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Supramolecular gel based on the cyclodextrin inclusion assembly of Ag-Fe_3O_4 nanodimers and Pluronic F127

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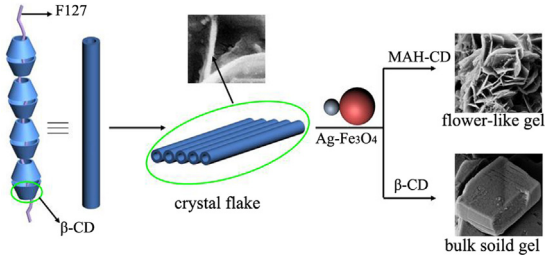
HIGHLIGHTS

- The supramolecular gel with a flower-like morphology structure has been prepared.
- The Ag-Fe_3O_4 nanodimer and carboxylated cyclodextrin play a key role to the gel morphology.
- The introduction of nanodimers to gel may bring potential applications from both Ag and Fe_3O_4.

GRAPHICAL ABSTRACT

The inclusion between carboxylated cyclodextrin (MAH-CD) and block polymer F127 forms a column-like structure, which may be close-packed to produce a crystal flake. With the help of anchoring cyclodextrin through the carboxyl group on Ag-Fe_3O_4, a flower-like gel morphology could be built by the directionally arranged flakes. Without carboxyl, however, the inclusions with normal β-CD could only result in a gel with a bulk solid morphology.



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ABSTRACT

Being considered as building blocks, the inorganic nanodimer particles such as Ag-Fe_3O_4, Cd-Se and Pt-Fe_3O_4, have attracted much attention because of their capability of dual surface functionalization and potential applications in field-emission, data storage and photovoltaic devices. For these motivations and as a continuation of our previous study, a gel with flower-like morphology based on Ag-Fe_3O_4 nanodimers has been constructed with the carboxylated cyclodextrin (MAH-CD) and Pluronic F127 molecules in mixed solvent of cyclohexane and water. The morphology of Ag-Fe_3O_4 nanodimers and structure of MAH-CD were characterized by transmission electron microscopy (TEM) and nuclear magnetic resonance (NMR) respectively. The mechanism of gel formation is discussed along with the data obtained from rheological measurement, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Fourier transformation infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Each Ag-Fe_3O_4 particle was coated by lots of MAH-CD molecules, which were threaded by F127 chains. The gel fabrication is controlled by the inclusion of MAH-CD with F127, the interaction between the carboxyl group and the Fe_3O_4 surface. The cyclohexane molecules in gel were trapped with F127 by cyclodextrin, which may be packed orderly through hydrogen bond. Meanwhile, the Fe_3O_4 side of nanodimers provides the anchoring position for carboxyl group to induce the formation of gel. Such an Ag-Fe_3O_4 nanodimer initiated gel can be used either based on Ag side for catalytic and sensing properties, or based on superparamagnetism from Fe_3O_4 side.

1. Introduction

During the past few decades, the Janus or nanodimer nanoparticles (NPs) have attracted more and more attention, because of

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their dual surface functionalization capability and potential applications in field emission, data storage and photovoltaic devices [1–4]. Several assembling strategies are also developed, including body phase self-assembly [5], electric [6] or magnetic fields directed assembly [7], which can make NPs arranged directionally to form micelles [8], vesicles [9], disk-like aggregates [10], or two-dimensional superlattices [11]. Kumacheva and co-workers [11,12] successfully prepared modified Au-CdSe NPs and assembled them in body phase to obtain a hexagonal, banded super-lattice structure or thin film. Doyle and co-workers [13] synthesized the magnetic responsive Janus particles, which could form chain and mesh structures spontaneously under the magnetic field. Meanwhile, the organic Janus aggregates were also prepared using body-phase route based on the block copolymers [14–16]. However, most of these researches are focused on hard-template mediated assembly using simple or modified inorganic particles. With Janus or nanodimer particles as pseudo-gelator to induce or promote gel formation is less reported.

Choosing appropriate gelator and solvent is important in designing and preparing gels [17]. The cyclodextrin (CD) as a well-known and common organogelator [18] has been convinced to show little dispersibility in organic solvents, and good organogelation ability toward various organic solvents at ambient temperature [19,20]. Zhao et al. [21] have reported a new type of reversible heat-set organogels formed by anilines, β-CD and lithium chloride in N,N-dimethyl formamide (DMF). And also the macroporous cyclodextrin materials can be obtained by freeze-drying the aqueous solutions of α-, β-, and γ-CDs at ambient temperature. Then, with the organic solvents and oils adding, the organogel could be formed. These organogels can potentially be used as molecular containers and drug carriers [22]. Moreover, the gels doped with inorganic nanoparticles have been reported. Jing et al. [23] have produced a supramolecular hydrogel doped with gold nanoparticles, which can achieve the gel–sol transition after adding the 1-adamantan-amine hydrochloride. These hydrogels were formed based on the complex inclusion of CD and the physical and chemical crosslinks between F127 chains. Chen and co-workers [24] prepared the responsive polymeric hydrogels with the inorganic nanoparticles CdS covered by CD cavities. The so-called super-crosslink polymeric networks were built via the inclusion complexation with suitable guest molecules linked on polymer main chains [25]. Meanwhile, they substituted the capping copolymer on CdS with azobenzene functionalized PDMA-b-PNIPAM to obtain a dual stimuli-responsive supramolecular hydrogel [26]. However, all these gels were prepared with the isotropic and homogeneous inorganic nanoparticles.

Here, as a continuation of our previous research [23], a facile preparation of novel Ag-Fe_3O_4 NPs-based supramolecular gels using a soft template method has been established, in which both the magnetic Fe_3O_4 and the noble Ag are brought together at the same time. First, the Ag-Fe_3O_4 nanodimers were synthesized by a simple one-step reaction under mild experimental conditions according to the method as reported by Yang [27]. The maleic anhydride (MAH) modified β-CD (MAH-CD) was then prepared according to the procedures described previously [28]. The carboxyl group can help MAH-CD to anchor on the Fe_3O_4 side of Ag-Fe_3O_4 NPs [29,30]. The gel was then constructed from a mixed system of triblock copolymer (Pluronic F127), MAH-CD, cyclohexane, little deionized water and Ag-Fe_3O_4 NPs at ambient temperature. The gel of flower-like morphology may be induced by the directional arrangement of MAH-CD inclusion with F127. Meanwhile, due to the co-existence of Ag and Fe_3O_4 nanoblocks, the gel may present potential applications both in catlysis or sensing from Ag side and in superparamagnetism from Fe_3O_4 side.

2. Experimental

2.1. Materials

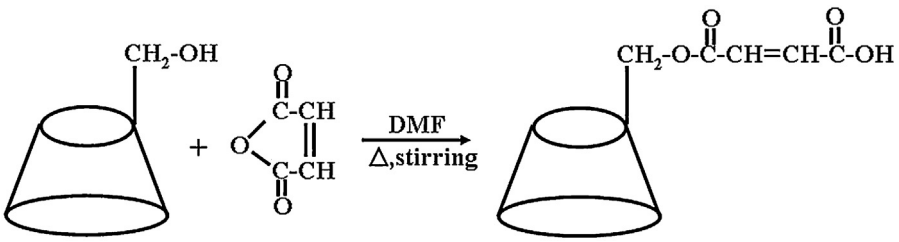
Ferric acetylacetonate (Fe(acac), 98%), oleylamine (80–90%), octadecene (ODE, 90%) and phenyl ether (DPE, AR) were obtained from Aladdin (Shanghai, China). N,N-dimethyl formamide from Tianjin Chemical Reagent limited Company was used after purification. Silver acetate (Ag(ac), AR) and β-cyclodextrin were purchased from Tianjin Kemiou. 1,2-Dodecanediol (HDD, >90.0%) from TCI (Shanghai), oleic acid (OAc) from Sinopharm (Beijing), maleic anhydride (MAH, ≥99.5%) from Tianjin Damao, and cyclohexane (≥99.5%) from Tianjin Guangcheng Reagent are all used without further purification. The used water was triply distilled.

2.2. Preparation of Ag-Fe_3O_4 NPs

The Ag-Fe_3O_4 NPs were prepared by a simple one-step reaction as established by Yang et al. [27]. First, the Ag(ac), Fe(acac), HDD and OAc were added in a three-neck flask with a specific percentage. Then, the comparable percent of ODE and DPE were added as solvent. The flask with mixed raw materials was sealed and heated up to 240 °C at a rate of 3.3 °C/min under a nitrogen atmosphere. In such a high temperature synthesis, the Ag nanoparticles through the reduction reaction of Ag(ac) were used as seeds. Then, the Fe(acac) was reduced to form a cubic-phase Fe_3O_4 and the nanocrystals were grown on the Ag nanosphere. By exactly control of the temperature and reaction time, the Ag-Fe_3O_4 nanodimer particles were prepared. The products were precipitated using absolute ethanol under centrifugation and the obtained Ag-Fe_3O_4 particles were dispersed in organic solvents.

2.3. Synthesis of MAH-CD

In order to obtain the carboxyl group modified β-CD, 8.52 g β-CD was first dissolved in 50 ml DMF. Afterwards, 7.35 g MAH was added. Then the solution was heated to 80 °C and refluxed for 10 h under continuously stirring, when the reaction shown in Scheme 1 was completed. The product was cooled to room temperature and the trichloromethane was added. Then, a white precipitate was produced and filtrated out, which was washed with acetone and dried in a vacuum at 80 °C for 4 days [28]. The carboxyl was covalently bonded to β-CD as confirmed by FTIR and NMR spectroscopic data.



Scheme 1. The carboxylation reaction of β-CD with maleic anhydride.