Materials Letters 151 (2015) 64–67

Contents lists available at ScienceDirect

Materials Letters

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

Charge transfer mediated magnetic response of cobalt ferrite nanoparticles

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ARTICLE INFO

Article history:
Received 6 February 2015
Accepted 9 March 2015
Available online 18 March 2015

Keywords:
Cobalt ferrite nanoparticles
Surface modification
Magnetic properties
Charge transfer effect

ABSTRACT

Herein, we have performed rational surface modification of $CoFe_2O_4$ nanoparticles (NPs) to tune its room temperature ferrimagnetic properties by using different non-ionic surfactants. The NPs have been prepared by surfactant-assisted chemical co-precipitation technique with a narrow size distribution. For our study, we have chosen four non-ionic surfactants of triton X and tween group having different chain-lengths. Interestingly, we have found that surfactant co-ordinated magnetic NPs show a maximum of $\sim$94% increase in coercivity along with a considerable decrease in magnetization as compared to the bare one. Systematic investigation reveals that both the nature and number of surfactant's head group and chain-length of its alkyl tail group have a remarkable impact on the magnetic properties of $CoFe_2O_4$ NPs. We believe that the tuned magnetic response of $CoFe_2O_4$ NPs depending on the nature of the surface binding ligand would open up many new opportunities as well as enhance their beneficial activities toward diverse application fields.

1. Introduction

During last few decades, $CoFe_2O_4$ nanomaterials have attracted enormous attention of the scientific community because of their high coercivity, moderate saturation magnetization, large magnetocrystalline anisotropy, low cost, remarkable chemical and mechanical stability [1]. All these features of $CoFe_2O_4$ nanostructures facilitate its wide range of applications in high-density magnetic recording, magnetic tunnel junction, magnetostrictive sensor, and magneto-optic devices [2]. It is very well documented that with gradual decrease of the size of magnetic nanoparticles (NPs) towards superparamagnetic size limit, the ambient thermal energy can easily randomize its direction of magnetization, resulting zero coercivity and remanent magnetization. However, the conservation of innate ferromagnetic character of magnetic nanomaterial with reduced size is of great importance in developing portable technological devices. There are numerous synthesis techniques which provide significant enhancement of magnetic properties of $CoFe_2O_4$ nanomaterials such as mechanical milling, [3] surface treatment [4], etc. Recent advancement of surface science suggests that surface modification of bare $CoFe_2O_4$ NPs using surfactants can significantly enhance its magnetic properties. However, rational surface modification to tune that enhanced magnetic properties is still scarce in the existing literatures. Hence, it would be of fundamental research interest to tune that enhanced magnetic properties of $CoFe_2O_4$ NPs by judiciously varying the surface binding ligands as well as to assign its quantum mechanical origin.

In this article, we have reported the tuning of enhanced coercivity and reduced magnetization of functionalized $CoFe_2O_4$ NPs by varying the number of same donor head and tail group of the surface binding ligand and also investigated the effect of nature of the donor head group on the magnetic properties of $CoFe_2O_4$ NPs. For the sake of understanding the role of donor head groups, we have chosen the ligands of tween and triton X groups where tween group of ligands have larger number of σ-donor head groups than triton X group of ligands along with a single π-donor head group. To distinguish the effect of chain-length, we have varied the chain-length of ligands within individual groups, such as triton X-100 (TX-100) has larger chain-length than triton X-114 (TX-114) and tween-80 (T-80) has longer chain than tween-20 (T-20). We have demonstrated the correlation between the surface binding ligand and magnetic properties of functionalized NPs in terms of charge transfer effect and Van-der Waal's interaction.

2. Experimental section

We have synthesized surfactant co-ordinated $CoFe_2O_4$ NPs by wet chemical route following our previous report [5] with a modification, which involves the use of four non-ionic surfactants named, TX-100, TX-114, T-20, and T-80. The phase and morphology of as-prepared

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http://dx.doi.org/10.1016/j.matlet.2015.03.040

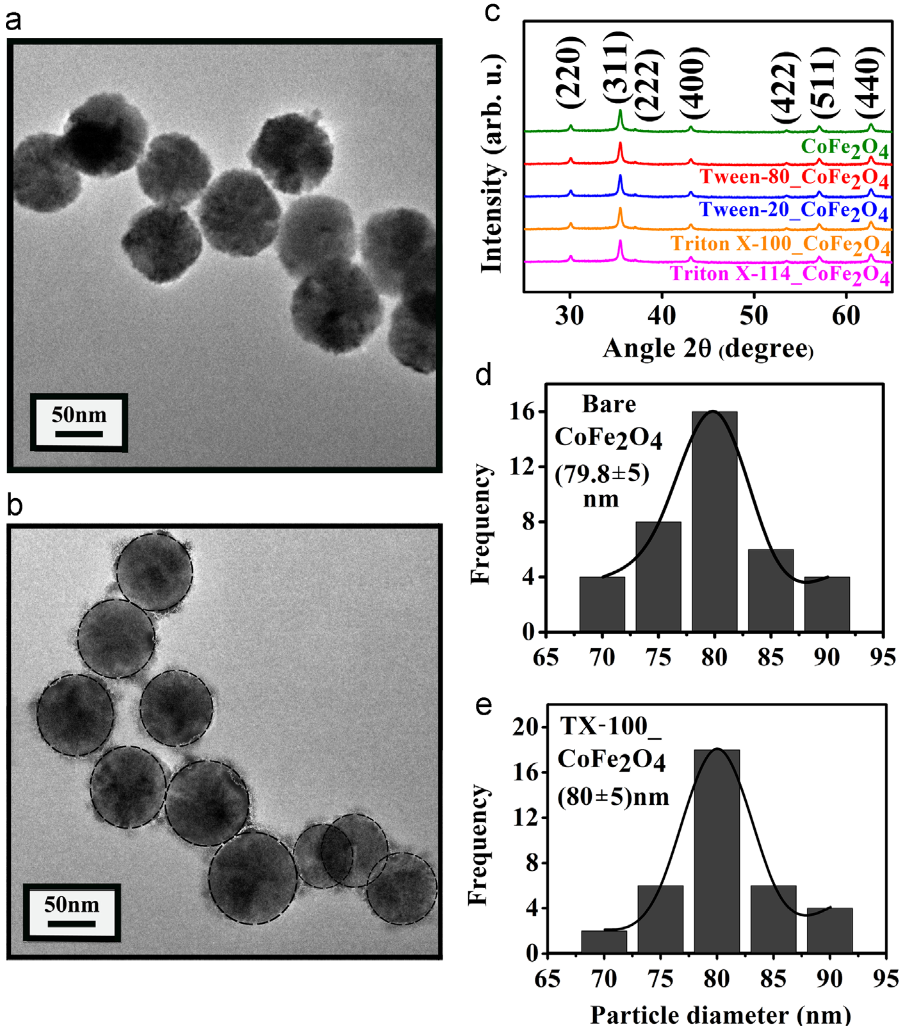

Fig. 1. TEM images of (a) bare, and (b) functionalized $CoFe_2O_4$ NPs. (c) XRD patterns of all $CoFe_2O_4$ NPs. Size distribution graphs of (d) bare, and (e) functionalized $CoFe_2O_4$ NPs.

Table 1

List of average particle diameter, coercivity (H_c), magnetization (M_s), anisotropy energy (E_A), and percentage change in H_c and M_s of surfactant co-ordinated $CoFe_2O_4$ NPs with respect to bare.

Type of $CoFe_2O_4$	Average particle diameter (nm)	H_c (kG)	M_s (emu/gm)	E_A (Joule/kg)	% increase of H_c	% decrease of M_s
Bare_ $CoFe_2O_4$	79 ± 5	0.391	40.13	4.45	0	0
TX-114_ $CoFe_2O_4$	78 ± 5	3.32	11.12	8.4	88.22	72.29
TX-100_ $CoFe_2O_4$	79 ± 5	4.91	15.23	19.97	92.03	62.05
Tween-20_ $CoFe_2O_4$	80 ± 5	5.73	17.36	26.17	93.18	56.74
Tween-80_ $CoFe_2O_4$	80 ± 5	6.4	27.86	48.7	93.89	30.57

$CoFe_2O_4$ NPs were studied by x-ray diffraction (XRD) and a transmission electron microscope (TEM) respectively. Room temperature magnetic measurements up to 1.6 T were performed using a vibrating sample magnetometer (VSM) and fourier transform infrared (FTIR) spectra of the samples were executed to ensure the attachment of surfactant molecule on the surface of $CoFe_2O_4$ NPs.

3. Results and discussion

Fig. 1(a and b) shows the TEM images of bare and functionalized $CoFe_2O_4$ NPs. They reveal that all the particles were spherical in shape and fairly monodispersed with a particle diameter in the range of 70–90 nm. The XRD patterns of as-prepared $CoFe_2O_4$ NPs (Fig. 1c) confirm their single phase inverse spinel face centred cubic structure (JCPDS Card no. 22-1086). The size distribution graphs (Fig. 1d and e) demonstrate that average size of the particles is ~80 nm. The list of average particle size of all as-synthesized $CoFe_2O_4$ NPs is mentioned in Table 1.

To investigate the interaction of ligand with the NP surface, a comparative FTIR spectroscopic study has been performed on both the ligand and surfactant co-ordinated $CoFe_2O_4$ NPs as shown in Fig. 2. The ligand T-20 shows five characteristic bands (in the range of 1200–3000 cm^{-1}) at 1249, 1467, 1736, 2871, and 2923 cm^{-1} which are associated with the stretching of ester C–O, bending of CH_2, stretching of ester C=O, and symmetric and antisymmetric stretching of alkyl C–H bonds respectively and a characteristic band in the range of 3300–3400 cm^{-1} belongs to the stretching of