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Preparation of spherical caged superparamagnetic nanocomposites with completed inorganic shell via a modified miniemulsion technology

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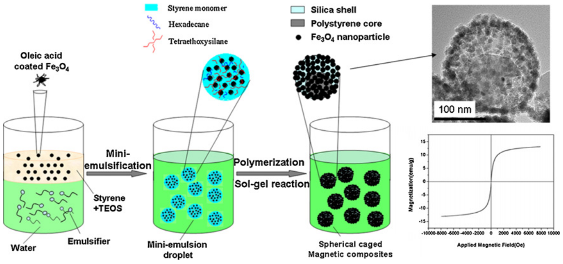
HIGHLIGHTS

- Magnetic spherical caged inorganic–organic composites (SCNs) were prepared.
- Mechanism of structure formation via a one-pot synthesis was studied.
- Prepared hollow mesoporous Fe_3O_4/silica microspheres using SCNs as template.
- The SCNs have regular structure, SiO_2 surface and superparamagnetism.

GRAPHICAL ABSTRACT

Spherical caged polystyrene/Fe_3O_4@silica composites with regular structure, SiO_2 surface and superparamagnetism have been prepared via a simple method in a high yield.



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ABSTRACT

A one-pot facile method is developed to synthesize spherical caged polystyrene/Fe_3O_4@SiO_2 nanocomposites (SCNs) microspheres with intact inorganic shells in a high yield via a combining process of miniemulsion polymerization and sol–gel reaction. It is revealed that St to TEOS ratio, the controlled hydrolysis and condensation rate of TEOS both play important roles in the structure formation. Control experiments are performed to understand the possible mechanism. With iron oxide nanoparticles as inorganic seeds, this one-pot synthetic method shows apparent advantage over multi-step layer-by-layer coating and selective etching regarding the simpleness and efficiency. Regular hollow magnetic mesoporous silica composites could easily be prepared using the caged magnetic microspheres as the template. The novel and facile method for preparing the magnetic composites with intrinsic space and intact shell could promote the development of drug carrier or photocatalysis system.

1. Introduction

Yolk/shell nanocomposites (YSNs) and spherical caged nanocomposites (SCNs) have attracted a lot of interest from material scientists and chemists due to their unique characteristics

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in physical or chemical properties and potential applications [1–5]. So far, the development of these complex systems has been expanded to several basic nanoparticle systems, such as Au nanoparticles [6], metal oxide [7,8], silica [9], semiconductive nanocrystals [10], and polymeric nanomaterials [11] since the first report of Au@polymer YSNs by Xia and coworkers in 2003 [12]. Various approaches have been developed for the preparation of YSNs and SCNs, such as, Ostwald ripening or galvanic replacement reaction [13,14], bottom-up or soft-templating process [15], selective etching approaches [16–18], "ship-in-bottle" approach [19], Kirkendall effect based methods [20], in situ template process [21] and spray-drying method [22]. Among them, recently, our group had developed a facile way to prepare magnetic YSNs with polymer core and Fe_3O_4 @ silica hybrid shell in a very high yield [21]. However, the big opening on the inorganic shell of YSNs still needed to be improved. More and more YSNs structures were designed as multifunctional system for cancer imaging and therapy [23]. In some cases, the shell needs to be complete if the cavity between the core and the shell is used for drug storage [24]. Otherwise, multi-shell hollow or yolk/shell spheres [25] are needed for higher payload and prolonged release of drugs. Despite the rising requirement of YSNs facing various practical applications, few efforts have been devoted to tuning the subtle structure of YSNs composites [26,27]. To the best of our knowledge, tuning the shell integrity of YSNs and formation of the regular spherical caged magnetic nanocomposites via a facile approach still remained challenging. Herein, we report a one-pot method for synthesizing high quality SCNs with intact shell structure via a modified process of combined miniemulsion polymerization and sol–gel reaction [28]. The SCNs microspheres composed of a polystyrene latex core and Fe_3O_4@silica hybrid shell could be produced in a straightforward fashion and high yield. Using the SCNs as the template, hollow mesoporous silica magnetic composites could be prepared through a sol–gel reaction.

2. Materials and methods

2.1. Materials

All reagents used were analytical grade and available commercially. Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous chloride ($FeCl_2{\cdot}7H_2O$), anhydrous ethanol and oleic acid (90%) were purchased from Shanghai Chemical Reagents Company. Styrene (St), 2,2-azobis(isobutyronitrile) (AIBN), triethylamine, and ammonia (NH_4OH, 28 wt.%) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Tetraethoxysilane (TEOS) and sodium dodecyl sulfate (SDS) were purchased from Sigma–Aldrich. Hexadecane (HD) was purchased from Acros Organics. Hexadecyltrimethoxysilane (C_{16}TMS) was purchased from Alfa Aesar. The aforementioned chemicals were used as received. Styrene was washed first with 5 wt.% sodium hydroxide solution and stored at −20 °C before use. Deionized (DI) water was used throughout the entire experiment.

2.2. Synthesis of magnetic spherical caged nanocomposites (SCNs) and hollow mesoporous microspheres

2.2.1. Synthesis of magnetic spherical caged nanocomposites (SCNs)

First, preparation of 10 nm oleic acid adsorbed iron oxide (OAIO) nanoparticles was carried out according to the well-established coprecipitative reaction protocol [21]. The obtained OAIOs were dispersed in octane and dried under rotary evaporation for further use. SCNs were prepared via our previously reported combined process of miniemulsion polymerization and sol–gel reaction [28]. In a typical process, water phase was prepared by dissolving 0.092 g of SDS in 40 g of DI water. HD (0.4 g) and OAIOs powder (0.055 g) were dissolved in St monomer (8 g). TEOS (1 g) was finally resolved into the monomer phase. The oil dispersion was dropped dropwise to the water phase under 200 W sonication. Miniemulsion droplet systems were prepared by sonicating the emulsions for 15 min at 500 W with a duty cycle of 50% with a Scientz-IID sonifier (Ningbo, China) in an ice bath. Before polymerization, the miniemulsion system was transferred to a three-neck flask and degassed with N_2 for 30 min under stirring after adding 0.08 g of AIBN. The polymerization of the St monomer was started when the flask was moved into the 70 °C water bath with condenser and under nitrogen atmosphere. After 60 min, 0.035 mL of NH_4OH was added rapidly into the reaction. Right after NH_4OH addition, the reaction system was taken out of the heating bath and kept stirring for another 12 h at room temperature.

In control experiments, the Styrene to TEOS mass ratio, the polymerizing period of the system before NH_4OH addition, and the type of sol–gel reaction catalyst were studied individually, keeping other conditions the same as the typical process.

2.2.2. Synthesis of hollow mesoporous Fe_3O_4@silica microspheres

Using the SCNs as the template, hollow mesoporous magnetic microspheres could be prepared via a typical sol–gel reaction with TEOS precursor and C_{16}TMS as porogen. The porogen and polymer core were removed by heating. In a typical process, a certain amount of ethanol solution of TEOS and C_{16}TMS (molar ratio is 4.7:1) was dropped into the reaction system at the rate of one drop each 10 s. The reaction stopped after being stirred at room temperature for 6 h. The obtained product was washed with ethanol and DI water each for two times and then calcinated at 550 °C for 6 h. In this way, hollow mesoporous Fe_3O_4@silica microspheres were obtained.

2.3. Characterization

The obtained SCNs and other magnetic composite products were washed twice in DI water by using an external magnetic field. The structure and chemical composition of the product were identified by transmission electron microscopy with Energy dispersive X-ray (EDX) analysis (TEM-EDX, Philips Tecnai 20). A scanning electron microscope (JEOL SM4800, Japan) was employed to investigate the surface morphology of the product. Thermogravimetric analyzer (NETZSCH TG209) and the vibrating sample magnetometer (LakeShore 7407, USA) were used to analyze the properties of SCNs and hollow mesoporous Fe_3O_4@silica microspheres.

3. Results and discussion

3.1. Illustration of pathway for synthesis of SCNs

As described in our previous work, yolk-shell magnetic composites have been produced via phase separation between polymeric and inorganic components in a combined process of miniemulsion polymerization and sol–gel reaction [21]. However, usually, big opening on the surface of yolk-shell composite was inevitable when the thick silica shell layer shrank due to the rapid phase separation. In this study, with a similar pathway for synthesis of yolk-shell composites, in order to prepare SCNs with nearly intact inorganic shell, the balance between growth of polymer latex and formation of inorganic shell must be well controlled. The preparation process for the SCNs is sketched in Fig. 1. OAIOs were first prepared by a coprecipitation method [21]. Sodium dodecyl sulfate (SDS) aqueous solution and an oil phase including styrene (St) monomers, a co-stabilizer, OAIOs, and TEOS

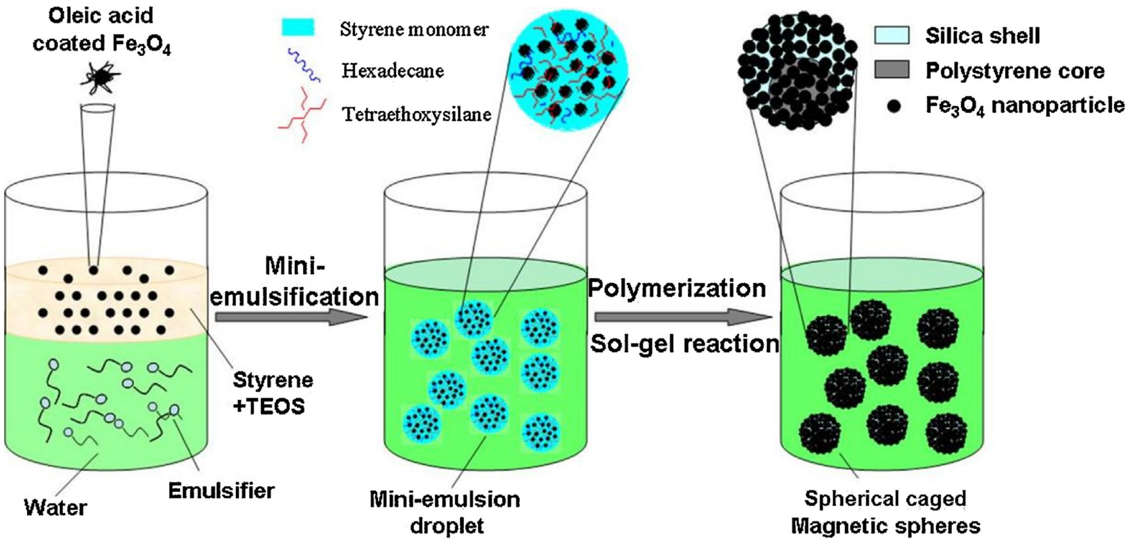

Fig. 1. Illustration of the preparation pathway of the magnetic spherical caged nanocomposites with completed inorganic shell via a combining process of miniemulsion polymerization and sol–gel reaction.

were mini-emulsified to get mini-emulsion droplets system. Polymerization of St monomers was initiated first by an oil-soluble initiator AIBN at 70 °C. On an appropriate occasion, NH_4OH was added to the reaction. The final product was obtained after another 12 h of reaction at room temperature. It was worth noting that St to TEOS ratio at 8:1 and conduction of sol–gel reaction at room temperature after NH_4OH addition were the typical parameter for SCNs formation.

In the typical condition for SCNs synthesis, our intention was to slow down the sol–gel reaction and lessen the thickness of formed silica layer. In this regard, two parameters, St to TEOS ratio and the reaction temperature after NH_4OH addition were optimized, which proved to be critical in preparation of SCNs. In a typical miniemulsion polymerization process, each miniemulsion droplet acts as an isolate "reactor" for polymerization of St monomer [29]. In this process, sol–gel reaction for silica formation also started in the droplets. So, the droplets stabilized by surfactants provided isolated sites for phase separation between polymeric and inorganic components. Without NH_4OH, OAIOs fast separated from the polystyrene chains gradually during the first hour polymerization of St monomer to polystyrene chains. When NH_4OH was added, heating was removed to slow down the sol–gel reaction. Besides, the thickness of silica shell was controlled by tuning TEOS feeding. Last, pure polystyrene nodules within the product were washed away in the presence of an extra magnetic field. The SCNs were successfully synthesized.

3.2. Structural information about the SCNs

In our previous work, most of the polystyrene/Fe_3O_4@silica composite microspheres exhibited obvious openings on the surfaces of inorganic hybrid shells. And a few of them had almost hemisphere geometry [21]. In the present work, it was found from Fig. 2A and C that SCNs here possessed nearly perfect spherical caged structure with the pristine intact inorganic shell in high yield. The Fig. 2A inset displays an individual polystyrene core inside the inorganic shell and clear space between the core and shell. Based on that proposed formation mechanism for the magnetic yolk-shell composite microspheres [21], it is interesting that this kind of cage-like structure with complete shell could be obtained by changing only two parameters, the St to TEOS ratio and the reaction temperature after NH_4OH addition. As abovementioned, due to the reduction of TEOS input regarding to the St monomer, the thickness of inorganic silica was obviously lessened. Meanwhile, the sol–gel reaction was carried out at room temperature after 1 h of polymerization of St monomer. The comparably slow growth of silica on the iron oxide nanoparticles matrix directly led to the thin but intact inorganic shell of the SCNs. The HRTEM images were taken to examine the thin silica shell in high resolution. Fig. 2B and D confirm a silica shell of around 3.5 nm thick covering the iron oxide nanoparticles via TEM-EDX analysis. The occurrence of elements of Si, Fe and O confirmed the chemical composition of the shell. From the SEM observation, the surface morphology and the cavity of the SCNs could also be clearly identified (Fig. 2C). With thin silica coating, the superparamagnetic nanocomposites not only owned increased chemical stability but also were endowed with capability for further surface functionalization [30].

3.3. The superparamagnetic property of SCNs

For preparing the SCNs, iron oxide nanoparticles played an important role as the matrix for silica coating. Furthermore, in the presence of many Fe_3O_4 nanocrystal seeds (~10 nm), the SCNs were superparamagnetic with a saturation at 13 emu g^{-1} (Fig. 3A). According to the TG analysis in Fig. 3B, the polystyrene accounted for 86 wt.% of the SCNs spheres. The results indicated that the SCNs possessed good magnetic property.

3.4. Formation mechanism of SCNs

For further understanding of the formation mechanism of SCNs, some control experiments were designed and conducted. According to the proposed mechanism, the yolk-shell magnetic composites or the caged composites formed as a result of the phase separation between the polymer matrix and inorganic components. During the polymerization of St monomer, the oleic acid modified iron oxide nanoparticles (OAIOs) separated rapidly from the polystyrene chains and it has been found that almost all OAIOs have totally separated. Fig. 4 A shows that OAIOs entirely separated from the polystyrene phase by the end of the first 1 h of miniemulsion polymerization before NH_4OH addition. These Fe_3O_4 nanoparticles surrounded the PS nodule homogeneously, acting as heterogeneous nucleation sites for silica component once NH_4OH was added. In the typical process, the St:TEOS ratio was fixed at 8:1, and NH_4OH was

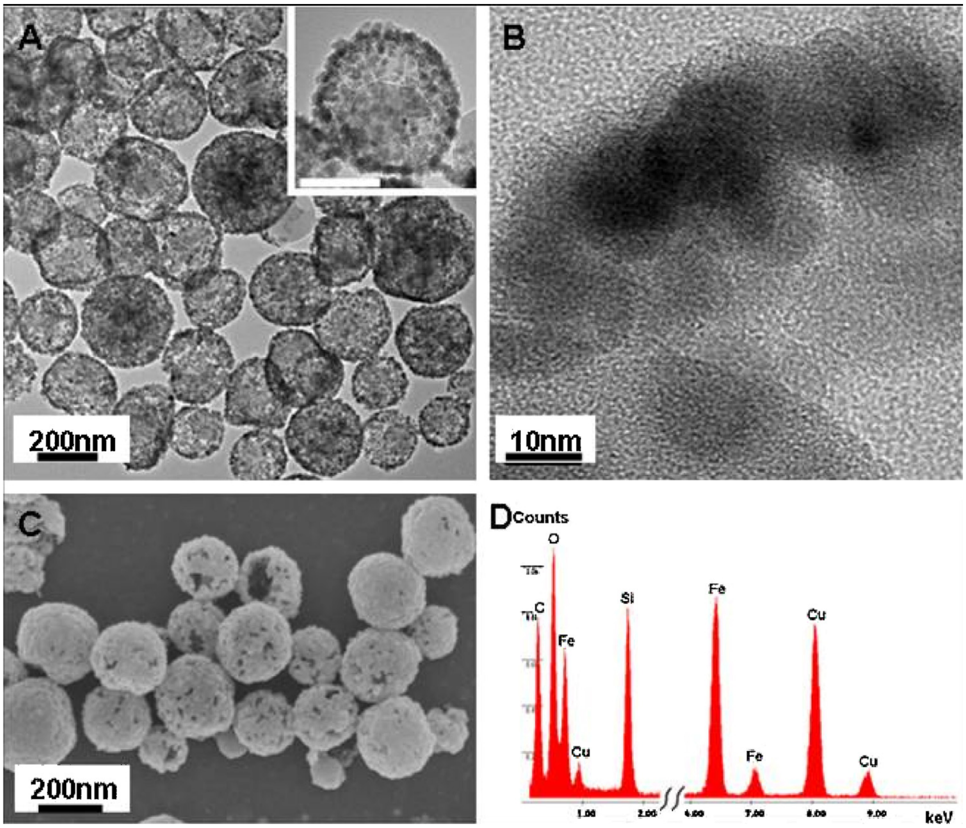

Fig. 2. (A) TEM, (B) HRTEM, (C) SEM images of the spherical caged magnetic nanocomposites, and (D) TEM-EDX spectrum of the inorganic shell of the spherical caged magnetic composites. The scale bar in inset of A is 100 nm.

added 1 h after the polymerization of the St monomer was initiated at 70 °C. In the control experiments, two parameters were tuned separately: the St:TEOS ratio and the polymerizing time before NH_4OH addition. The intention for changing the sol–gel reaction temperature was to adjust the growth rate of silica on the iron oxide nanoparticles matrix. As shown in Fig. 4B, in the process of SCNs synthesis, when St to TEOS ratio was changed to 8:2 instead of the typical ratio of 8:1 and with other condition unchanged, the incomplete inorganic shell was formed with the thickness of silica layer increased. That means more TEOS input changed the structure of final product by influencing the separating and growth behavior of the silica. In the same way, the extent of St polymerization before NH_4OH addition also affected the final product structure. Addition of NH_4OH after 2.5 h of polymerization of monomer turned most of the product into the hybrid structure with polystyrene microspheres partially covered by many inorganic nanoparticles (Fig. 4C). After 2.5 h polymerization, most St monomers were transferred to polystyrene. It was believed that the prolonged polymerizing period before NH_4OH addition further promoted phase separation between the polystyrene and inorganic components. The remaining iron oxide nanoparticles and TEOS precursor in the droplets were inadequate for formation of the intact inorganic shell. NH_4OH played two roles in the process of SCNs syntheses. One is to act as the catalyst to trigger the sol–gel reaction. On the other hand, addition of NH_4OH could facilitate the hybridization of silica and hydrophobic iron oxide nanoparticles. When triethylamine, a more hydrophobic organic base, was used instead of NH_4OH, the uniformity of the coverage of inorganic shell on polymer core is changed (Fig. 4D). The result indicated the good aqueous solubility of the catalyst may be necessary for the SCNs synthesis. The result

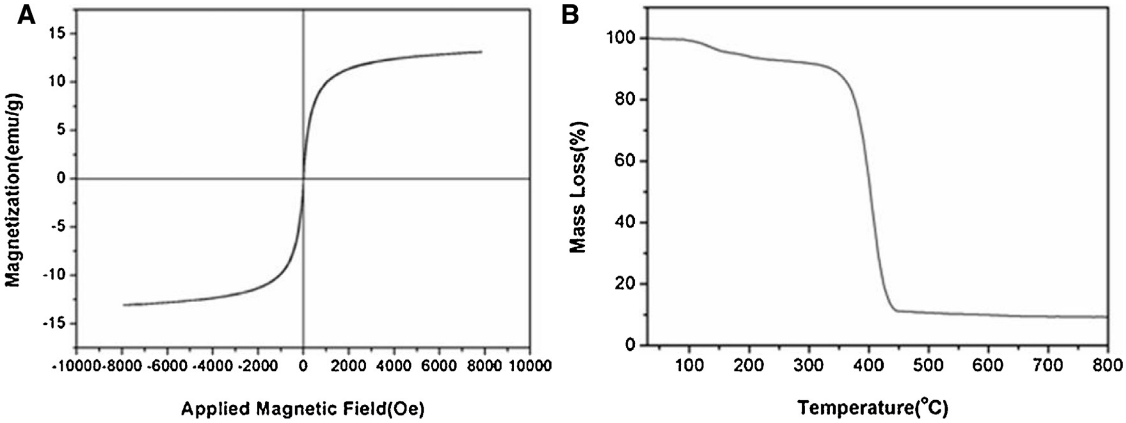

Fig. 3. (A) Magnetization curves (at 300 K) and (B) TG analysis curve of the magnetic cage like composites.

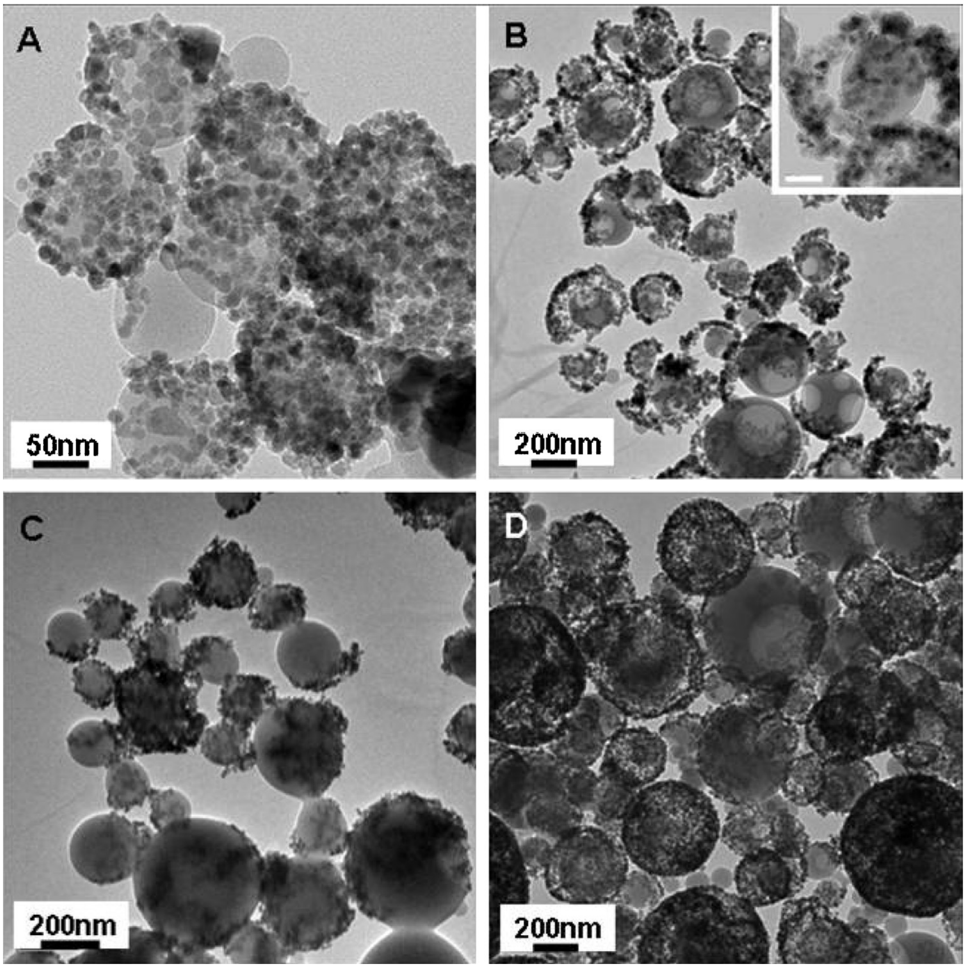

Fig. 4. TEM images of the samples obtained from the typical synthesis: (A) after 1 h of polymerization of St monomer before NH_4OH added. (B) St to TEOS ratio of 8:2, scale bar of inset is 50 nm, (C) NH_4OH was added after polymerization of St monomer lasted for 2.5 h, and (D) using triethylamine to replace NH_4OH as the catalyst for sol–gel reaction.

shows that both the inorganic and organic base could catalyze silica formation, resulting in the magnetic composites.

3.5. Hollow mesoporous Fe_3O_4@silica microspheres

One of the strengths of SCNs over YSNs was improved availability for drug/gene delivery. Furthermore, hollow mesoporous Fe_3O_4 @ silica microspheres could be easily synthesized using SCNs as the template. Hexadecyltrimethoxysilane (C_{16}TMS) was co-reacted with TEOS to act as the porogen in the sol–gel process and could be calcinated with polymer core at the same time. The morphology of the hollow mesoporous Fe_3O_4 @ silica microspheres is shown in Fig. 5A. Fig. 5B gives the magnetization property of the hollow mesoporous Fe_3O_4@silica

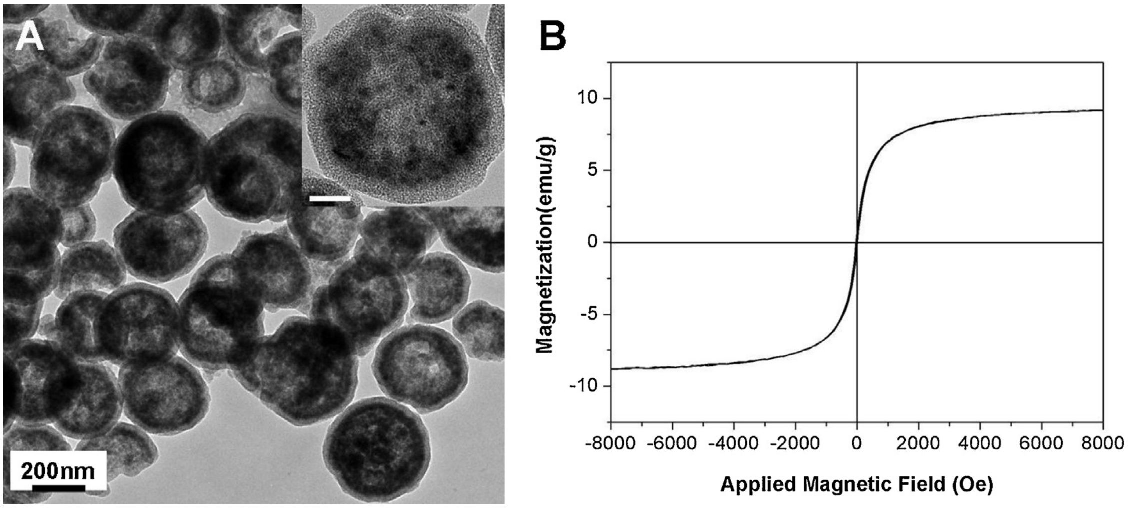

Fig. 5. (A) TEM image and (B) the magnetization curve of the hollow mesoporous Fe_3O_4@ silica microspheres. The scale bar in inset is 50 nm.

microspheres. The superparamagnetic property was well remained after calcination [31].

4. Conclusions

We have developed a simple method for the preparation of spherical caged polystyrene/Fe_3O_4@silica nanocomposites (SCNs) with almost intact inorganic shells in a high yield. The possible mechanism involved was studied. It was found that St to TEOS ratio and the phase separation between polymer and silica played important roles in the process. Hollow mesoporous Fe_3O_4@ silica microspheres were synthesized using the SCNs as template. The obtained magnetic composites with regular intrinsic cavity and silica shell have a good magnetic property and could be surface modified with chemical groups, reflecting the potential in some applications of drug carrier, catalysis or lithium ion battery.

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