Materials Research Express

PAPER

CoFe$_2$O$_4$–Fe$_3$O$_4$ bimagnetic heterostructure: a versatile core-shell nanoparticle with magnetically recoverable photocatalytic and self heating properties

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Keywords: exchange coupled, magnetic hyperthermia, photocatalytic

Supplementary material for this article is available online

Abstract

CoFe$_2$O$_4$–Fe$_3$O$_4$ (Fe/Co = 2.3, 2.75 & 3.5) core-shell magnetic nanocomposite (MNC) was successfully prepared by combined sonochemical and reverse co-precipitation method using cost effective and readily available precursor. The structure, morphology, thermal, optical and magnetic properties of the MNC was extensively studied and the product was found suitable for use as an environmentally safe recyclable photocatalyst for pollution control. The self-heating properties of the MNC was also investigated for magnetic hyperthermia application. The studies of Infrared (IR) and Ultraviolet-visible (UV-Vis) spectroscopy confirmed the synthesis and formation of the bimagnetic heterostructure. The x-ray Diffraction studies and Transmission Electron Microscopy (TEM) analysis confirmed the formation of subnanometer clusters (<10 nm) in the asprepared samples. The results of Differential Scanning Calorimetry (DSC)/Thermo-Gravimetric Analysis (TGA) analysis of the as prepared samples showed transformation of intermediate Fe-phases to Fe$_3$O$_4$ during sample heating at 420 °C. This transformation accompanied structural changes in the asprepared sample that led to the formation of the core-shell structure which was observed in the TEM images of the annealed sample with Fe/Co ratio (x = 3.5). The magnetization-hysteresis (M-H) studies was done on the asprepared and annealed samples using the Vibrating Sample Magnetometer (VSM). The VSM studies showed significant improvement of magnetization and coercivity in the annealed samples making it suitable for re-usability in photocatalytic reaction and magnetic hyperthermia application. The degradation of phenolphthalein (a non-biodegradable organic chemical) in the presence of UV light irradiation was used as a reference reaction to confirm the photocatalytic properties of the CoFe$_2$O$_4$–Fe$_3$O$_4$ MNC, which could be well isolated from the media at the end of degradation, by applying an external magnetic field and reused. The nanocomposite was also investigated for magnetic hyperthermia using induction heating properties and the result infer that it is also a promising material for hyperthermia application.

1. Introduction

Nanoscale magnetism of a magnetic nanoparticle system composed of a magnetically hard and soft phases has stimulated great interest in the recent years due to their importance in many technological applications [1, 2]. Compared to traditional single-phase material, such two-phase systems have high magnetization and coercivity [3], which are the most important parameters describing a permanent magnet. However, a bimagnetic core/shell nanoparticle system, where the shell in addition to being magnetic (ferro- or ferri-magnetic) also show good optical property has been less studied. The study of such nanoparticle system is interesting due to their
potential in magneto-optical, electromagnetic, biomedical, photocatalytic and permanent magnetic applications. Therefore, it is tempting to consider composites of material consisting of bi-magnetic phases, one of which provides a high nucleation field for irreversible magnetization reversal at the core and the other material with high magnetization saturation, \( M_s \) and good optical property at the shell. Here, we report the fabrication of core-shell MNC of CoFe\(_2\)O\(_4\) (core) and Fe\(_3\)O\(_4\) (shell), using reverse co-precipitation technique under the assistance of ultrasonic irradiation \([4, 5]\). CoFe\(_2\)O\(_4\) nano-particle is a well-known hard magnetic material \([5–7]\), which has been studied in detail due to its high coercivity, moderate magnetic saturation, remarkable chemical stability and mechanical hardness. On the other hand, Fe\(_3\)O\(_4\) (magnetcite) with large saturation magnetic moment and low coercivity nanoparticles could serve as an ideal soft magnetic material for the nanocomposite \([8]\). Moreover, due to the well-known optical properties, biocompatibility and excellent ferrimagnetic properties exhibited by the Fe\(_3\)O\(_4\) nanoparticles, their applications could also be explored in several areas of science and technology. These areas include magnetic recording technology, pigments, catalysis and photo-catalysis \([9–13]\), as well as the medical uses with emphasis on the cell separation \([14]\), biological sensing and probing \([15, 16]\), Magnetic hyperthermia \([17, 18]\) making it a truly multifunctional nanocomposite. Erikson \textit{et al} \([19]\) has studied the nonstoichiometry, cation distribution and electrical properties of CoFe\(_2\)O\(_4–\)Fe\(_3\)O\(_4\) nanocomposite prepared by resin intermediate method (P. PECHINI, US Patent 3,330,697, July 11, 1967) at high temperature. So far no elaborate application oriented study on magnetic and optical properties of such core-shell CoFe\(_2\)O\(_4–\)Fe\(_3\)O\(_4\) nanocomposite system prepared by sonochemically assisted reverse co-precipitation technique has been done. A study of these conjugates may provide an insight into developing nanostructured material with enhanced magnetic and optical properties for possible use as an effective photo-catalyst in environmentally safe cost effective pollution control and hyperthermia applications. There are different technologically important methods such as aqueous coprecipitation, \([20, 21]\) sonochemical reactions, \([22, 23]\) hydrolysis of precursor, \([24, 25]\) mechano-chemical synthesis, \([26, 27]\) hydrothermal process, \([28, 29]\) microwave synthesis, \([30]\) micelle microemulsion, \([31]\) and others \([32, 33]\). Chemical routes are commonly used to fabricate ultra-fine powder having high volume of crystalline structure and uniform size distribution \([34, 35]\). Among numerous chemical methods, co-precipitation is considered to be the simplest, cost-effective and most efficient pathway to obtain magnetic nanoparticles \([36–38]\). In our approach, both CoFe\(_2\)O\(_4\) and Fe\(_3\)O\(_4\) are incorporated as nanometer scale building blocks in a single step reaction by the reverse co-precipitation technique under the assistance of ultrasonic irradiation \([4, 5]\). The reverse co-precipitation technique is a simple fast and inexpensive approach to synthesize these nanocomposites since it does not involve any intermediate steps. In addition, it is also easy to control the stoichiometric composition and crystallite sizes, which have many important effects on the magnetic and optical properties. The Fe/Co ratio (2.3 to 3.5) in Co\(_x\)Fe\(_{3-x}\)O\(_4\) (where \( x = 0.67 \) to 0.91) can be easily varied to obtain a nano-composite of desired properties by tuning the composition of the individual building blocks. In this paper, we have prepared highly stable cobalt ferrite/ferric oxide nanocomposite by combined sonochemical and reverse co-precipitation method. This is achieved by adding off-stoichiometric ratios of mixed acidic solution of metal salts (FeCl\(_3\) and CoCl\(_2\),6H\(_2\)O) to a large amount of basic solution, which maintains the solution pH until all the components gets precipitated completely \([39]\). The main aim of the present work is to investigate the influence of Fe/Co ratio on the structural, magnetic and optical properties of the nanocomposite. We also emphasize on the development of an effective tool for the degradation of environmental pollutants such as phenolphthalein (a non-biodegradable organic chemical). The investigation also analyses the application prospects of the nanocomposite for magnetic hyperthermia applications.

2. Experimental

The raw material used in the synthesis of CoFe\(_2\)O\(_4–\)Fe\(_3\)O\(_4\), was obtained from Merck and used as purchased. The raw materials are cobalt chloride hexahydrate CoCl\(_2\),6H\(_2\)O (purity 98%), Iron chloride FeCl\(_3\) (purity 97%) and sodium hydroxide NaOH (purity 96%).

2.1. Synthesis of CoFe\(_2\)O\(_4–\)Fe\(_3\)O\(_4\) nanocomposite:
The CoFe\(_2\)O\(_4–\)Fe\(_3\)O\(_4\) MNC was synthesized by taking two aqueous solutions of FeCl\(_3\) (2.399 g, 14.7 mmol, 50 ml) and CoCl\(_2\),6H\(_2\)O (1 g, 4.2 mmol, 50 ml) mixed in a 200 ml flat bottom flask. The mixed acidic solution was added drop-wise to an aqueous NaOH solution (4 g, 250 mmol, 25 ml) in a 500 ml beaker. The reaction was done under argon atmosphere with continuous ultrasonic irradiation using a JEIO TECH, Lab Companion Ultrasonic bath (Model: 1505), operating at a frequency 40 KHz and a power of 40 KW. Prior to mixing, all these three solutions were sonicated for 30 min to remove any dissolved oxygen. During mixing, the pH of the solution was continuously monitored and maintained in a range of 13–14. After the completion of the mixing, the temperature of the sonicator bath was raised up to 330 K and was further sonicated for 30 min in air.
atmosphere. The black precipitate formation was observed and the reaction mixture was then centrifuged at 14000 rpm at ambient temperature for 15 min. The black precipitate was separated from supernatant liquid and washed off with copious amount of distilled water and ethanol. A sample of the precipitate formed was analyzed in TEM-EDX and the formation of CoFe$_2$O$_4$–Fe$_3$O$_4$ nanocomposite was confirmed from the Fe and Co ratio (Fe/Co = 3.5). We have repeated the above steps by taking two more concentration of FeCl$_3$ as 1.8812 g (11.6 mmol) and 1.5702 g (9.68 mmol) in 50 ml water to obtain the desired ratios of Fe and Co (Fe/Co = 2.3 and 2.75). To study the microstructural and magnetic properties of the nano-crystalline particles, the material was annealed in nitrogen atmosphere for 12 h using a custom made tubular muffle furnace at temperature of 500 °C and was quenched using compressed nitrogen gas at room temperature.

2.2. Characterization

The crystalline nature of the synthesized CoFe$_2$O$_4$–Fe$_3$O$_4$ sample was investigated by XRD pattern recorded on a Bruker AXS D8 using Cu-K$_\alpha$, radiation (λ = 1.54178 Å). The crystallite size of the CoFe$_2$O$_4$–Fe$_3$O$_4$ nanoparticles was obtained from the XRD pattern using Scherer’s formula. The IR studies were recorded using a PerkinElmer RXI FT-IR spectrometer in KBr pellets. The crystallinity and particle-size of the CoFe$_2$O$_4$–Fe$_3$O$_4$ nanoparticles were examined by TEM (JEOL JEM2100). The sample for TEM analysis was prepared by taking a micro drop of dilute ethanol solution of the dispersed nano-particles, deposited on a carbon-coated copper grid (400 mesh size). The nanoparticle was observed in bright field TEM imaging at a maximum resolution of 20 nm with a magnification range of 50–200KX. The magnetic properties were observed under the application of a magnetic field upto 20 kOe, for the various samples using a VSM (Lakeshore 7410). UV–Vis spectra of the nanoparticles as well as the photocatalytic degradation were recorded in a Varian Cary 50 bio UV–Vis spectrophotometer.

The specific surface area was measured by the application of Brunauer–Emmett–Teller (BET) equation and Barrett–Joyner–Halanda (BJH) method. The sample was first degassed for 2 h at 200 °C and then analyzed by a Backman Coulter (SA 3100) surface area and pore-size Analyzer. Induction heating variations were analyzed by using Easy Heat AMBRELL 8310.

2.3. Photocatalytic degradation of phenolphthalein by CoFe$_2$O$_4$–Fe$_3$O$_4$ nanocomposite

The evaluation of photocatalytic activity for the prepared samples was measured by degrading phenolphthalein in aqueous solution at ambient temperature. The experiment was carried out in a 200 ml quartz glass vessel. The core-shell CoFe$_2$O$_4$–Fe$_3$O$_4$ MNC (0.02 g) was placed into the tubular quartz vessel containing 100 ml of 1 × 10$^{-3}$ M phenolphthalein aqueous solution. Then the mixture was stirred in dark to obtain absorption/desorption equilibrium until a uniform concentration of phenolphthalein was obtained. The mixture was then illuminated with a 12 mW UV lamp (wavelength of 400 nm) with continuous stirring. After the reaction began, the mixture was sampled at different times and separated by a magnet to discard any sediment. The absorption spectra was obtained through a wavelength scan from 220–350 nm with aid of quartz cells (10 mm optical path length) on a UV–Vis spectrophotometer.

3. Results and discussion

3.1. Structural and morphological analysis

In the present study, we report the microstructural, magnetic and optical properties of a series of nanocomposites of CoFe$_2$O$_4$–Fe$_3$O$_4$ with Fe/Co ranging from 2.3 to 3.5 synthesized by the sonochemically assisted reverse co-precipitation method. The TEM observation of the as prepared samples shown in figures 1(a)–(d) indicate the formation of clusters of approximately 4–8 nm in diameter with particle-particle contact surrounding the CoFe$_2$O$_4$ nanoparticle. It is highly possible that subnanometer phases such as FeOOH (akageneite), Fe$_3$H$_2$O$_4$, H$_2$O (Ferrihydrite), Fe(OH)$_3$, etc along with CoFe$_2$O$_4$ nanoparticle may be formed due to off-stoichiometric ratios of NaOH and FeCl$_3$ in the reaction [40]. These intermediate phases are more prominently observed in the TEM images of the as prepared samples with Fe/Co equal to 3.5.

The IR spectra of the as prepared samples in figure 2 have been used to locate the band positions in the region between 350 cm$^{-1}$ and 4000 cm$^{-1}$ and their values are given in table 1. The higher frequency band observed at around 600 cm$^{-1}$ ($\nu_1$) and the lower frequency at around 400 cm$^{-1}$ ($\nu_2$) are an indication of formation of CoFe$_2$O$_4$ spinel structure [41]. These bands are assigned to intrinsic vibration in the tetrahedral and octahedral interstices [42]. In the present system we have also observed prominent peaks around 1623 cm$^{-1}$ and 3410 cm$^{-1}$ which also suggest the formation of the intermediate Fe-phases and the hydroxyl ions that were entrapped on the surface of the nanoparticle during the sonication process. Figure 3 shows the DSC/TGA curves of the sample with Fe/Co ratios (x = 3.5) recorded on a NETZSCH 449 F3 Jupiter under nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$. The DSC-TGA curves showed a complicated behavior arising from the simultaneous
dehydration and oxidation of the Fe-phase. The TGA curve showed an initial weight loss of ∼17 % up to 200°C due to de-absorption of OH ions. Further, a close examination of the DSC curve also showed peaks which are attributed to transformation of the intermediate Fe-phase to Fe₂O₃ at 269.3°C and finally to Fe₃O₄ at 420°C [40]. This transformation accompanied structural changes in the as-prepared sample that led to the formation of

| Observed Fe/Co (x) | ν₁ (cm⁻¹) | ν₂ (cm⁻¹) |
|--------------------|-----------|-----------|
| 2.3                | 581       | 400       |
| 2.75               | 586       | 405       |
| 3.5                | 591       | 410       |

Figure 1. (a) Bright field TEM images and (b) HRTEM images of CoFe₂O₄–Fe₃O₄ as prepared nanocomposite for Fe/Co = 2.3. (c) Bright field TEM images and (d) HRTEM images of CoFe₂O₄–Fe₃O₄ as prepared nanocomposite for Fe/Co = 3.5.
the coreshell structure. Therefore, to form highly crystalline and well defined nanocomposites of CoFe$_2$O$_4$ and Fe$_3$O$_4$, all the samples were annealed at 500 °C for 12 h under nitrogen atmosphere.

The UV-Vis analysis of the annealed samples in figure 4 showed absorption bands around 400 nm. The direct band gap corresponding to these absorption bands was observed between 2.19 eV–2.57 eV which was calculated by plotting $(\alpha \nu)^2$ versus $\nu$ (figure 4(b)) using equation (1) [43].

$$\alpha \nu = \text{Const}(\nu - E_0)^n$$  \hspace{1cm} (1)

The value of $\alpha$ is obtained from equation (2) [42]

$$\alpha = 2.3026A \frac{A}{t}$$  \hspace{1cm} (2)

Where $A$ is absorption and $t$ is the thickness of the sample.

The CoFe$_2$O$_4$ nanoparticle is identified by a charge transfer band around 350 nm [44]. In CoFe$_2$O$_4$–Fe$_3$O$_4$ nanocomposite we have observed this band at 400 nm. This shift in the charge transfer band indicates the formation of CoFe$_2$O$_4$–Fe$_3$O$_4$ NP. Compared to traditional Fe$_3$O$_4$ [45], these bands showed a red shift with a prominent absorption in the near-ultraviolet spectral region suggesting its suitability for photo-catalytic activity [46]. Figure 5 shows the XRD of annealed CoFe$_2$O$_4$–Fe$_3$O$_4$ nanocomposite. The diffraction peaks and relative intensities of all patterns matched well with a cubic spinel structure of CoFe$_2$O$_4$ and Fe$_3$O$_4$ (JCPDS–International
center diffraction data, PDF cards 22–1086 and 1–1111). However, the small difference in the lattice parameter of both compounds makes it difficult to differentiate them. Further, no other impurity phase other than CoFe₂O₄ and Fe₃O₄ was found in all the patterns. The profile of the SAED patterns in figures 7(b) and (c) also showed peaks which matched well with the cubic spinel structure of CoFe₂O₄ and Fe₃O₄ and is consistent with the XRD analysis. The crystallite size as calculated by Scherer’s broadening analysis [47] of the spinel 311 reflection, are shown in table 2.

The nanostructure of the heat-treated samples (figures 6(a)–(d)) was also investigated using TEM. Again, because of the similarities in the crystal structures it was difficult to distinguish between the CoFe₂O₄ and Fe₃O₄ phases in the TEM images. High resolution TEM (HRTEM) has been done to clearly distinguish the phases. The HRTEM image of the annealed sample (Fe/Co = 2.3) in figure 6(b) showed some coalescence but, the phases in the sample (Fe/Co = 3.5) in figure 6(d) remained isolated with the formation of a core-shell structure. The particle size distribution of the TEM images shown in figures 7(a) and (d) and table 2 showed an increase in average particle size for higher Fe ratio. This may be due to the coalescences of the Fe-phase upon annealing that
lead to the formation of a Fe$_3$O$_4$ shell and was more prominently observed for the sample Fe/Co = 3.5. However, the CoFe$_2$O$_4$ MNP at the core showed good structural stability [22]. The formation of the cobalt ferrite/ferric oxide core-shell heterostructure has been schematically shown in figure 8.

**Table 2.** Some physical parameters of CoFe$_2$O$_4$–Fe$_3$O$_4$ nanocomposite prepared by combined sonochemical and reverse co-precipitation method.

| Observed Fe/Co (x) | Crystallite size (nm) | Particle size (nm) | Coercivity $H_c$ (Oe) annealed (300 K) | Magnetization $M_s$ (emu/g) annealed (300 K) |
|--------------------|-----------------------|--------------------|----------------------------------------|------------------------------------------|
| 2.3                | 22.75                 | 24                 | 812                                    | 63                                       |
| 2.75               | 30.44                 | —                  | 865                                    | 69                                       |
| 3.5                | 44.32                 | 50                 | 867                                    | 73                                       |

Figure 6. (a) Bright field TEM images and (b) HRTEM images of CoFe$_2$O$_4$–Fe$_3$O$_4$ annealed nanocomposite for Fe/Co = 2.3. (c) Bright field TEM images and (d) HRTEM images of CoFe$_2$O$_4$–Fe$_3$O$_4$ annealed nanocomposite for Fe/Co = 3.5.
Figure 7. (a) Particle size distribution and (b) SAED pattern of annealed CoFe$_2$O$_4$–Fe$_3$O$_4$ nanocomposite with Fe/Co = 3.5. (c) SAED pattern and (d) Particle size distribution of annealed CoFe$_2$O$_4$–Fe$_3$O$_4$ nanocomposite with Fe/Co = 2.3.

Figure 8. Schematic illustration of formation of the cobalt ferrite/ferric oxide core-shell hetrostructure.
3.2. Magnetic analysis

The magnetic behavior of the as-prepared and annealed samples has been explained on the basis of the magnetization curves measured at room temperature and at 80 K and are shown in figures 9 and 10. The inset in the figures 9 and 10 shows the expanded region around the origin to make the coercivity more visible at various temperatures. The magnetization and coercivity values were extracted from the magnetization curves as shown in table 2. The development of coercivity differed greatly between the single phase and two phase Co-Fe structure. Our previous studies on single phase CoFe2O4 structure prepared by this method have given a moderate coercivity which transformed to a hard magnetic structure after appropriate heat treatment [22, 39, and 49]. In the present study, we have observed a clear hysteresis for the annealed samples with Fe/Co ratio at 2.3 with a coercivity of 812 Oe which reached a maximum of 4KOE at 80 K for the sample Fe/Co = 3.5. Moreover, the hysteresis loops of the sample (Fe/Co = 3.5) measured at 80 K in figure 10 also showed a non-saturating behavior which may be attributed to strong magnetocrystalline anisotropy. As the field approached zero a prominent hump appeared in the demagnetization curve particularly for the sample Fe/Co = 3.5 and was more prominent in the hysteresis loops measured below 150 K. A similar feature has been observed in the magnetization-demagnetization curves of CoFe2O4-ZnFe2O4 core-shell structure reported by Ombretta Masala et al [48] and has been attributed to magnetic exchange coupling between the hard CoFe2O4 phase and soft ZnFe2O4 phase. Similarly, in our case the magnetic interaction across the grain boundaries of the hard CoFe2O4
phases and soft Fe₃O₄ phases of the core-shell structure has given rise to exchange coupling between the phases [49]. The evidence of core-shell structure in the annealed samples is also observed from the temperature dependence of the field-cooled (FC) and zero-field cooled (ZFC) magnetization curves of the annealed samples under an applied field of 100 Oe. Below the blocking temperature $T_B$, the FC and ZFC curves in figure 11 diverge and the ZFC values approach zero as the temperature approaches 10 K. From the figure 11 we also observed that the blocking temperature is independent of the sample composition and is same for the samples with Fe/Co = 2.3 and 3.5. We may conclude that the magnetization of both the phases in the core-shell type structure are correlated due to spin coupling at the interface and one value of blocking temperature is observed [48, 49].

3.3. Photocatalytic degradation of phenolphthalein:

The excellent magnetic and optical properties shown by this nanocomposite has prompted its use as an effective photocatalyst in environmentally safe and cost-effective pollution control which is an important area of research and needs immediate attention. Although there are several approaches for environmental cleanup such as adsorption, reverse-osmosis, chlorination, ozonisation etc, photocatalysis is an environmental friendly process that utilizes the radiation energy to perform catalytic reactions under ambient conditions. This technology has been widely investigated for eradication of pollutants that are present in the environment. Reduction of phenolic (phenolphthalein) compounds to their corresponding derivatives in the presence of UV light irradiation has been chosen as a standard reaction for monitoring the catalytic activity of the nanocomposite. The UV-VIS spectra of phenolphthalein during the UV irradiation are illustrated in figure 12. It can be seen that the maximum absorbance of 227 nm and 277 nm disappears completely after irradiation for about 5 h. A blank experiment in the absence of irradiation but with CoFe₂O₄–Fe₃O₄ MNC with Fe/Co ratios ($x = 3.5$) catalyst demonstrates that no degradation occurs as shown in the spectra. Another blank experiment in the absence of the catalyst but under irradiation shows that phenolphthalein cannot be degraded under the present experimental condition.

The CoFe₂O₄–Fe₃O₄ MNC is a new photocatalyst to degrade organic contaminants, such as phenolphthalein. The photo catalytic degradation percentage of phenolphthalein was calculated using equation (3).

$$ Degradation\% = \frac{A_O - A}{A_O} \times 100\% $$

Where, $A_O$ is the initial absorbance of phenolphthalein before degradation and $A$ is the absorbance after time $t$. It was found that the degradation % of phenolphthalein is 93% in 5 hour of UV irradiation. The observed high degradation may be attributed to (a) high band gap energy (2.57 eV) for the nanocomposite [50], and (b) small particle size (30–40 nm) which is associated with remarkably high surface area (BET surface area = 133.46 m² g⁻¹) as the photocatalysis occurs at the surface of the catalyst. The high photocatalytic activity shown by this nanocomposite can also be explained on the basis of electrical and optical properties of the sample. It is known that CoFe₂O₄ is a p-type semiconductor [51], but it was shown by Na and Lee [52] that Fe excess cobalt ferrite exhibited n-type conduction due to cation redistribution in spinel lattice. As electrons have higher mobility than holes, Fe-excess cobalt ferrite shows higher electrical conductivity [52]. To confirm the high
conductivity of the sample, we have also calculated the Urbach energy ($E_U$) of the sample which characterizes the extent of the exponential tail of the absorption edge \cite{53}. Although, Urbach energy ($E_U$) depend on parameters such as temperature, thermal vibrations in the lattice, induced disorder, static disorder etc, the main factor contributing to edge broadening in our sample is exciton-phonon coupling (dynamic disorder). The urbach energy calculated for our sample ($Fe/Ca = 3.5$) is $E_U \sim 0.84$ eV, which is higher than the Urbach energy of Fe$_3$O$_4$ reported by Ghandoor \textit{et al} \cite{54} and EI-Daisty \textit{et al} \cite{55}. These results suggest that our composite is more conducting than CoFe$_2$O$_4$ or Fe$_3$O$_4$ \cite{54}. Therefore, the photogenerated electrons during UV irradiation of our sample in solution are more efficiently generated and transferred to the surface of the nanoparticle which react with the trapped O$_2$ to produce superoxide radical anions, O$_2^-$, which on further protonation generates OH. These

**Figure 12.** UV-VIS absorption of phenolphthalein in the presence of CoFe$_2$O$_4$-Fe$_3$O$_4$ ($x = 3.5$) under UV irradiation at different time intervals.

**Figure 13.** Recovery of CoFe$_2$O$_4$–Fe$_3$O$_4$ nanoparticle by applying an external magnetic field at the end of the reaction.
'OH radicals is highly reactive to degrade organic molecules and enhances the photocatalytic activity of the sample. The as-prepared CoFe$_2$O$_4$–Fe$_3$O$_4$ MNC with combined the catalytic and magnetic properties could be isolated from the reaction mixture easily by an exterior magnet (figure 13) at the end of the reaction and successfully recycled.

3.4. Induction heating studies

The plot of self heating capabilities of the nanocomposite with Fe/Co ratio at 3.5 as a function of time is presented in the figure 14 (Field amplitude H = 8.98 kAm$^{-1}$ and constant frequency f = 337 kHz). We have chosen the field amplitude and frequency within the biological safety limit as suggested by Hergt [56]. However, in other systems (2.5 and 2.75) could not reach the hyperthermic temperature and therefore not shown here. Heating profile conclusively shows that the nanocomposite with ratio 3.5 and optimum concentration 2 mg ml$^{-1}$ attain the hyperthermic threshold temperature limit. The possible reason to act as a nano-heater of the nanocomposite with Fe/Co ratio 3.5 is due to the higher magnetization and coercivity compared to other nanocomposites. To analyze the hyperthermia efficiency of the nanocomposite, a well-known parameter, Specific Absorption Rate (SAR) has been calculated by using initial slope method [57] and is depicted in the figure 15. As can be seen, the SAR value decreases with particle concentration. Probably, the dipolar energy exert a disordering random torque-disrupting spin relaxation process due to competition between the interparticle interaction and interparticle anisotropy and hence SAR value decreases [38].
4. Conclusion

In conclusion, we have synthesized CoFe$_2$O$_4$–Fe$_3$O$_4$ nanocomposites using a combined sonochemical and reverse co-precipitation technique. A two-phase core-shell structure of CoFe$_2$O$_4$ and Fe$_3$O$_4$ was formed after annealing the asprepared sample at 500 °C which showed excellent magnetic and optical properties. Our approach suggests that this method can be used for the controlled synthesis of core-shell CoFe$_2$O$_4$–Fe$_3$O$_4$ nanocomposites using off-stoichiometric ratios of Co and Fe which may find potential application in the field of permanent magnet with excellent optical properties. The core–shell NPs also showed good magnetic recoverable photo-catalytic activity towards reduction of phenolphthalein under UV light irradiation and was magnetically recoverable and reusable. Also, the nanocomposite was demonstrated to be an efficient nano heater for hyperthermia application with moderate SAR value.

Acknowledgments

Financial support from DST (India) for TEM facility at CIF, IIT Guwahati (Grant No. SR/SS/NM-01/2005) is gratefully acknowledged. The authors would also like to acknowledge the support from IIT Guwahati and NIT Nagaland for the analytical facilities during the course of investigations.

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