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Regular Article

Single step synthesis of amine-functionalized mesoporous magnetite nanoparticles and their application for copper ions removal from aqueous solution

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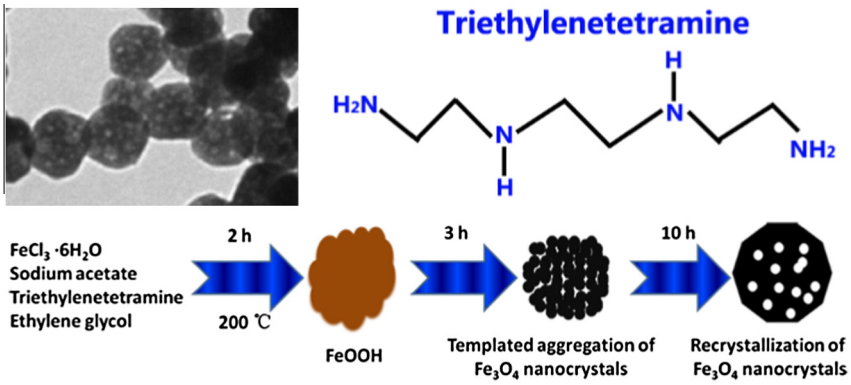
GRAPHICAL ABSTRACT

Amine-functionalized mesoporous superparamagnetic Fe_3O_4 nanoparticles with high Cu(II) removal capacity have been synthesized via a single step solvothermal method by the introduction of triethylenetetramine.



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ABSTRACT

Amine-functionalized mesoporous superparamagnetic Fe_3O_4 nanoparticles with an average size of 70 nm have been synthesized using a single step solvothermal method by the introduction of triethylenetetramine (TETA), a chelating agent recommended for the removal of excess copper in patients with Wilson's disease. The synthesized nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, nitrogen adsorption/desorption isotherm, vibrating sample magnetometer (VSM), and Fourier transform infrared spectroscopy (FTIR). It is confirmed that the magnetic nanoparticles have been functionalized with TETA during the synthetic process, and the concentration of TETA is crucial for the formation of monodisperse mesoporous nanoparticles. The obtained single-crystal magnetic nanoparticles have a high magnetization, which enhances their response to external magnetic field and therefore should greatly facilitate the manipulation of the particles in practical uses. Reaction parameters affecting the formation of mesoporous structure were explored, and a possible formation mechanism involving templated aggregation and recrystallization processes was

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proposed. The capacity of the synthesized amine-functionalized Fe_3O_4 nanoparticles toward Cu(II) removal from aqueous solution was investigated. The adsorption rate of Cu(II) on amine-functionalized Fe_3O_4 nanoparticles followed a pseudo-second order kinetic model. The results of this study demonstrated that the amine-functionalized mesoporous superparamagnetic Fe_3O_4 nanoparticles could be used as an efficient adsorbent in water treatment and would also find potential application for Cu(II) removal in vivo.

1. Introduction

Magnetic nanoparticles have received much attention in recent years due to their widely potential applications in magnetic resonance imaging, catalysis, biomedicine, and waste water remediation, etc. [1–4]. Magnetic materials with nanoscale pores exhibited enhanced performances in the field of adsorption, catalysis, and drug delivery owing to the enclosed nanocavities and increased surface area [5–7]. Mesoporous magnetic nanomaterials have been prepared through different template methods in recent years. Leung et al. reported the preparation of mesoporous Fe_3O_4 nano/microspheres using a method combining Fe_3O_4/poly(acrylic acid) hybrid sphere template and subsequent silica shell formation and removal [8]. Ha et al. reported the preparation of mesoporous magnetite nanospheres by a solvothermal method through a gas bubble induced mesoporous structure formation process [9]. Although the nanomaterials prepared by these template methods have high surface area, their surfaces usually lack functional groups and additional surface modification steps are needed to meet specific applications.

The surface properties of magnetic nanomaterials are crucial for their colloidal stability, biocompatibility, ability for further functionalization, and potential applications [10–12]. A variety of molecules have been used to modify the magnetic nanoparticles surface to achieve desired properties, and these modifiers are usually small molecules or polymers bearing charged carboxylate groups [13–15]. Among various functional groups, carboxylate and amino groups are well studied for their wide applications in bioconjugation chemistry [16]. Besides the conjugation with carboxylate group containing molecules by the aid of a 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) linker, amino groups are also intensively explored for affinity with transition metal elements. Amine-functionalized magnetic nanoparticles were widely used as adsorbent for the removal of toxic heavy metal ions from water [17–19]. Direct synthesis of mesoporous magnetic nanoparticles with amine-functionalized surfaces is desirable for their diverse applications. Guo et al. reported the direct preparation of amine-functionalized magnetite nanoparticles with mesoporous structure by the introduction of ethylenediamine in a solvothermal system. The added ethylenediamine not only modified the surface as a capping agent but also affected the nucleation and structure of prepared magnetic nanoparticles [20]. However, the use of toxic ethylenediamine may limit their potential biomedical applications, and the formation mechanism needs to be explored when amino group containing molecule is used as additive.

As a low toxic chelating agent, triethylenetetramine (TETA) is recommended for administration to lower the copper concentration in Wilson's disease [21]. The well-acknowledged biocompatibility coupled with longer chain length and increased nitrogen atoms of TETA made it more suitable for adsorption and biomedical applications than ethylenediamine. TETA functionalized Fe_3O_4 nanoparticles have been synthesized directly or by more complex post-grafting methods. For instance, O'Connor et al. reported a simple one-pot synthesis method using TETA as both solvent and stabilizing agent to prepare water-soluble amine-functionalized 7 nm Fe_3O_4 nanoparticles, it was showed that the surface amino groups are available for either attachment of a different nanomaterial or biomolecules conjugations [22]. However, the small sized nanoparticles prepared by this method have a low magnetization per particle, so it is difficult to effectively separate them from suspensions or control their movement in blood using moderate magnetic fields. Fathallah et al. prepared nanoadsorbents for Cu(II) removal through surface coating of Fe_3O_4 nanoparticles with silicon oxide followed by covalent surface bonding with TETA [23]. The silica layer mediated surface functionalization method is complex and time consuming which may prevent them from being used in large-scale applications, the incorporation of silica onto the magnetic nanoparticles also decrease the magnetic responsiveness of the nanocomposites. Therefore, it remains a great challenge to develop a facile and simple strategy for the large-scale synthesis of monodisperse magnetic nanoparticles with a biocompatible functional surface to facilitate its covalent coupling to bioactive molecules and with high magnetization to achieve the fast manipulation and the sensitive magnetic signal to meet the specific requirements for biomedical applications.

Herein, we reported the preparation of amine-functionalized mesoporous superparamagnetic magnetic nanoparticles via a simple one-step solvothermal method by the introduction of TETA. The biocompatible nitrogen rich TETA molecule not only endowed the nanoparticle surface with functional amino group, but also directed the formation of mesoporous structure through modification of the nucleation and growth mode. A plausible formation mechanism involving templated aggregation and recrystallization processes has been proposed based on the systematic investigation of reaction parameters and the porous structure formation processes. The adsorption performance of Fe_3O_4 nanoparticles toward Cu(II) in aqueous solution was evaluated. The synthesized Fe_3O_4 nanoparticles may find potential applications in water treatment and Cu(II) removal in vivo.

2. Experiment section

2.1. Materials

Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), sodium acetate (CH_3COONa), ethylene glycol, copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), and nitric acid (HNO_3, trace select ultra for analysis) were purchased from Sigma-Aldrich. Triethylenetetramine (TETA) was purchased from Alfa-Aesar. All reagents were used as received without further purification. The water used throughout all experiments was purified with a Millipore Milli-Q system.

2.2. Synthesis of Fe_3O_4 nanoparticles

Amine-functionalized Fe_3O_4 nanoparticles were prepared by a modified solvothermal method in the presence of triethylenetetramine (TETA). Typically, 0.54 g $FeCl_3{\cdot}6H_2O$ was dissolved in 12.5 mL ethylene glycol to form a homogenous solution, followed by the addition of 1.5 g sodium acetate and 2.5 mL TETA. To investigate the effect of TETA on the formation of monodisperse nanoparticles, TETA was varied from 0 mL to 15 mL while the total