



# Modifying graphite oxide with grafted methyl acrylate brushes for the attachment of magnetite nanoparticles



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## ABSTRACT

Surface-grafted polymer brushes of methyl acrylate of graphite oxide (GO) have been constructed to anchor poly(amidoamine) 2.0G (PAMAM 2.0G) dendrites for the attachment of magnetite nanoparticles. Monomers of methyl acrylate were copolymerized on the GO sheets by atom transfer radical polymerization. Then the PAMAM 2.0G was attached via covalent bond at the end of the grafted chains. Thus the inexpensive Fe(III) of ferric trichloride could coordinate with the remaining amino groups of PAMAM 2.0G and were reduced by the added sodium borohydrite at appropriate pH value to obtain nano magnetite-decorated GO hybrid materials. The hybrids exhibited a powerful catalysis on the degradation of aqueous solutions of hydroquinone.

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## 1. Introduction

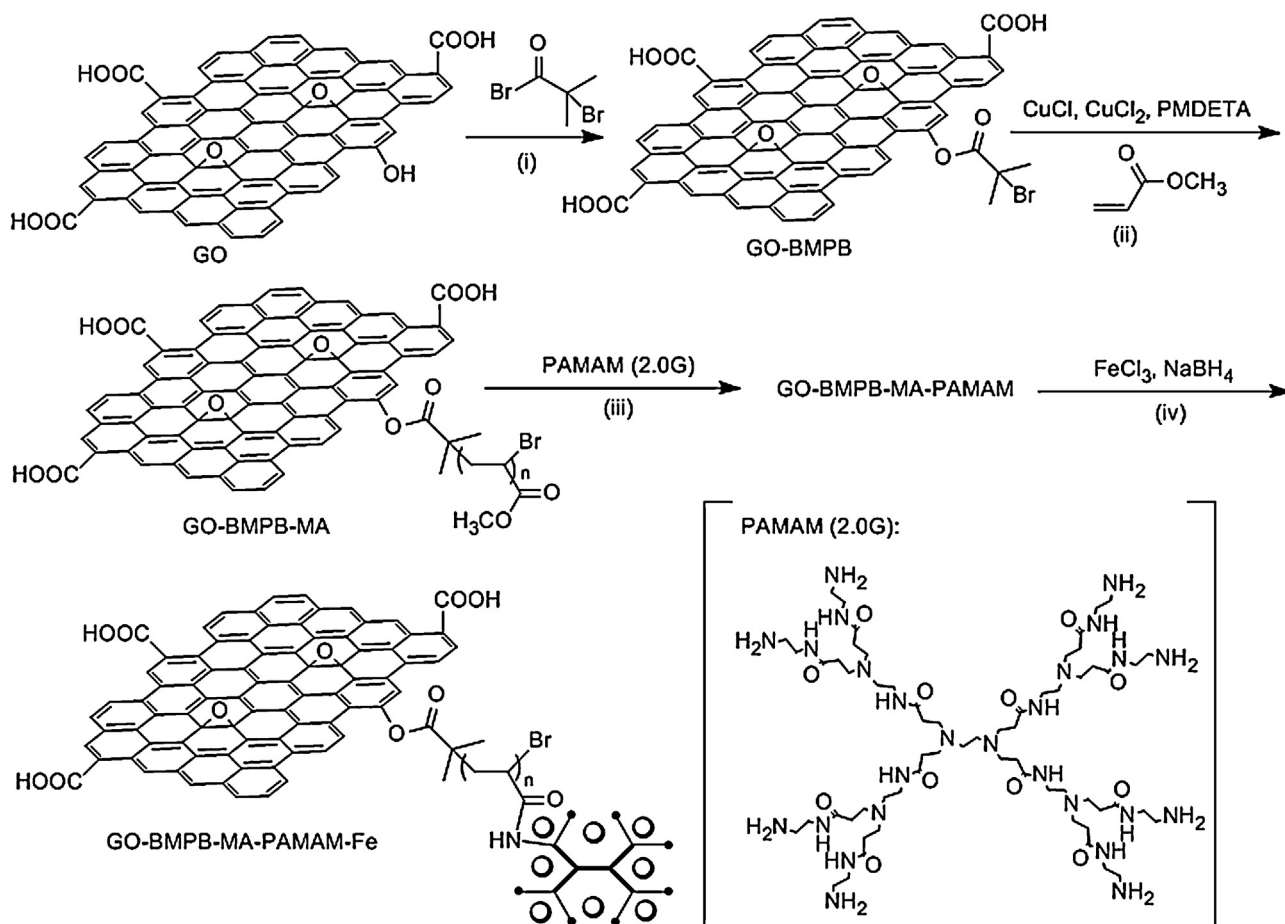
Graphite oxide (GO) is an interesting material due to its novel structure of pseudo-2D with large amount of active groups such as hydroxyl, carboxyl and epoxy which generated in the course of the preparation. These functional groups are capable of involving many sorts of reactions [1–9] which are utilized as effective avenues to realize some proper modifications on GO. Such chemical ornaments give rise to wider applications of GO [3,4,10]. The hydroxyls of GO reacted with N-(trimethoxysilylpropyl) ethylenediamine triacetic acid to introduce a multi-carboxyl species onto GO and thus stable suspensions were obtained in ethanol/Nafion solutions [10]. Such mixtures were deposited on a glass carbon electrode forming a stable film which displayed high ion selectivity in an electrochemical catalysis. The hydroxyls of GO could also be activated by 2-bromo-2-methylpropanoyl bromide (BMPB) to introduce the initiators onto its surface leading to surface-grafted copolymerization of methacrylates by technique of atom transfer radical polymerization (ATRP). After reduced with hydrazine hydrate the polymer brush-modified GO enhanced piezoelectric  $\beta$ -polymorph poly(vinylidene fluoride) formation [4]. The side carboxyls of GO could be esterified by N-hydroxysuccinimide and subsequently reacted with ethylenediamine so as to introduce primary amino groups. Hence the initiator molecules such as BMPB could be attached to surface of GO by amidation reaction. Consequently, monomer of 2-(dimethylamino)ethyl methacrylates

were grafted copolymerized on GO [5]. Additionally, the surface functional groups of  $-\text{OH}$  or  $-\text{COOH}$  of GO were utilized to anchor Mg/Ti catalyst species giving a nanoscale catalyst system of synthesizing polypropylene on GO [3]. Treatments on GO with isocyanates brought an enhanced stability in polar aprotic solvents such as N,N-dimethylformamide (DMF), N-methylpyrrolidone, dimethyl sulfoxide (DMSO) which resulted from the reaction between hydroxyls and isocyanate groups [7]. Apparently, many of these novel applications of GO were derived from the appropriate modifications on GO chemically. However, some precursors with polar carbonyls, such as ferric triacetylacetonate [11,12] or ferric pentacarbonyl [13], could interact with unmodified GO by hydrogen bonds after a thorough dispersion in supersonic dealing. Then the mixtures were heated to a high temperature to obtain nano magnetite/GO composites which exhibited a surprising magnetoresistance [13] and peroxidase-like activity [14]. The nano magnetite possesses the catalysis on degradation of p-nitrophenol based on the chemical activities and the large specific surface area [15]. This property was utilized to deal with environmental pollutants such as phenolic wastewater.

Despite the unmodified GO sheets possess the capability of loading nano magnetite [11,13,16], which based on the direct interactions between the precursors and surface functional groups of GO, we believe that the appropriate modifications on GO will capture more precursors of nanoparticles and improve their loading capabilities. PAMAM dendrites with plenty of outside amino groups had been applied in preparing metallic nanoparticles by the coordination of amino groups with corresponding ions by means of in situ reducing reaction in the presence of reductants. The PAMAM 2.0G

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**Fig. 1.** The stepwise modifications on GO were described schematically. The initiated GO (represented with GO-BMPB) was obtained by reaction (i) in the first place. Then MA were grafted copolymerized on GO (abbreviated with GO-BMPB-MA) by means of ATRP technique (ii). The end esters of the grafted polymer brushes reacted with PAMAM 2.0G by virtue of amidation reaction (iii) to obtain the composites of GO-BMPB-MA-PAMAM. Thus the Fe(III) were captured and were reduced through reaction (iv) under appropriate conditions to generate magnetite-decorated GO hybrid materials (denoted with GO-BMPB-MA-PAMAM-Fe).

molecules can link with GO by covalent bonds as long as the GO is mended properly. Such PAMAM/GO hybrids will increase the loading of Fe(III). Hence ferric trichloride (FeCl<sub>3</sub>) rather than ferric triacetylacetonate or ferric pentacarbonyl can be chosen as an inexpensive Fe(III) source in preparing magnetite/GO hybrids. This approach will be described in this work in detail. The whole procedure is depicted schematically in Fig. 1.

## 2. Experimental

### 2.1. Materials

Ammonia (30%), tetrahydrofuran (THF), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), methyl acrylate (MA), sodium borohydride (NaBH<sub>4</sub>), FeCl<sub>3</sub>, DMF and DMSO were purchased from Guoyao Chemicals (Shanghai, China). BMPB, cuprous chloride (CuCl), cupric chloride (CuCl<sub>2</sub>), N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA) and hydroquinone were commercially provided by Xiya Chemicals (Chengdu, China). Solvents of THF were dehydrated with anhydrous calcium chloride before use. Other chemicals were used as received without any purification. GO was prepared by Hummer's method using graphite flakes oxidized with H<sub>2</sub>SO<sub>4</sub> and KMnO<sub>4</sub> [17]. PAMAM 2.0G was synthesized by successive addition reaction between ethylenediamine and MA as well as amidation between the resultant esters and ethylenediamine which reported elsewhere [18].

### 2.2. Preparation of grafted polymer brushes on GO surface

About 100 mg GO and 20 mL THF were mixed by ultrasonication for 30 min. Then the mixtures were transferred into a reactor followed with dropwise addition of 1.5 mL BMPB depicted in (i) of Fig. 1. Such reaction system was oil-sealed to hinder ambient water vapors and lasted for 5 h at 35 °C with a magnetic agitation. The products, GO-BMPB, were obtained by vacuum filtration with three times washing of anhydrous alcohol and subsequently dried at 50 °C.

About 25 mg GO-BMPB mixed with 20 mL DMSO under supersonic disposal for 30 min. Subsequently, 3 mL MA, 100 mg CuCl (1.01 mmol), 50 mg CuCl<sub>2</sub> (0.372 mmol) and 0.1 mL PMDETA were added to the GO-BMPB/DMSO suspensions. The reaction system was airtight with an oil-sealed device and was kept under flowing N<sub>2</sub> for at least 10 min so as to vent the air. Such reaction (ii, depicted in Fig. 1) proceeded for 6 h at 60 °C. The products (GO-BMPB-MA) were filtrated and washed with copious water for many times and anhydrous alcohol for three times.

### 2.3. Attachment of PAMAM 2.0G to the side chains of grafted polymer brushes of GO-BMPB-MA and generation of nano magnetite

About 25 mg GO-BMPB-MA were dissolved in 20 mL DMSO with supersonic disposal for 30 min followed with dropwise

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