Materials Chemistry and Physics 173 (2016) 364–371

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Influence of physicochemical interactions of capping agent on magnetic properties of magnetite nanoparticles

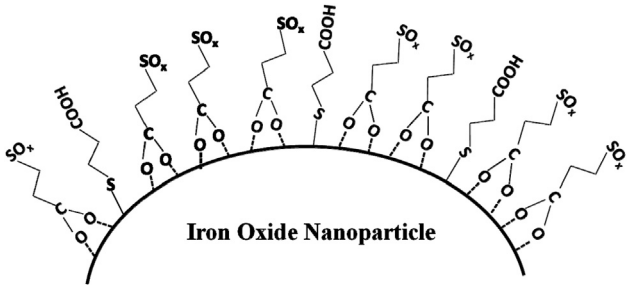
S. Sathish, S. Balakumar*

National Centre for Nanoscience and Nanotechnology, University of Madras, Guindy Campus, Chennai 600 025, India

HIGHLIGHTS

- Organic capped magnetite nanoparticles have been prepared by polyol method.
- The crystal structure and morphological analysis were studied by XRD, FESEM.
- Ethylene diamine (EDA) capped nanoparticles exhibit non saturation behavior.
- Mercaptopropionic acid (MPA) capped nanoparticles approaching the saturation state.
- Sulfur atom present in the MPA is chemically bonded with surface iron atom.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 October 2015
Received in revised form
26 January 2016
Accepted 6 February 2016
Available online 12 February 2016

Keywords:
Magnetic materials
Chemical synthesis
X-ray photo-emission spectroscopy
Magnetic properties

ABSTRACT

The properties of nanoparticles can be significantly altered by surface modification. In this present work the effect of surface inorganic–organic interactions on magnetic properties of magnetite nanoparticles have been investigated. Hence the mercaptopropionic acid (MPA) and ethylene diamine (EDA) capped magnetite nanoparticles have been prepared by polyol method. The magnetic study signifies that all the samples prepared by this method possess superparamagnetic behavior. The as-prepared, calcinated and EDA capped nanoparticles exhibit non saturation behavior, the MPA capped sample approach the saturation state and exhibit high value of magnetization whereas its calcinated sample shows complete saturation. The XRD results reveal that all the particles have nearly similar grain size so it is believed that the significant differences in magnetic properties are caused by the different interactions between the surface iron atoms and organic molecules. The XPS analysis indicates that sulfur atoms present in the MPA are chemically bonded with the surface iron atoms on the other hand, the EDA is physically adsorbed on iron oxide nanoparticles. Herein, we analyze and propose the possible interactions that could occur between the surface iron atoms and capping agent thereby influencing the magnetic properties of the nanoparticles.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Functionalization of magnetic iron oxide nanoparticles by organic molecules have attracted considerable attention in recent years because of their unique applications in biomedical field such

* Corresponding author.
E-mail address: balasuga@yahoo.com (S. Balakumar).

http://dx.doi.org/10.1016/j.matchemphys.2016.02.024
0254-0584/© 2016 Elsevier B.V. All rights reserved.

as targeted drug delivery [1–3], cancer treatment (hyperthermia) [4] and magnetic resonance imaging [5–7]. Indeed, for in vivo application as well as for nanoparticle self-assembly, the functionalization step is of fundamental importance to ensure suspension stability and to bring bioactivities. Besides improving its durability and suspensibility in biological environments and biocompatibility, the functional coating/shell can be used for tailoring the bio-distribution and immobilizing of foreign molecules. For these technological applications, the grafting of the molecules at the surface of nanoparticles is essential.

The magnetic properties of magnetic nanoparticles are considerably altered when coated with organic molecules. So understanding the influence of surface chemistry on the magnetic properties of nanoparticles certainly facilitates our fundamental understanding of the unique magnetic behavior of nanoparticles. However, most of the reported studies deal with the influence of the nanoscale on magnetic properties and only few investigations have been devoted to the specific effect of the organic coating. Especially, magnetic properties variation by surface modification of magnetic nanoparticles was mostly studied on maghemite nanoparticles [8–11]. Despite the large amount of work that has been focused on the decrease in the value of the saturation magnetization, they have invariably attributed to finite size effect, structural disorder in the whole particle and to surface effects. The surface effects have been mostly ascribed to a large fraction of surface subcoordinated atoms and/or a disordered (spin-glass) or magnetically different surface layer, inducing spin canting [12–25]. Limited work has been contributed on incomplete magnetic saturation behavior of the nanoparticles coated with organic molecules [20,26,27].

However, the origin of such anomalous magnetic properties is not fully understood till now. So it is necessary to broaden the research range for further insight into the mechanism. Therefore, in the present work, the effect of surface inorganic–organic interactions on the magnetic properties of magnetite nanoparticles functionalized by carboxylic and amine molecules have been investigated. The mercaptopropionic acid (MPA) and ethylene diamine (EDA) capped magnetite nanoparticles were prepared by polyol hydrolysis process. These capping agents were selected for two reasons: first, MPA acts as carboxyl functional group whereas EDA acts as amine functional group and second, they are known to effectively control the particle size and shape.

2. Experimental details

2.1. Materials

Iron (III) chloride hexa-hydrate, $FeCl_3.6H_2O$ (Sigma–Aldrich, 99%, ACS reagent), Iron (II) chloride tetra-hydrate, $FeCl_2.4H_2O$, sodium acetate, diethylene glycol (DEG), mercaptopropionic acid and ethylene diamine (Merck, 99%, for synthesis), NH_4OH (Merck, 25%), double distilled (DD) water, ethanol and acetone.

2.2. Synthesis of magnetite nanoparticles

The magnetite nanoparticles were prepared by polyol method with certain modifications as reported in the literature [28,29]. In a typical procedure, the precursor salts, $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ in a stoichiometric ratio (2:1) were added to a given volume (200 mL) of diethylene glycol. 0.5 M concentration of MPA (capping agent) was added into the above solution. The hydrolysis ratio and the acetate ratio were fixed to 6.8 and 3 by the addition of water and sodium acetate respectively. The pH of the solution was adjusted to 8 by adding ammonia solution. Under reflux condition, the mixture was heated to boiling temperature (256 °C) for 12 h with continuous stirring to obtain the final product as a pure solid phase. A black suspension was obtained, which was left undisturbed overnight and later centrifuged. During centrifuging, the obtained magnetite precipitate was washed twice with DD water, ethanol and acetone. Magnetite powders thus prepared were dried at 100 °C for 2 h under vacuum condition. The similar procedure was repeated by adding EDA instead of MPA as a capping agent. In order to get the calcinated samples the as-prepared nanoparticles have been calcinated at 200 °C and 300 °C for 2 h under vacuum condition. Hereafter the sample calcinated at 200 °C is simply called as calcinated sample.

2.3. Characterization techniques

The thermal degradation property of the sample was studied by using thermal gravimetric analysis (Perkin Elmer). The samples were heated in an inert atmosphere from room temperature (32 °C) to 950 °C at the rate of 20 °C min^{-1}. The structural and phase analysis of the samples were carried out by X-ray diffractometer (XRD, X'PERT PRO PANalytical) using a Cu K_α source ($\lambda = 1.5406$ Å). XRD patterns were recorded in the range of 10–80° (2θ) at the scan rate of 3.3°/min. Morphology was determined from Field Emission Scanning Electron Microscopy (FESEM) images using Hitachi SU6600, Singapore. Fourier-transform infrared (FTIR) spectra of purified and dried nanoparticles were recorded using an attenuated total reflection FTIR (Varian 3100 FT-IR). Magnetic properties of the samples were studied by using vibration sample magnetometer (Lakeshore – VSM 7410) in a maximum magnetic field of 1.5 T. Surface analysis were carried out using X-ray Photoelectron Spectroscopy (XPS), Omicron nanotechnology.

3. Results and discussion

3.1. Thermal analysis (TGA)

Fig. 1 shows the TGA plot of as-prepared magnetite nanoparticles. The weight loss of about 9% at below 200 °C may be due to removal of water and some of the organic content. The weight loss of about 12% at 220–380 °C is may be associated with the removal of DEG that has been coated on magnetite nanoparticles as well as the transition of magnetite into maghemite phase [28,30,31].

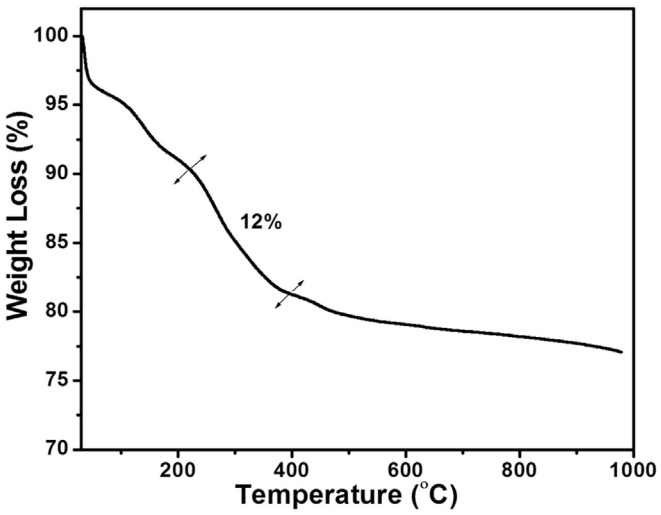


Fig. 1. TGA plot of as-prepared magnetite nanoparticles.

Download English Version:

https://daneshyari.com/en/article/1520702

Download Persian Version:

https://daneshyari.com/article/1520702

Daneshyari.com