposed. The obtained reduced graphene oxide (RGO) that bears adsorbed GG (G-RGO) was characterized by Fourier transform infrared spectroscopy, X-ray diffraction spectroscopy, Thermogravimetric analysis, Raman spectroscopy, X-ray photoelectron spectroscopy and Atomic force microscopy. The results showed that GG can efficiently reduce GO and adsorb onto the RGO nanosheets giving a stable G-RGO aqueous dispersion. Parameters affecting the stability of G-RGO aqueous dispersion, such as pH and ionic strength, were also studied. This work promised a new green strategy for large scale production of RGO with highlighting multiple functions of the natural, nontoxic and biodegradable macromolecule of GG. Moreover, GG was found to be able to promote reducing $HAuCl_4$, $AgNO_3$ or H_2PtCl_6 to Au, Ag or Pt nanoparticles respectively onto G-RGO surfaces providing noble metal nanoparticle-G-RGO nanohybrids that exhibit good electrochemical activities with potential applications in the fields of catalysis and energy storage.

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1. Introduction

Graphene, a single layer of sp^2-hybridized carbon atoms arranged in a perfect honeycomb hexagonal lattice [1,2], has been attracting substantial attention due to its unique electrical

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properties [3–5], excellent mechanical properties [6–8], and superior thermal properties [9]. Just because of these remarkable properties, graphene shows huge potential applications in many areas of technology such as nanoelectronic devices [10], solar cells [11], supercapacitors [12] and composite materials [6,13].

In order to take full advantage of these aspects, large-scale production of graphene is a priority. So far, several physical and chemical methods have been used to prepare graphene [14]. The physical methods include micromechanical cleavage [15], epitaxial growth [16], chemical vapour deposition (CVD) [17,18] and cutting carbon nanotubes [19]. Although these physical methods can yield high quality graphene, they are too low-yield and low-throughput to industrially scalable process. The chemical methods consist of intercalation followed by solution-based exfoliation [20–22], synthesis of small aromatic compounds through stepwise organic chemical reactions [23,24] and chemical reduction of graphene oxide [25]. Among of them, chemical reduction of graphene oxide offers great superiority over the other two methods in terms of cost effectiveness and bulk-scale productivity [26,27]. At present, a number of chemical reducing agents and corresponding reduction procedures have been developed even though these reduction mechanisms involve remain unproven [28]. Hydrazine [26,29,30] and its derivatives [6,27] are extensively used reducing agents to date for their high reduction efficiency. These reduction process can be implemented in water or organic solvents such as N,N-dimethylformamide (DMF) [31] and N-methyl-2-pyrrolidinone (NMP) [32] at ambient or under hydro/solvothermal conditions. However, hydrazine and its derivatives are very toxic and potentially explosive that should be avoided in actual process, especially in large-scale production [33].

Afterwards, other chemical reducing agents such as hydroquinone [34], sodium borohydride [35], sodium hydrogen sulfite [35], poly(amidoamine) [36], hydrohalic acid [37], p-phenylene diamine [38], and pyrrole [39] are found to be efficient reducing agents for GO. Unfortunately, these chemical reducing agents are still toxic to some extent being harmful to both humans and environment. In response, attempts have been made to develop safe and environmentally friendly reducing agents, like L-ascorbic acid [40] and L-lysine [41]. Although they are non-toxic, irreversible agglomerates will be formed during the reduction process owing to the strong tendency of π-π stacking between the chemical reduced GO (RGO) sheets. Therefore, aggregation of graphene nanosheets in chemical reduction process is another obstacle for large-scale production of graphene. This problem can be solved by using noncovalent functionalization [20,42–45] and covalent modification [29,35,46–48] of the graphene, but the presence of excess stabilizers is generally undesirable for most applications. Recently, many efforts have been made to settle aforementioned problems by using natural resources as reduction agents and stabilizers instead of toxic reducing agents and foreigner stabilizers. For example, reducing sugar [49], protein bovine serum [50], green tea [51], dextran [52], chitosan [53] and wild carrot root [54] have been employed as reduction agents and stabilizers in reducing GO.

Additionally, graphene nanosheet is an attractive substrate for immobilizing metal nanoparticles due to its excellent conductivity and large specific surface area. Such hybridization of graphene can usually enhance the catalytic activities and reactivities of metal nanoparticles. The main preparation of graphene/metal nanoparticles hybrids methods consist of in situ growth, solution mixing, solid reaction and so on [55]. Recently, biomacromolecules such as DNA [56], bovine serum albumin [50], dextran [52] and chitosan [53] – functionalized graphene nanosheets served as a template for the direct synthesis of graphene/metal nanoparticles hybrids have been reported. We also utilized a pyrene/hyaluronan conjugate -stabilized RGO as a template to directly build up various nanosized noble metal nanoparticles [57]. Although the preparation of RGO and RGO based hybrids have been developed, an environmentally friendly and cost-effective reducing agent for the synthesis of stable graphene dispersions and graphene based hybrids still remains highly desirable [58].

Gellan gum (GG) is an extracellular bacterial polysaccharide produced in high yield by the non-pathogenic strain *Sphingomonas elodea*, possessing a tetrasaccharide repeat unit consisting of two glucose residues, one glucuronic acid residues, and one rhamnose residue [59]. It has widespread applications in food and cosmetics mainly as a multi-functional gelling, stabilizing and suspending agent, and has received both US FDA and EU (E418) approval for these purposes. Additionally, GG has been utilized for biomedical purposes as controlled drug delivery systems [60–64] and tissue engineering materials [65–69] attributed to its peculiar gelation and rheological properties. Recently, Sheetal Dhar et al. have shown that GG can be used as reducing and stabilization agent for gold or silver nanoparticle synthesis in aqueous solution and that the resulting gellan-coated nanoparticles are biocompatible [70–73]. In addition, Panhuis et al. have used GG to disperse carbon nanotubes in aqueous media which enables subsequent processing into useful architectures by various technologies [74–77]. In this paper, we report an environmentally friendly and efficient approach for the synthesis of both RGO and RGO-based noble metal nanohybrids by using GG as a reducing and stabilization agent. The advantage of this method is that GG as a conventional food additive, is nontoxic, biodegradable, cheap and easy to get, and thereby it is facile to prepare RGO and RGO-based nanohybrids. Most importantly, we found that the obtained noble metal nanoparticle-RGO nanohybrids showed good electrochemical activities in alkaline methanol solutions.

2. Experimental

2.1. Materials

Graphite powder (100 mesh, 99.9995%) was purchased from Alfa-aesar Co., Ltd. Concentrated sulphuric acid (H_2SO_4, 95–98%), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), sodium nitrate ($NaNO_3$), concentrated hydrochloric acid (HCl), ammonia solution ($NH_3 \cdot H_2O$, 25%), chloroauric acid ($HAuCl_4$), chloroplatinic acid (H_2PtCl_6), silver nitrate ($AgNO_3$) and other regents were all obtained from Sinopharm Chemical Reagent Co., Ltd. (SCRC). GG ($M_w = 100$, 400 and 600 kDa, respectively) was acquired from Zhejiang DSM Zhongken Biotechnology Co., Ltd. All chemicals were analytical grade and used as received without further purification. All aqueous solutions were prepared with ultrapure water (>18 MΩ) from a Milli-Q Plus system (Millipore).

2.2. Sample preparation

2.2.1. Preparation of GO

GO was prepared from graphite powder based on the well-known modified Hummers method [78,79]. In brief, concentrated H_2SO_4 (23 ml) was added into a 250 ml flask filled with graphite (1 g) at 0 °C (ice bath), followed by the addition of $NaNO_3$ (0.5 g). Then solid $KMnO_4$ (3 g) was slowly added into the solution with stirring while the temperature of the mixture was kept below 20 °C for 2 h. Next, the mixture was stirred for another 30 min after the temperature was increased to 35 °C. Then excess ultrapure water was added to the mixture and the temperature was increased to 80 °C. Finally, 30% H_2O_2 was added dropwise until the colour of the mixture changed to brilliant yellow and no more gas was being produced. The dispersion was filtered and washed several times

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