



# Green synthesis of biocompatible chitosan–graphene oxide hybrid nanosheet by ultrasonication method



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## ARTICLE INFO

### Article history:

Received 16 January 2016

Received in revised form 27 March 2016

Accepted 28 March 2016

Available online 28 March 2016

### Keywords:

Supercritical CO<sub>2</sub>

Ultrasound

Graphene oxidation

Chitosan

Amidation

## ABSTRACT

Ultrasound-induced synthesis of chitosan-modified nano-scale graphene oxide (CS-NGO) hybrid nanosheets, which has great potential pharmaceutical applications, in supercritical CO<sub>2</sub> without catalyst was presented for the first time. The preparation process does not require organic solvent and post-processing, and CO<sub>2</sub> easily escapes from the product. The morphology and structure of the CS-NGO, characterized using scanning electron microscopy, transmission electron microscopy, infrared spectroscopy, X-ray photoelectron spectroscopy and thermogravimetric analysis, confirms that it was combined via the amide linkage, and had excellent dispersibility and stability toward acidic and physiological aqueous solution, which implies that it could be used as a drug-carrier. The sonication power played a crucial role in inducing forming amidation, and the conversion rate increased with the sonication time. The mechanism of this reaction was explained.

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## 1. Introduction

Graphene oxide (GO), a single-layer graphene sheet consisting of carboxylic acid, epoxide and hydroxyl groups, is one of the most important derivatives of graphene [1]. GO has a great potential in pharmaceutical and biochemical applications because it has a big surface area, like graphene [2], and other superiorities. GO has good hydrophilicity and can be easily modified because it has oxygen-containing groups, like epoxide (—O—) and hydroxyl (—OH) groups [3]. In addition, GO can be a good drug-carrier loading drug via  $\pi$ – $\pi$  interactions with aromatic pharmaceuticals due to its surface  $\pi$  electrons [4]. Besides, monolayer GO can be largely produced from graphite [5].

To enable GO application in a biomedical field, GO modification with biocompatible molecules is usually required because the modified-GO has been proved to be nontoxic [6–9]. Moreover, GO with smaller size has lower toxic performance [10]. Chitosan is one of the most widely used biomaterial due to its good biocompatibility, biodegradability, low immunogenicity, and antibacterial property [11–13]. It was reported that the chitosan-modified GO, formed via interaction of either noncovalent [14–16] or covalent conjugation [17–23], had the merits of both chitosan and GO, and had a great potential to be a drug carrier [17,19], a biosensor [16], a catalyst [20], a superior absorbent [21,23], and a tissue engineering material [22]. The chitosan-modified GO, formed via cova-

lent conjugation of the amide linkage between the carboxylic groups of GO and the amine groups of chitosan, has a wide range of applications because of its stable structure. However, the previously published synthesis methods require both a catalyst and organic solvent, which would bring impurities in the final product or complicated post-processing steps.

Supercritical CO<sub>2</sub> technique is a green process, and has been widely applied in the fields of food, pharmacy and chemicals et al. because it is nontoxic, non-flammability, inertness, cheapness, and it would not remain in the final product [24]. Ultrasonication method is also a green way in chemical synthesis or engineering process, and it exhibits great effects in enhancing reactivity and acceleration, energy saving, and getting cleaner products [25–27].

The purpose of this study is to develop a new route, being simple and green, of synthesizing chitosan-modified nano-scale GO (CS-NGO) via amide linkage by ultrasonication in supercritical CO<sub>2</sub> (named as USSC). The CS-NGO was characterized using scanning electron microscopy, transmission electron microscopy, infrared spectroscopy, X-ray photoelectron spectroscopy and thermogravimetric analysis. The reaction mechanism was explained.

## 2. Materials and methods

### 2.1. Materials

Graphite with purity of 99.99% was purchased from Sinopharm Co., Ltd. Chitosan (viscosity < 200 mPa s) with 88% degree of

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deacetylation was purchased from Aladdin. N-(3-dimethylamino propyl)-N'-ethylcarbodiimide hydrochloride (EDC, purity > 99.0%) and N-hydroxysuccinimide (NHS, purity > 99.0%) were supplied by Sinopharm Co., Ltd. Other reagents were obtained from Lingfeng Chemical Reagent Co., Ltd. and were of analytical grade.

## 2.2. Preparation of nano-scale graphene oxide (NGO)

The aqueous GO suspension was prepared using an improved method developed by Marcano [28], including the multiple-washing process using diluted hydrochloric acid (10%) and deionized water, from which the GO powder was obtained by a freeze-dried method. Furthermore, the NGO nanoparticles (NGO) were generated by SCCO<sub>2</sub> using the GO powder as starting materials. The processing schematic is shown in Fig. 1. Briefly, 200 mg of the dried GO powder was first put inside the kettle (6). Then, CO<sub>2</sub> (1) was pumped into the kettle by a high-pressure piston pump (3) via condenser (2) until the system pressure increased to 10 MPa. Meanwhile, the kettle was heated to 40 °C by a temperature-controlled heating mantle (5). After the pressure and temperature reached the desired value, a power-adjustable ultrasonic probe started to run (4) (frequency of 20 kHz) for a certain time. After the processing completed, the NGO was collected.

## 2.3. Preparation of CS-NGO

As contrast, the chitosan-modified GO (CS-GO) was first prepared via the amidation of the GO and the chitosan based on the previously published method assisted with catalyst in water (named as AWCW) [17]. Briefly, 500 mg of the chitosan and 100 mg of the NGO were dispersed in 50 mL of water containing 1% acetic acid by a bath sonication for 2 h, and then 652 mg of the EDC and 782 mg of the NHS were added slowly into the reactive mixture, and the mixture solution was continually stirred and reacted for 24 h. After the reaction, the suspension was filtered, and the filter precipitate was washed with acetic acid solution (5%) and deionized water in turn to remove excess the chitosan, EDC and NHS. Furthermore, the filter pasty precipitate was dialyzed (MWCO 8000–14,000) by deionized water for 3 days, and finally the dry CS-GO powder was obtained by a freeze-dry process

In our developed new route of preparation of CS-NGO using an ultrasound in supercritical CO<sub>2</sub> (USSC) technique, the reaction system is as same as that of the processing NGO, shown in Fig. 1. A certain amount of the chitosan was first adequately grinded and then put inside the kettle with 100 mg of the NGO together, into which CO<sub>2</sub> was pumped. After the pressure and temperature reached 10 MPa and 40 °C, the sonication probe was started to induce reaction. The ultrasonic power and period were examined on reaction efficiency. The resultant CS-NGO was collected after emptying the CO<sub>2</sub> of the kettle.

## 2.4. Analytical methods

The structure of the resultant products were analyzed by a four-ier transform infrared spectrometer (FTIR, Spectrum 100, Perkin Elmer, America) at the wave number of 4000–400 cm<sup>-1</sup>. The samples were prepared using KBr disc technique. To fully avoid the disturbance of the residue unreacted chitosan, the CS-NGO was dialysed with water for 3 days. An X-ray photoelectron spectrometer (XPS, AXIS ultraDLD, Kratos, Japan) was used for the surface chemistry analysis.

The morphologies of the resultant products were observed using a field emission scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The samples were dispersed on the electronic conductive adhesive stucked to an aluminum stub, and then coated with platinum using a sputter coater (1.2 kW, E-1045, Hitachi, Japan) for 60 s. The samples were observed using a transmission electron microscope (TEM, JEM-2100, JEOL, Japan) after they were dispersed in ethanol and dripped on copper meshes with carbon films followed with infrared drying.

The thermodynamic property was analyzed by a thermogravimetric analyzer (TGA, TGA 7, Perkin Elmer, America) under nitrogen atmosphere at a heating rate of 10 °C/min from 50 to 550 °C.

## 3. Results and discussion

### 3.1. Influence of ultrasonic power and period on NGO

Fig. 2 shows the morphologies of the GO and the NGO. As shown in the SEM (Fig. 2a) and TEM (Fig. 2b) images, the size of the GO is bigger than 100 μm, which is not suitable for a drug carrier. How-

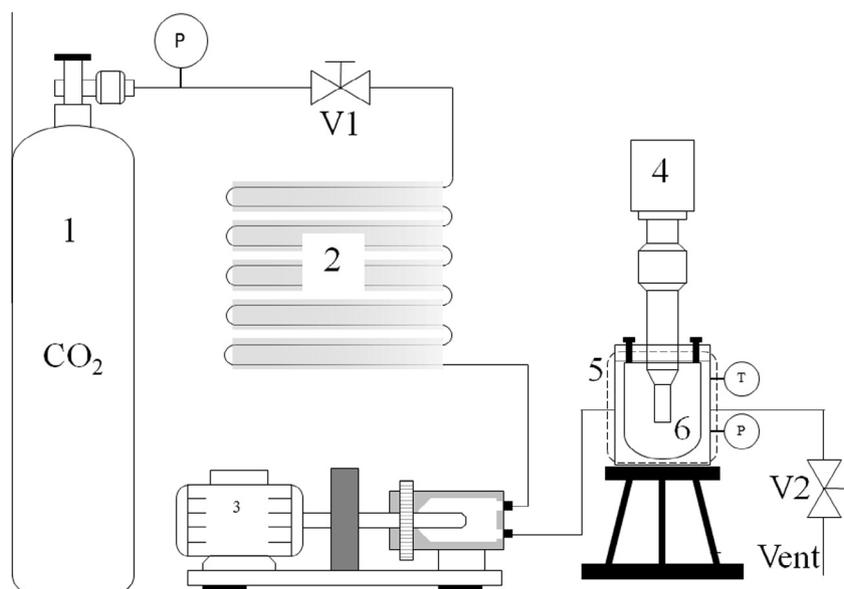


Fig. 1. The schematic of the apparatus.

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