Magnetic Nanoparticle Embedded in Functionalized Mesoporous Silica for Removal of Radioactive Cesium

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1. Introduction

Radioactive cesium which comes from nuclear power plants accident should be extracted because of its high radioactivity (through emission of gamma rays), long half-life (30 years) and cause severe harm to human health and organism [1]. Methods involving Solvent extraction, precipitation and solid phase extraction method have been used for capturing hazardous cesium [2]. Among them, solid phase extraction is reported to a better method due to high selectivity, rapid separation, high thermal and radiation stabilities and high efficiency [3]. Recently, silica substrates functionalized with metal ferrocyanide show exceptional adsorption capacity towards radio-cesium [3]. In the current study, magnetic iron oxide nanoparticles (IONPs) embedded in functionalized mesoporous silica have been used to capture cesium because of its biocompatibility, easier magnetic separation, high surface area for effective dispersion of functional groups, high adsorption capacity and effective reusability. Monodisperse IONPs of desired size is obtained using a large-scale thermal decomposition method. These nanoparticles are then phase transferred and surface area enhanced with mesoporous silica coating. In future, the IONPs with mesoporous silica structure will be functionalized with metal ferrocyanide (IONPs@mSiO$_2$@EDA@Cu FC) for capturing radioactive cesium. The captured radioactive cesium with our system can be collected by using a strong magnet. The radioactive cesium attached to the functional groups can be desorbed for the reusability of IONPs @mSiO$_2$@EDA @Cu FC.

2. Methods and Results

2.1 Synthesis of iron oleate complex

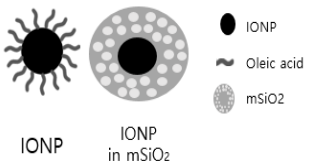
10.8 g of Iron chloride hexahydrate is dissolved in a mixture of 60 ml of water, and 80ml of ethanol, to which 36.5 g of sodium oleate mixed in 140ml of hexane is added and stirred at 200 rpm for 10 min. The solution mixture is then heated to 70 °C and kept at that temperature for 4 hours under stirring. The resultant solution shows a reddish brown colored upper phase and a turbid bottom phase. After the bottom phase is removed, the remaining reddish brown colored upper phase is washed three times with 30 ml of water and then dried at room temperature for 30 days.

2.2 Synthesis of Iron oxide nanoparticles

The synthesis of IONPs is performed using a reported procedure [4] with some modification. The iron oleate complex (7.2 g) is dissolved in a mixture of 1-octadecene (50 ml) and oleic acid (2.3 g). The reaction solution is degassed at 120 °C for 1 hour, and then the reaction temperature is increased to 320 °C with a heating rate of 6.6 °C/min under the inert Ar gas flow (100 mL/min). After aging for 20 minutes at 320 °C, the product solution is rapidly cooled down to room temperature. The entire reaction in the flask is carried out at a constant stirring of 200 rpm and in the presence of Ar gas. The as-synthesized IONP solution (5 ml) is washed three times with a mixture of hexane (2 ml) and acetone (40 ml), which involves centrifugation at 6000 rpm for 20 min for each washing to collect IONPs.

2.3 Synthesis of magnetic nanoparticle embedded in mesoporous silica (IONPs@mSiO$_2$)

The silica coating of IONPs is performed with a reported procedure [5]. The 5.46mg of synthesized IONPs dissolved in 0.5ml of chloroform is mixed with cetyltrimethyl ammonium bromide (CTAB) solution(103mg/10ml) at 65 °C and the mixture is stirred until the chloroform have been evaporated. To form mesoporous silica coating layer on CTAB-capped IONPs, the solution is diluted with 20.48 ml of water and the pH of the solution is increased to 12 by the adding 12.45 mg of NaOH. After the temperature reached 70 °C, 0.307 ml tetraethyl orthosilicate (TEOS) and 0.541 ml of ethyl acetate (EtOAc) are added to solution with a constant stirring for 2 hours. The synthesized core-shell particles are centrifuged and washed with ethanol for three times. The IONPs with mesoporous silica structures are formed through removal of CTAB and oleic acid from iron oxide surface by calcination at 550 °C for 8 hours.



Scheme 1. Synthesis of functionalized with mesoporous silica embedded with IONPs.

2.4 Functionalization IONPs@mSiO$_2$ (Future work)

The IONPs@mSiO$_2$ powder is dispersed in toluene and the solution is stirred vigorously for one hour. Ethylenediamine (EDA) terminated silane [[1-(2 aminoethyl)-3-aminopropyl] trimethylsilane] is added in refluxing solution to functionalize silica surface with EDA [3]. The IONPs@mSiO2@EDA is treated with copper chloride solution in water to form IONPs@mSiO$_2$@EDA@Cu, filtered and dried. The particles are then added to sodium ferrocyanide solution and stirred vigorously. After reaction, particles are collected by centrifugation, washed with water and ethanol.

3. Results and discussion

3.1 Morphological and magnetic characterization of IONPs with and without silica coating

The transmission electron microscopy (TEM) measurement of as-synthesized IONPs and mesoporous silica coated IONPs are shown in Figure 1. The TEM images of as-synthesized IONPs show that the size of IONPs are 12 nm with a size distribution of less than 5% which clearly indicates that the synthesized particles are monodisperse (Figure 1a). The TEM images of IONPs@mSiO$_2$ show a nearly monodisperse core-shell morphology with magnetic iron oxide as core and mesoporous silica as shell (Figure 1b). The magnetization curves of IONPs with and without silica shell is measured (Figure 1c). Both the IONPs exhibits superparamagnetism with a saturation magnetization of 18.5 emu/g (without silica) and 5.97 emu/g (with silica shell). This clearly indicate that silica coated IONPs can magnetically recovered by the application of strong field.

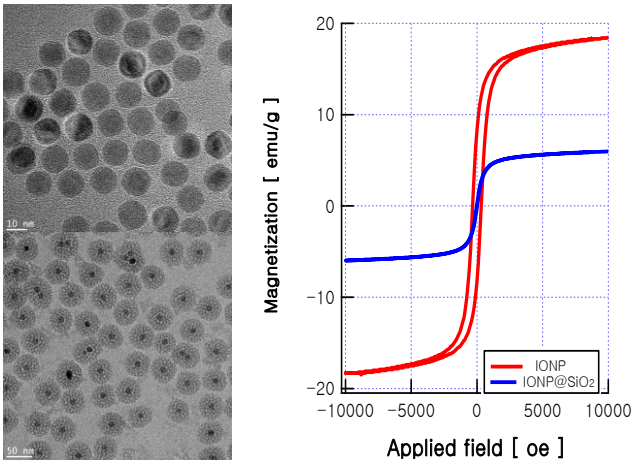


Figure 1. TEM images for (a) monodisperse IONPs of size 12 nm (b) IONPs embedded in mesoporous silica and (c) magnetization curves.

3.2 Adsorption of radioactive cesium (Future work)

The IONPs@mSiO$_2$@EDA@Cu FC structure can be dispersed in cesium solution to collect radioactive cesium. The radioactive cesium can be effectively adsorbed due to the large surface area which provide more platform for the adsorbing functional groups. The adsorbed cesium on the surface of IONPs @mSiO$_2$@EDA@Cu FC can be collected using a strong applied magnetic field. The adsorption efficiency will be evaluated by amount of remaining cesium in the solution. The adsorbed radio-cesium in the collected IONPs@mSiO$_2$@EDA@Cu FC can be desorbed from the surface for the recyclability of system [6].

4. Conclusions

We have synthesized monodispersed IONPs by thermal decomposition of iron oleate complex. The synthesized IONPs are then coated with uniform thickness of mesoporous silica (IONPs@mSiO$_2$) which provide large surface area for the effective functionalization of adsorbing groups. In the future work, we will functionalize the mesoporous silica surface with EDA-Cu-FC and evaluate the radioactive cesium capturing efficiency. Also, the reusability of synthesized IONPs@mSiO$_2$@EDA@Cu FC will be studied.

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