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Synthesis of 1D Fe_3O_4/P(MBAAm-*co*-MAA) nanochains as stabilizers for Ag nanoparticles and templates for hollow mesoporous structure, and their applications in catalytic reaction and drug delivery

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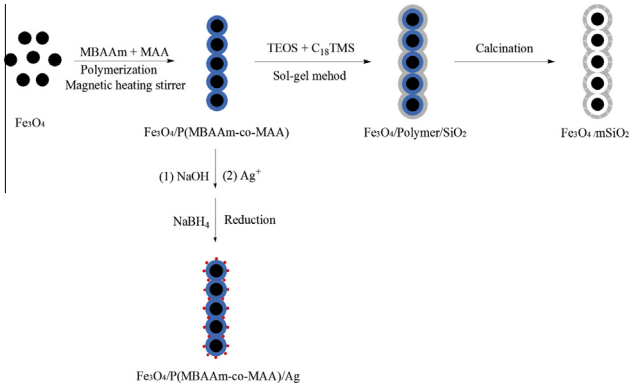
GRAPHICAL ABSTRACT



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ABSTRACT

One-dimensional (1D) magnetic Fe_3O_4/P(MBAAm-*co*-MAA) nanochains were prepared by distillation–precipitation polymerization of MBAAm and MAA in the presence of Fe_3O_4 nanoparticles as building blocks under a magnetic heating stirrer, which played two critical roles: serving as magnetic field to induce the self-assembly of Fe_3O_4 nanoparticles into 1D nanochains and providing thermal energy to induce the polymerization of MAA and MBAAm on the surface of the Fe_3O_4 nanoparticles. The thickness of the P(MBAAm-*co*-MAA) layer can be easily tuned by adjusting the successive polymerization steps. The polymer layer that contained carboxyl groups was used as stabilizers for loading Ag nanoparticles and the reaction locus for deposition of outer silica layer via a sol–gel method in presence of C_{18}TMS as the pore directing agent for tri-layer nanochains. The corresponding hollow mesoporous silica nanochains with movable maghemite cores (γ-Fe_2O_3@*m*SiO_2) were produced after removal of the polymer mid-layer and the alkyl groups of the pore directing agent via calcination of the tri-layer nanochains at high temperature. The Fe_3O_4/P(MBAAm-*co*-MAA)/Ag nanochains exhibited a highly catalytic efficiency and well reusable property toward the reduction of nitrophenol. Furthermore, the γ-Fe_2O_3@*m*SiO_2 nanochains possessed hollow mesoporous structure and high specific surface area (197.2 $m^2\ g^{-1}$) were used as a drug carrier, which displayed a controlled release property.

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1. Introduction

In the past few decades, magnetic nanomaterials have received a great deal of attention due to their broad applications in many fields, including medicine [1], catalysis [2–4], drug delivery [5,6], magnetic separation [7], and magnetic resonance imaging [8,9]. Among a wide variety of magnetic nanomaterials, the ordered magnetic one-dimensional (1D) nanomaterials have been intensively studied because of their unique structures and interesting properties as well as wide applications [10]. To date, numerous techniques have been developed for fabrication of 1D magnetic nanomaterials, such as template-directed synthesis [11], electrospinning [12], dipole-directed self-assembly [13,14], magnetic -field-induced assembly [15–17], and so on. Owing to its relative simplicity and versatility, magnetic-field-induced assembly of magnetic nanoparticles is one of the most attractive approaches to prepare magnetic 1D nanostructures. Generally, an applied external magnetic field could induce self-assembly of magnetic nanoparticles along the easy magnetic axis, which might result in formation of 1D nanostructure. For example, Sun et al. [18] demonstrated an alternating magnetic field-induced assembly of Fe_3O_4 nanoparticles that is in close relationship with the surface charge. Chen et al. [19] have prepared 1D weak ferromagnetic nanochain structure of polycrystalline magnetite nanoclusters by applying a simple magnetic-field-induce assembly approach.

Nevertheless, it is usually difficult to maintain the ordered 1D chain-like structure of the magnetic nanoparticles after removal of the external magnetic field. To address this challenge, silica [20,21], carbon [22,23], polyelectrolyte [24], and cross-linked polymer [25–27] were commonly used to covalently link the closely spaced magnetic nanoparticles and fix the nanochains into mechanically robust wires. These 1D magnetic hybrid nanochains have attracted more attention due to its multi-functions via combining the different properties of these distinct materials [28,29]. On the one hand, due to the existence of the magnetic particles, these hybrid 1D nanomaterials can be manipulated and easily separated/recovered by an external magnetite, and can also be used as the heating agents by high-frequency magnetic fields, or the contrast materials for magnetic resonance imaging (MRI). For instance, Yin et al. [30] have fabricated individually fixed Fe_3O_4@SiO_2 photonic chains with a magnetically responsive photonic property by combining magnetic assembly with sol–gel processes. Duan et al. [31] have reported that self-polymerization of polydopamine (PDA) around aligned magnetic nanoparticles is able to "polymerize" the nanoparticles into nanochains. Then loading Au nanoparticles on the nanochains via localized reduction by PDA give rise to magnetically recyclable, self-mixing nanocatalysts, which exhibited a high recyclable catalytic activity. On the other hand, the protective layer on the surface of the nanochains not only enhances their chemical and thermal stability either in bulk or in solution, but also endows the nanochains with additional functions. For example, Lou et al. [32] have developed a novel magnetic field-induced solvothermal method to synthesize 1D Fe_3O_4/C composite microrods, which display much better lithium storage properties with a high reversible capacity of 650 mA h g^{-1} retained after 100 charge/discharge cycles. Based on the magnetic field-induced assembly and microwave-assisted route, their group has prepared 1D Fe_3O_4/C/CdS coaxial nanochains, which exhibited excellent photocatalytic activity for the degradation of RhB dye under visible-light irradiation [33]. Zhou et al. [34] have synthesized the multifunctional 1D magnetic nanochains to combine the enhanced MRI contrast, fluorescent imaging ability, and combined chemo-/photothermal therapeutic ability into a single 1D nano-object, which displayed great potential for various biomedical application. However, it is still urgent to develop a facile method for preparation of 1D magnetic nanochains with a protective shell and endow the magnetic nanochains with additional functions.

Herein, we reported a facile approach to prepare robust 1D magnetic Fe_3O_4/P(MBAAm-*co*-MAA) nanochains with a well-defined core–shell structure through distillation–precipitation polymerization under a magnetic heating stirrer. The thickness of the P(MBAAm-*co*-MAA) layer of the nanochains can be easily controlled via adjusting the successive polymerization steps. The functional polymer layer contained plenty of carboxyl groups was used as a scaffold for loading silver nanoparticles, as well as the reaction locus for deposition of the outer silica layer via a sol–gel method in the presence of C_{18}TMS as the pore directing agent for tri-layer nanochains. The corresponding hollow mesoporous silica nanochains with movable maghemite cores (γ-Fe_2O_3@*m*SiO_2) were developed after selective removal of the polymer mid-layer and the organic component of the pore directing agent via calcination of the tri-layer nanochains at high temperature. The catalytic activity of the magnetic Fe_3O_4/P (MBA Am-*co*-MAA)/Ag nanochains was studied by reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AnP) as a model reaction. Furthermore, the γ-Fe_2O_3@*m*SiO_2 was used as a carrier for doxorubicin hydrochloride (DXR), which displayed a controlled drug release process.

2. Experimental section

2.1. Materials

Ferric chloride ($FeCl_3{\cdot}6H_2O$) and sodium acetate (NaAc) were purchased from Tianjin Guangfu Fine Chemical Engineering Institute. Trisodium citrate (Na_3Cit) was obtained from Tianjin Chemical Reagents I. *N*,*N*′-Methylenebisacrylamide (MBAAm, Tianjin Bodi Chemical Engineering) was recrystallized from acetone. Methacrylic acid (MAA) was purchased from Tianjin Chemical Reagent II and purified by vacuum distillation. 2,2′-Azo bisisobutyronitrile (AIBN) was obtained from Chemical Factory of Nankai University and recrystallized from methanol. Tetraethylorthosilicate (TEOS) and *n*-octadecyltrimethoxysilane (C_{18}TMS) were purchased from Aldrich and used without any further purification. Doxorubicin hydrochloride (DXR) was provided by Beijing Huafeng United Technology Co. and used as received. Dialysis chamber with a molecule weight cut-off of 8000–15,000 g/mol (φ = 36 mm) was purchased from Beijing Dingguo Biotech Co. for drug release. All the other reagents were of analytical grade and used without any further treatment.

2.2. Synthesis of magnetite (Fe_3O_4) nanoparticles

Magnetic (Fe_3O_4) nanoparticles were synthesized through a solvothermal method according to the literature with a minor modification [35,36]. The procedure was as following: 3.6 g of $FeCl_3{\cdot}6H_2O$ and 0.72 g of Na_3Cit were dissolved in a mixture of ethylene glycol/ethanol (90 mL/10 mL) solution through ultrasound irradiation. 4.8 g of NaAc was then added under vigorous magnetic stirring for 30 min. Finally, the resultant mixture was transferred into a Teflon-lined stainless-steel autoclave (with a capacity of 200 mL) for reaction at 200 °C for 10 h. After that, the autoclave was carefully taken out to cool to room temperature. The resultant black products were thoroughly washed with ethanol and de-ionized water for three times, respectively, and finally dried in vacuum oven.

2.3. Synthesis of 1D magnetic Fe_3O_4/P(MBAAm-co-MAA) nanochains

The 1D magnetic Fe_3O_4/P(MBAAm-*co*-MAA) nanochains were prepared through two-stage distillation–precipitation