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Synthesis and magnetic properties of prussian blue modified Fe nanoparticles

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ABSTRACT

Fe nanoparticles are prepared using a unique polyol process and modified with prussian blue (PB) at various concentrations. The presence of PB in the Fe nanoparticles are confirmed from thermal, Fourier transform infrared spectroscopy and electron microscopic analyses. The prussian blue existed on ;the surface of the nanoparticles when the concentration is 200 μM and in excess with 1000 μM. ;Fe nanoparticles are reduced in size using Pt as nucleating agent and modified with the optimum concentration of PB. The saturation magnetization decreases with the concentration of PB whereas the coercivity is influenced by the size of the Fe nanoparticles. The presence of oxide layer in Fe nanoparticles helps in the surface modification with PB. The Fe nanoparticles of particle size 53 nm modified with 200 μM of PB showed a saturation magnetization of 110 emu/g. The magnetic properties suggest that the PB modified Fe nanoparticles are better candidates for detoxification applications.

1. Introduction

Surface modified magnetite nanoparticles are extensively used in biomedical applications such as magnetic particle hyperthermia, drug delivery and as MRI contrast agents [1–3]. However the synthesis of magnetic nanoparticles with higher magnetization for radiotoxin decontamination is not explored. The insoluble form of prussian blue (PB) is useful for the removal of radioactive Cesium (Cs) as it has the tendency to attach with PB [4]. For detoxification of radioactive contaminants using an applied magnetic field, highly magnetic nanoparticles are required. The saturation magnetization of bulk magnetite is 92 emu/g [5] whereas the magnetization reduces to 55 emu/g [6] and below with size reduction due to surface spin effects. Surface modification of the magnetite nanoparticles reduces the magnetization further. The surface modified Fe nanoparticles could have a larger saturation magnetization compared to magnetite of the same size.

Chemical methods are preferable for the synthesis of magnetic nanoparticles due to their easy and cost effective surface modification process. However it is difficult to synthesize Fe with higher saturation magnetization using chemical methods due to the highly oxidizing nature of Fe nanoparticles [7]. Surface treatment of Fe nanoparticles reduces the magnetization drastically and therefore the size of Fe nanoparticles plays an important role in obtaining better magnetic properties. On the other hand, the presence of oxide layer on the surface of Fe is advantageous for surface modification. In this paper, we present the first attempt on the surface modification of Fe nanoparticles with prussian blue and present their magnetic properties.

2. Synthesis of Fe nanoparticles

The Fe nanoparticles were synthesized by using a unique polyol process using high purity $FeCl_2.4H_2O$ and NaOH in ethylene glycol. The ethylene glycol (100 ml) was heated to 170 °C with constant mechanical stirring in a reaction vessel and $FeCl_2.4H_2O$ granules were added under continued mechanical stirring. When the ethylene glycol solution turned green, NaOH pellets were added within 5–6 s. The molar concentration of Fe was 0.2 M and the OH/Fe ratio was maintained at 20. Violent reaction of NaOH with ethylene glycol started within 3 s followed by the formation of black Fe precipitate. The total reaction duration was 2 min after which, the reaction vessel was removed from the heater and allowed to reach room temperature. For size reduction, $H_2PtCl_6.6H_2O$ with various molar concentrations was used from the stock solution prepared in water. Pt precursor was introduced 2 s prior to the addition of ferrous salt. The final greenish black colored solution was centrifuged by adding equal amount of methanol, washed several times with methanol and finally the Fe nanoparticles were separated using a magnet and stored in alcohol.

The reduction of Fe in polyol process is given by [8]

$$2CH_3CHO + FeCl_2 \xrightarrow[-2NaCl]{\text{Excess NaOH} > 373\ \text{K}} CH_3\ COCOCH_3 + 2H_2O + Fe^0 \quad (1)$$

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As per Eq. (1), reduction of Fe could be facilitated with Fe^{2+} ions, which is reduced to Fe. In the above process, excess NaOH enhances the reaction rate and a temperature above 373 K is required for the removal of water. Presence of water in the system would result in the production of Fe oxides. Therefore any deviation from the reaction steps and duration would not result in the formation of Fe or would end up in obtaining Fe oxides.

2.1. Synthesis of prussian blue modified Fe nanoparticles

Fe nanoparticles (100 mg) were taken in a 10 ml solution containing HCl along with $K_4[Fe(CN)_6]\cdot 3H_2O$ at appropriate concentrations and stirred for 30 min at 60 °C. The molar concentration of HCl used in the experiments was 10 mM then 10 ml of $FeCl_3$ solution was added to the above solution and stirred for 30 min. The final powder was collected by using magnetic separation and washed several times with HCl solution and double distilled water. The concentration of insoluble prussian blue (PB) was increased from 200 μM to 1000 μM.

2.2. Characterization

The synthesized Fe and PB modified nanoparticles were characterized by X-ray diffraction (XRD), thermo magnetic analysis (TMA), vibrating sample magnetometer (VSM), Fourier transform infrared spectroscopy (FTIR) and transmission electron microscope (TEM). XRD patterns were obtained using a Rigaku Ultima III X-ray diffractometer equipped with a Cu Kα. FTIR spectra were obtained using a Thermo Fisher Nicolet iS5 spectrophotometer. Thermo magnetic analysis was performed using an EXSTAR 6200 TG/DTA under N_2 atmosphere with a flow rate of 300 ml/min. Hysteresis loop at room temperature was recorded using a vibrating sample magnetometer (VSM) (Model 7404, Lakeshore, USA). The imaging and selected area diffraction pattern (SAED) of the synthesized particles were recorded using a FEI make 300 kV TEM.

3. Results and discussion

The asprepared Fe nanoparticles (hereafter referred to Fe nanoparticles prepared without using Pt as nucleating agent) synthesized using the unique polyol process was modified with PB at various concentrations from 200 to 1000 μM. Preliminary experiments showed that PB concentration above 1000 μM reduces the magnetization drastically. Pt was used as nucleating agent for size reduction and the size reduced Fe nanoparticles prepared using 10^{-7} M of Pt was modified with PB of 200 μM in order to study the attachement of PB addition with size reduction. Fig. 1 shows the XRD pattern of (a) Fe (b) Fe with 200 μM of prussian blue (PB) (c) size reduced Fe using 10^{-7} M of Pt and modified with 200 μM of PB (d) Fe with 1000 μM of PB and (e) prussian blue. The Fe sample prepared without prussian blue showed single phase behavior corresponding to the bcc phase of Fe as shown in Fig. 1(a). The average grain size for the asprepared Fe nanoparticles found using Scherrer formula was 56 nm. The asprepared Fe nanoparticles or the size reduced Fe nanoparticles modified with 200 μM of prussian blue did not exhibit peaks corresponding to PB and showed Fe peaks as shown in Fig. 1 (b) and (c) respectively. Moreover, the Fe particles undergo surface oxidation resulting in the formation of magnetite which was difficult to identify as the peaks hardly appear in the XRD pattern due to the thin layer [8].

The Fe nanoparticles prepared using Pt as nucleating agent showed an average grain size of 31 nm indicating the effect of Pt in reducing the size of Fe. Fig. 1(d) corresponds to the asprepared Fe nanoparticles modified with 1000 μM of PB. With the increase in

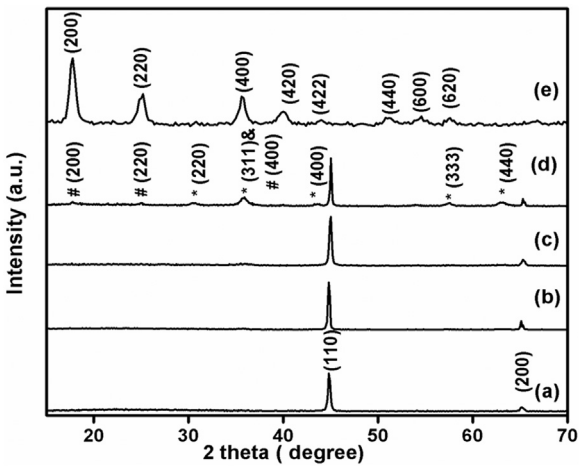

Fig. 1. The XRD pattern of (a) Fe, (b) Fe with 200 μM of prussian blue (PB), (c) size reduced Fe using 10^{-7} M of Pt and modified with 200 μM of PB, (d) Fe with 1000 μM of PB and (e) prussian blue (# – PB peaks, * – Fe_3O_4 peaks).

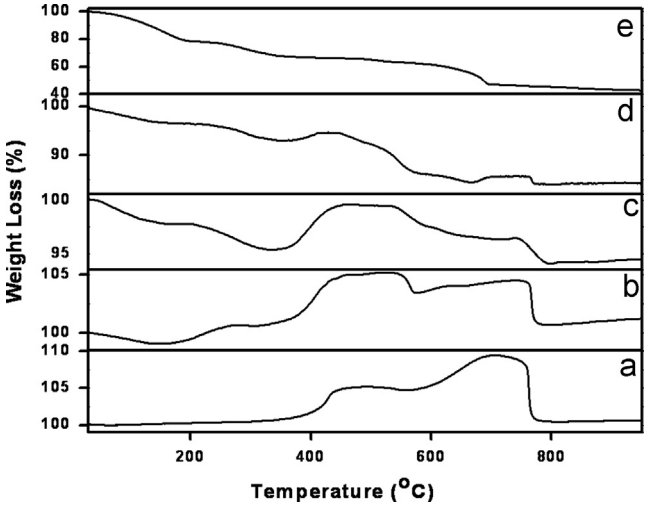

Fig. 2. Thermomagnetic analysis curves of (a) Fe, (b) Fe with 200 μM of prussian blue (PB), (c) size reduced Fe using 10^{-7} M of Pt and modified with 200 μM of PB, (d) Fe with 1000 μM of PB and (e) prussian blue.

the concentration of PB from 200 μM, the Fe oxide peaks begin to appear and are quite evident at a PB concentration of 1000 μM along with the (200) peak corresponding to PB. The (400) peak of PB coincides with the Fe_3O_4 high intensity peak. It is to be noted here that the main peak of PB (200) is lesser in intensity compared to the (311) peak of Fe_3O_4. Therefore it is understood that the fraction of Fe_3O_4 is higher than PB. The increase in the formation of Fe-oxide is due to the addition of higher concentration of Fe^{3+} ion for the formation of insoluble PB. The Fe^{2+} is obtained from the addition of HCl which oxidizes the Fe. The formation of Fe-oxide can be inferred as Fe_3O_4 due to the favorable conditions prevalent in the Fe-Cl-H_2O system [9]. Although pure PB is crystalline as seen from Fig. 1(e) and showed an average grain size of 13 nm, the PB peaks could not be identified for the Fe modified with PB (Fig. 1(b and c)). The PB in a poorly crystalline form or insufficient concentration would result in the nonappearance of peaks in the XRD pattern and therefore further analysis is required to confirm its presence.

Fig. 2 shows the thermomagnetic analysis curves of (a) Fe (b) Fe with 200 μM of prussian blue (PB) (c) size reduced Fe using 10^{-7} M of Pt and modified with 200 μM of PB (d) Fe with 1000 μM of PB