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Thermal Annealing Synthesis of Fe_4N/Fe Nanocomposites from Iron Oxide (Fe_3O_4) Nanoparticles

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A facile sono-thermal approach using inexpensive and non-toxic chemicals was applied for the large-scale synthesis of iron nitride/iron (Fe_4N/Fe) nanocomposite. The as-synthesized iron oxide (Fe_3O_4) nanoparticles by sonochemical method were treated in a thermal annealing chamber in presence of hydrogen (H_2) and ammonia (NH_3) gases to obtain Fe_4N/Fe nanocomposite. X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) analyses revealed that the Fe_4N/Fe nanocomposite had been successfully synthesized using this simple method. Transmission electron microscopy (TEM) data demonstrated that the sizes of the as-synthesized Fe_4N/Fe nanocomposite were larger compared to the sizes for the initial Fe_3O_4 NPs. The magnetization curve obtained using vibrating sample magnetometer (VSM) measurements showed that the magnetization had been significantly increased in the synthesized Fe_4N/Fe nanocomposite compared to that in the freshly-prepared Fe_3O_4 magnetic NPs.

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I. INTRODUCTION

During the last few decades, the synthesis of nanoparticles has drawn much interest due to their tremendous prospects in diverse fields. This increasing interest is not only in scientific purposes but also in biomedical applications, such as magnetic resonance imaging (MRI) [1–4], cell and protein separation [5–7], and drug delivery [8], as well as in ever-increasing technological applications, such as the tenability of their magnetic properties [9,10] and their extensive use in catalysis [11], magnetic recording [12], high-performance electromagnetics [13], spintronics [14] and ecological remediation [15,16]. For these diverse ecological and biomedical applications, the magnetic nanocomposite should have high magnetic moment value as well as be stably dispersed in water. Iron-nitride nanoparticles and nanocomposites have been considered as potential candidates for magnetic applications among other magnetic counterparts [17], and Iron-nitride nanoparticles and nanocomposites have been prepared by using various methods, such as laser pyrolysis [18], mechanical alloying [19] and gas-solid nitrogenation [20]. Recently, with quality improved, high-temperature organic-solution phase methods have also been developed for the synthesis of iron-nitride systems.

In this study, an unsophisticated sono-thermal approach using inexpensive and non-toxic chemicals was applied for the large scale synthesis of iron nitride/iron

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(Fe_4N/Fe) nanocomposite. Firstly, Iron oxide (Fe_3O_4) NPs were synthesized through sonochemical route. After that, the dried Fe_3O_4 NPs were treated in a thermal annealing chamber in the presence of both hydrogen (H_2) and ammonia (NH_3) gases for 6 hours for reduction. Finally, we successfully obtained Fe_4N/Fe nanocomposite. By optimizing the preparation conditions, such as the temperature of annealing and the reaction time, we successfully synthesized Fe_4N/Fe nanocomposite with an average size of 70 nm, which implies that this modified simple sono-thermal method may be a good candidate for synthesis of various nanoparticles.

The as-synthesized Fe_4N/Fe nanocomposites were characterized and analyzed by different techniques like X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectrometer (EDS), and the magnetic hysteresis loop was measured using vibrating sample magnetometer (VSM) at 300 K. The X-ray diffraction (XRD) and the transmission electron microscopy (TEM) results indicate that the as-synthesized Fe_4N/Fe nanocomposite has a reasonable size distribution and moderate monodispersity in both polar and non-polar solvents.

II. EXPERIMENTS AND DISCUSSION

A two-step sonochemical method has been applied to synthesize Fe_4N/Fe nanocomposite. In the first step, a prepared mixture of 3 g of $FeCl_3.6H_2O$ (99%, Aldrich) and 2 g of $FeCl_2.4H_2O$ (90%, Aldrich) in 120 ml of distilled H_2O was sonicated for 60 minutes. An aqueous solution of $28 - 30\%$ ammonia (20 ml) was injected into the reaction vessel after 10 minutes from starting the ultrasonication. More details of the synthesis process are described in a previously-published paper [21]. The obtained Fe_3O_4 NPs were washed with distilled water and ethanol a few times and then dried in a vacuum evaporator. Then, the synthesized Fe_3O_4 NPs were annealed in a thermo annealing chamber to synthesize the Fe_4N/Fe nanocomposite. Fe_3O_4 NPs samples (100 mg) were well distributed in a ceramic boat and placed into the annealing chamber. Before starting the annealing, we evacuated the annealing champer by using rotary and diffusion pumps to make an oxygen-free environment inside the chamber. Subsequently, the chamber was filled with H_2, and the sample was annealed for up to 6 h at 500 °C. The as-synthesized Fe_4N/Fe nanocomposite were kept in an air-tight container for some specific time before being used for measurements.

The crystalline structure of the synthesized Fe_4N/Fe nanocomposite was examined by using XRD technique with Rigaku RiNT 2200 equipment. The size and the morphology of the Fe_4N/Fe nanocomposite were measured using TEM (Tecnai G2 F20). Elemental analysis was done by using an energy dispersive spectroscopy (EDS) that was embedded in the TEM. The VSM (Lake Shore 7400) which has an external magnetic field ranging from −13 to 13 kOe, was used to measure the magnetic properties of the sample.

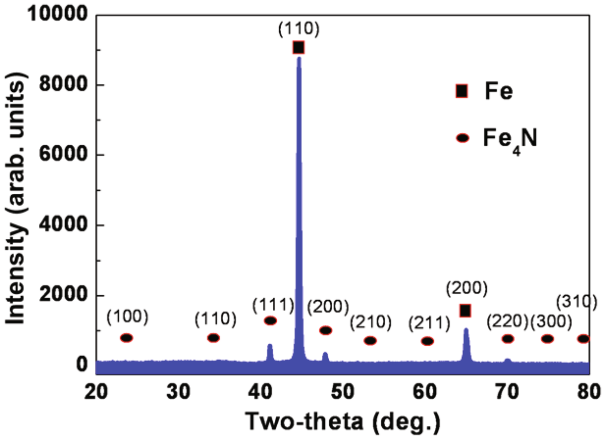

Fig. 1. (Color online) The XRD pattern of the sample shows peaks for the Fe_4N/Fe nanocomposite phase.

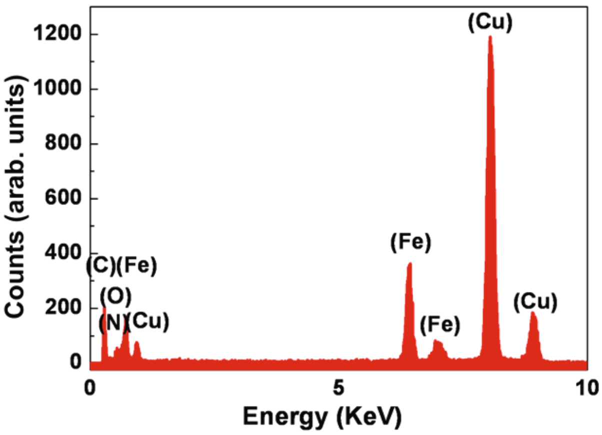

Fig. 2. (Color online) The EDS pattern for the Fe_4N/Fe nanocomposite clearly shows the presence of Fe and N elements in the NPs. The small amount of oxygen present is due to the oxidation of the Fe_4N/Fe nanocomposite in air. The Cu and C peaks are due to carbon copper grid.

Figure 1 shows the X-ray diffraction patterns of the synthesized Fe_4N/Fe nanocomposite. From the X-ray diffraction patterns, the peaks can be indexed to the (100), (110), (111), (200), (210), (211), (220), (300) and (310) planes of a cubic unit cell of Fe_4N, and the peaks at (110) and (200) to Fe based on comparisons with the standard patterns of Fe_4N and Fe.

A typical EDS analysis of the Fe_4N/Fe nanocomposite in Fig. 2 reveals that the material is mainly composed of Fe and N elements, which indicates that a Fe_4N/Fe nanocomposite had been synthesized. The small peak for O is due to a thin iron-oxide shell that formed on the outside of the Fe_4N/Fe nanocomposite core due to oxidation of the samples in air before the TEM and the EDS measurements. This oxide shell is considered to

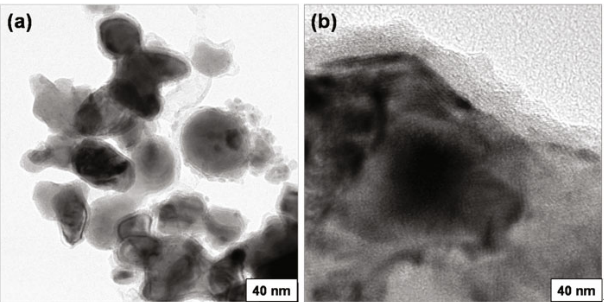

Fig. 3. TEM images of (a) Fe_4N/Fe nanocomposite and (b) Fe_3O_4 shell due to surface oxidation of the Fe_4N/Fe nanocomposite.

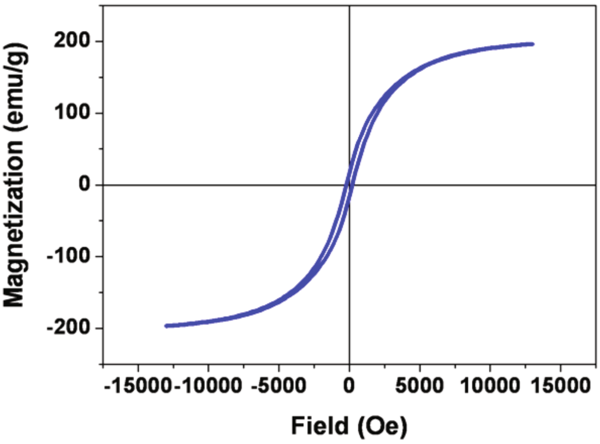

Fig. 4. (Color online) Magnetization curves of the Fe_4N/Fe nanocomposite measured at room temperature.

be very important as a protective agent against further oxidation.

Figure 3 shows typical TEM images of the as-prepared Fe_4N/Fe nanocomposite. The images (Fig. 3(a)) reveal that the as-synthesized Fe_4N/Fe nanocomposite were moderately monodisperse and nearly spherical in shape with an average size of about 80 nm. Due to the oxidation of the Fe_4N/Fe nanocomposite sample, an oxide shell had been produced, which is shown in Fig. 3(b) and is supported by the EDS analysis. From Figs. 3(a) and (b), EDS and XRD analyses, clearly the inside core is Fe_4N/Fe, and a TEM image of the synthesized Fe_4N/$FeFe_3O_4$ nanocomposite shown that the core is covered with thin oxide layer.

Magnetic measurements were carried out on the synthesized Fe_4N/Fe nanocomposite powders precipitated from the ethanol dispersion and the results is shown in Fig. 4. The as-prepared high magnetic Fe_4N/Fe nanocomposite were nearly superparamagnetic, with a saturation magnetization of about 196 emu/g, whereas Fe_3O_4 had a value of 80 emu/g before annealing [21].The saturation magnetization of the as-synthesized Fe_4N/Fe nanocomposite is significantly higher than that of the initial Fe_3O_4 NPs.

III. CONCLUSION

In summary, iron nitride/iron Fe_4N/Fe nanocomposite have been successfully synthesized by using a facile sono-thermal approach with non-hazardous chemicals and sonochemically-synthesized Fe_3O_4 NPs treated in a thermal annealing chamber in the presence of hydrogen (H_2) and ammonia (NH_3) gases. XRD and EDS analyses and (TEM) data demonstrated that the sizes the as-synthesized Fe_4N/Fe nanocomposite were increased compared to those of the initial Fe_3O_4 NPs. The magnetization curve showed that the magnetization had been significantly increased in the as-synthesized Fe_4N/Fe nanocomposite compared to that in the freshly- prepared Fe_3O_4 magnetic NPs. TEM and EDS data also suggested that a thin oxide layer that had been produced on the core Fe_4N/Fe nanocomposite due to oxidation in air could act as protective layer to add further stability to the core. This high magnetic Fe_4N/Fe nanocomposite can be used in bio-sensing and many other applications.

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