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Facile synthesis of Cu^{2+}-modified mesoporous silica-coated magnetic graphene composite for enrichment of microcystin-LR followed by mass spectrometry analysis

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ABSTRACT

MCs is a group of potent hepatotoxic peptides produced by cyanobacterial in eutrophic water, among which microcystin-LR is the most abundant and toxic. Long-time accumulation of even trace dosage from drinking water would cause significantly hepatic injury to animal and humans. Here we reported a novel Cu^{2+}-modified mesoporous silica coated magnetic graphene composite (magG@mSiO$_2$@-Cu^{2+}) through mild sol-gel process and surface modification. Next, the composites were successfully applied for enrichment and separation of microcystin-LR followed by MALDI-TOF MS analysis based on the virtues of excellent hydrophilicity, high surface area (261 $cm^2\ g^{-1}$), sensitively magnetic separation property, accessible porosity (3.10 nm) and large amount of modified Cu^{2+} ions. Even performed in a lower concentration (0.5 μg/L), at which microcystin-LR could not be detected directly, after treatment with the composites the S/N ratio could appear to be 82.93. Furthermore, the novel composites also exhibited high enrichment efficiency in real water sample. It provided a sensitive and efficient technique for enrichment and detection of microcystin-LR and developed a potent method for separation of pollutant in contaminated water.

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1. Introduction

Microcystins (MCs) is a family of manocyclic heptapeptides produced by cyanobacterial in eutrophic water, which shares a general $_D$-Ala-X-$_D$-MeAsp-Z-Adda-$_D$-Glu-Mdha structure yielding more than 80 variants of MCs [1]. Among the MCs group, microcystin-LR containing leucine (L) and arginine (R) amino acids is the most toxic and frequent one in variants of MCs. It has been reported that MCs could causes skin irritation, vomiting, diarrhea and critically lead to a significant hepatotoxic to lives for animals and humans [2–6]. The widespread blooming of MCs has attracted an increasing worldwide concern in water environment on account of the water eutrophication. The increased occurrence of cyanobacterial bloom inevitably leads to the abundantly burst of MCs and contamination to the drinking water. Exposed to that even trace dose of microcystin-LR in water would significantly disturb cellular process and the World Health Organization (WHO) has set out a guideline of 1 μg L^{-1} for total microcystin-LR in drinking water [3,7,8]. In addition, Microcystin-LR has a specific cumulativity because of its chemical stability and property of hard-degradation, so that long-term drinking of contaminated water would cause damage to the liver because of the potential carcinogens [5,9]. Thus, the development of an efficient and convenient method for microcystin-LR detection is urgently needed especially at low concentration.

Various methods and techniques have been developed for microcystin-LR detection in water, include high-performance liquid chromatography (HPLC) [10], liquid chromatography/mass spectrometry (LC/MS) [11], enzyme-linked immunosorbent assays (ELISA) [12], surface-enhanced fluorescence (SEF) [13]. However, HPLC and LC/MS require long time for analysis. ELISA would lead to interference results for identifying while large molecules would interfere with the affinity and specificity to the small target. SEF with Au-nanoparticles exhibit a higher limit of detection for microcystin-LR. Nevertheless, beyond that matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) is a rapid and sensitive technique that could be capable of identifying individual homogeneous substances [14]. In previous studies, MALDI-TOF MS had been successfully applied to detection of MCs, but the method had a higher detecting limitation that is well above the WHO advisory level for drinking water [15]. Therefore, a simple and efficient method for enrichment of microcystin-LR in water sample followed by MALDI-TOF MS analysis is required.

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Recently functionalized nanomaterials have been widely applied in sample extraction and pre-treatment in biomedical analysis and environmental analysis [16–18]. And the most commonly used method for enrichment and pre-concentration of microcystin-LR is adsorbent-based adsorption before analysis. Activated carbon is a frequently-used adsorbent for microcystin-LR but require large dose and is difficult to be separated from solution [19,20]. In recent years, mesoporous silica, mesoporous carbon and graphene have been used for the separation of microcystins based on their accessible porosity structure, high surface area and activate sites on the surface outer or inner the pores [21–26]. In the meantime, magnetic materials have been developed rapidly and attracted specific interests in separation of microcystin-LR due to their magnetic property. Deng et al. have reported magnetic mesoporous microspheres with a Fe_3O_4@SiO_2 core and perpendicularly aligned mesoporous SiO_2 shell for removal of microcystins [27]. Due to the advantages of high specific surface areas, uniform mesopores, thermal and mechanical stability, as well as variety of modification, several functionalized mesoporous materials also have been developed for separation of microcystins in our previous works. For example, Lu et al. have synthesized a novel mesoporous silica coated magnetic carbon nanotubes and applied the composites as absorbent for the fast removal of microcystins. Liu et al. have prepared magnetic mesoporous silica microspheres for fast extraction of microcystins [24,28]. Moreover, ionic materials (such as Cu^{2+} ion, Fe^{3+} ion) have been applied as an adsorbent for adsorption of microcystin-LR relying on the combination of metal ions and carboxyl groups and amino groups.

Herein in this work, we synthesized a novel Cu^{2+}-modified polydopamine (PDA)-introduced magnetic graphene coating with mesoporous silica composite (denoted as magG@*m*SiO_2-Cu^{2+} composite), which integrates the merits of hydrophilicity, high surface area, accessible porosity, abundant metal ions and sensitively magnetic separation. Then the magG@*m*SiO_2-Cu^{2+} composite was performed as a substrate for efficient enrichment of microcystin-LR in real water sample and directly for MALDI-TOF MS analysis. It suggests that the magG@*m*SiO_2-Cu^{2+} composites have a potential in enrichment and separation of pollutant in future.

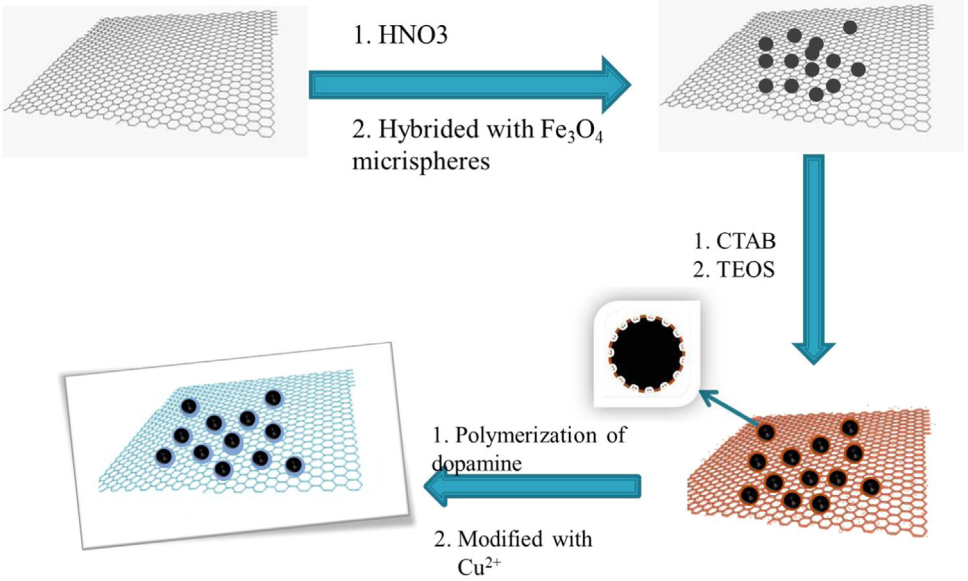
2. Materials and methods

2.1. Chemicals and materials

Graphene was purchased from Shanghai Boson Technology Co. Ltd. Dopamine hydrochloride and Tris(hydroxymethyl)aminomethane were purchased from Sigma-Aldrich (St. Louis, MO, USA). Trimesic acid was purchased from Alfa Aesar (Ward Hill, MA, USA). Microcystin LR and α-Cyano-4-hydroxycinnamic acid (CHCA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile (ACN) and trifluoroacetic acid (TFA) were purchased from Merck (Darmstadt, Germany). All of other chemicals are analytical grade and used as received. All aqueous solutions were prepared using water purified by a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Preparation of the magG@*m*SiO_2-Cu^{2+} composites

The synthetic route of the magG@*m*SiO_2-Cu^{2+} composites was shown in Scheme 1. Firstly, graphene was dispersed in 50 mL of nitric acid and stirred at 60 °C for 8 h. The graphene treated by nitric acid was washed to neutral with deionized water and dried in vacuum at 50 °C. Then, the magnetic graphene was synthesized through a hydrothermal reaction. Briefly, 200 mg of $FeCl_3 \cdot 6\,H_2O$ were dissolved in 40 mL of ethylene glycol, and then the pretreated graphene (150 mg), trisodium citrate (150 mg), anhydrous sodium acetate (1.8 g) and polyethylene glycol 2000 (1.0 g) were added into the solution obtained. After magnetic stirring for 2 h, the mixture was sealed in a Teflon-lined stainless-steel autoclave and heated at 200 °C for 12 h. Afterward, the product was collected by magnetic separation and washed with deionized water for several times. The obtained magG was then dried in vacuum at 50 °C as reserved. The magG@*m*SiO_2-Cu^{2+} composites were prepared via a surfactant involved sol-gel process according to the previous method [17]. The as-prepared magG (50 mg) and cetyltrimethyl ammonium bromide (CTAB) with a ratio of 50 mg/500 mg in quality were dispersed in 50 mL of H_2O and ultrasonically treated at a frequency of 40 kHz (note: ultrasonication process was performed at this frequency throughout this work) for 30 min. Next, 450 mL of sodium hydroxide (NaOH) aqueous solution (1.1 mM) was added into the resultant dispersion and ultrasonicated for 5 min to form a uniform dispersion for further heating at 60 °C for 30 min. Afterwards, 2.5 mL of



Scheme 1. The synthetic route of the magG@*m*SiO_2-Cu^{2+} composites.

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