Original Article

Tuning hyperthermia efficiency of MnFe₂O₄/ZnS nanocomposites by controlled ZnS concentration

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Magneto-fluorescence MnFe₂O₄/ZnS nanocomposite with varying ZnS concentration were successfully synthesized by co-precipitation method. Its structural, morphological, optical and magnetic properties are comprehensively characterized by XRD, HRTEM, FTIR, UV-Vis, Photoluminescence (PL) spectroscopy and VSM techniques. XRD Results indicate that the prepared nanocomposite comprises of cubic Spinel structure of MnFe₂O₄ and cubic zinc blende structure of ZnS. FTIR analysis exhibits conjugation of ZnS with surface of MnFe₂O₄ nanoparticles through surfactant PEG. The photoluminescence study shows the shifting of emission peaks due to strong quantum confinement effect and the absorption spectra show the trend of increasing band gap with increasing concentration of ZnS. Room temperature magnetic study shows that the saturation magnetization increases with increasing ZnS concentration. The prepared nanocomposite investigated for hyperthermia application at different concentration of ZnS. The result infer that the nanocomposite is a promising material for hyperthermia and also heating efficiency can be tuned by changing the ZnS concentration in the MnFe₂O₄/ZnS nanocomposite.

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1. Introduction

Opto-magnetic nanocomposites have drawn attention from the research community because of their multifunctional properties and broad range of application in military [1,2], catalysis [3–8], devices [9–15] and others [16–22]. Recently magnetic fluorescence nanocomposites considered as one of the most promising therapeutic agent due to its exciting magnetic and optical properties and their potential range of photocatalysis and biomedical application such as targeted drug delivery [23], magnetic resonance imaging [24], diagnosis [25], tissue engineering [26], mediator to convert electromagnetic energy into heat energy, when expose to A.C magnetic field [27–30]. Spinel Metal ferrite (MFe₂O₄ where M = Mn, Ni, Co, Zn etc) nanoparticles are superior for hyperthermia owing to their tunability, biocompatibility, chemical stability [31]. Among the ferrites, MnFe₂O₄ is a decent candidate which has been widely used as MRI contrast agent, targeted drug delivery and magnetic hyperthermia agent [32–34]. MnFe₂O₄ nanoparticles shows mixed spinel structure due to their Mn³⁺ and Fe³⁺ ions distribution over tetrahedral A site and octahedral...
2.1. precipitation

Fe band
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the
sample.
Table
MnFe
3+

Sample name | Crystallite size of MnFe₂O₄ from W-H plot (nm) | Crystallite size of ZnS from W-H plot (nm) | Lattice constant of MnFe₂O₄ Nelson Riley plot (Å) | Lattice constant of ZnS Nelson Riley plot (Å)
---|---|---|---|---
MnFe₂O₄ | 9.53 ± 0.002 | – | 8.51 | –
MnFe₂O₄/PEG | 41.2 ± 0.001 | – | 8.509 | –
MnFe₂O₄/ZnS (1%) | 6.00 ± 0.006 | 6.6 ± 0.010 | 8.509 | 5.344
MnFe₂O₄/ZnS (3%) | 6.87 ± 0.010 | 4.1 ± 0.001 | 8.509 | 5.343
MnFe₂O₄/ZnS (5%) | 8.55 ± 0.016 | 3.74 ± 0.002 | 8.509 | 5.343

B site (Mn²⁺ Fe³⁺)₈ (Mn²⁺ Fe³⁺)₈O₄. This cation distribution leads exchange interaction between two sites which increase the saturation magnetization of MnFe₂O₄ nanoparticles. Due to fascinating size dependent electronic and optical properties, II-VI semiconductor structures have attracted increasing attention [35,36]. Among this semiconductor group ZnS (direct band gap 3.68 eV) is an excellent contestant due to its significant optical properties like high photo stability, active size dependent physio-chemical properties, cell imaging, tuneable and narrow emission spectra motivated worldwide enthu- siasms of scientists [37–39].

Several groups have investigated various types of magnetic luminescence nanocomposites adopting different methods to analyse its optical and magnetic properties. He et al. [40] reported lanthanide doped nanoparticles to prepare Fe₃O₄@LaF₃:Ce:Tb opto-magnetic nanoparticles. Acharya et al. [41] succeeded to visualise recognition of targeted cancer cells by a multifunctional magneto-fluorescent nanocomposites. Cui et al. [42] develop a fluorescent magnetic nanoprobe for vivo targeted imaging and hyperthermia therapy of prostate cancer and showed highly selective targeting, fluorescent imaging and magnetic resonance imaging of the prostate cancer cells and solid tumours under vitro alternating magnetic field irradiation.

Here in our work, we synthesis a MnFe₂O₄/ZnS mag- netic fluorescence bi-functional nanocomposites by co-precipitation method, considering MnFe₂O₄ as a core and its surface is functionalised by organic polymer PEG and ZnS used as a shell. We have investigated structural, morphological, optical and magnetic properties of the nanocomposites. In this work we have reported the moderate hyperthermic efficiency of the nanocomposite and also study the effect of the concentration of ZnS in the nanocomposite to optimized heating efficiency.

2. Experimental studies

2.1. Synthesis of MnFe₂O₄ nanoparticles

MnFe₂O₄ magnetic nanoparticles were synthesis by a simple
co-precipitation technique using hydrolysis of Mn²⁺ and Fe³⁺ salts of molar ratio 1:2. The aqueous solution of precursor materials MnCl₂, 4H₂O and 2FeCl₃ were prepared at room temperature. A NaOH solution of 2.0 M was added drop-wise to Mn²⁺ and Fe³⁺ mixture under continuous stirring till the pH level of the solution reached 7–8. After this, the prepared solution was stirred for 30 min at 100 °C. The obtained black coloured solution then sonicate for half an hour at 50 °C and then cooled the solution up to room temperature. The black precipitate solution were vacuum pumped and the obtained precipitate washed 5 times by de-ionised water, then dried for 8 h at 100 °C. The solid product reduce to powder. The obtained powder again heated at 200 °C for 4 h.

2.2. Synthesis of ZnS nanoparticles

ZnS nanoparticles were synthesised by co-precipitation method where Zinc acetate [Zn(CH₃COO)₂] of 0.2 M and sodium sulphide [Na₂S·9H₂O] of 0.2 M were taken separately, then dissolved in 50 ml of de-ionised water and stirred for 30 min. With the Zinc acetate solution, the sodium sulphide solution was added drop wise under stirring at 70 °C until the pH value of the solution reached up to 7–8. The solution then cooled to room temperature. The obtained white precipitate washed several times by de-ionised water and then dried at 80 °C for 6 h. As prepared MnFe₂O₄ nanoparticles and PEG₄₀₀₀ were mixed separately in 25 ml of de-ionised water at stoichiometric ratio and then satired both the solution for 20 min. The mixed solutions stirred at 50 °C for 30 min. The solution then sonicate for 90 min at 50 °C and cooled it. The black coloured solution centrifuged at 3000 r.p.m for 15 min and the obtained black precipitate washed 4 times then dried at 60 °C for 12 h. The acquired solid product grinds to powder.

2.3. Synthesis of MnFe₂O₄@ZnS 1%, 3% and 5%

MnFe₂O₄/PEG and ZnS at the wt. percentage of 1% of MnFe₂O₄/PEG are dissolving separately in 25 ml of de-ionised water. After mixing both the solution satired continuously for
Fig. 2 – HRTEM image of MnFe$_2$O$_4$/ZnS nanocomposite with (a) 1% ZnS and the inset shows its SAED patterns (b) Enlarge view of 1% nanocomposites (c) 3% ZnS and the inset shows its SAED patterns (d) d-spacing of (111) plane of ZnS and (311) plane of MnFe$_2$O$_4$ in nanocomposites.

Fig. 3 – EDAX spectrum of nanocomposites with 3% ZnS and the inset shows the weight % of different elements in the nanocomposites.

Table 2 – The observed value of coercivity ($H_c$), saturation Magnetization ($M_s$) and Remanence ($M_r$) of MnFe$_2$O$_4$ with ZnS 1%, 3% and 5% in the nanocomposites.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Coercivity ($H_c$) (G)</th>
<th>Saturation Magnetization ($M_s$) (emu/g)</th>
<th>Remanence ($M_r$) (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>122.65</td>
<td>0.311</td>
<td>$0.80 \times 10^{-2}$</td>
</tr>
<tr>
<td>(ZnS) 1%</td>
<td>130.12</td>
<td>0.347</td>
<td>$0.85 \times 10^{-2}$</td>
</tr>
<tr>
<td>(ZnS) 3%</td>
<td>89.66</td>
<td>0.424</td>
<td>$0.80 \times 10^{-2}$</td>
</tr>
<tr>
<td>(ZnS) 5%</td>
<td>150.49</td>
<td>0.409</td>
<td>$1.14 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
half an hour at 50 ° and the resulting solution sonicate for 90 min at 50 °. The obtained precipitate centrifuge at the rate of 2000 r.p.m for 10 min and then washed 5 times by de-ionised water. The acquired black precipitate dried at 60 ° for 12 h and then grinds to powder. Similarly the sample for ZnS 3% and 5% also prepared.

Fig. 4 – FTIR spectra of MnFe₂O₄, MnFe₂O₄/PEG nanocomposites at different concentration of ZnS (1%, 3%, 5%).

Fig. 5 – Gaussian fitting PL spectra of (a) pure ZnS (b) 1% (ZnS) (c) 3% (ZnS) (d) 5% (ZnS) of MnFe₂O₄ nanocomposites.
3. Characterization

A powder X-ray diffractometer (Rigaku, RINT 2500 TRAX-III) using CuKα radiation (wavelength $\lambda = 1.5406 \text{Å}$) was used to take the XRD spectra of the samples to identify the phase. The morphology of the materials was studied by a high resolution transmission electron microscope (HRTEM) of (JEOL Model: JEM 2100). To observed the vibrational spectra of synthesised materials A Cary 630 Fourier transform infrared (FT-IR) (Agilent Technology) was used. The recorded Photoluminescence (PL) spectra of the samples were examined by fluorescence spectrometer [Thermospectronic AMINCO Bowman (series 2)]. A double beam spectrometer (HITACHI-U3210) in the range of 200–800 nm was used to record the absorption spectra of all the samples at a resolution of 0.1 nm wavelength. The magnetic parameters were studied by Vibrating Sample Magnetometer (VSM) (Model: 7410 series).

3.1. Induction heating

The Easy Heat 8310, Ambrell make, UK with a coil diameter of 8 turns was used to study the induction heating efficiency of pure MnFe$_2$O$_4$ and MnFe$_2$O$_4$/ZnS nanocomposites at different weight percentage. The 2 mg mass of each sample was suspended in 1 ml of distilled water, were sonicated for 15 min for suitable suspension, and then placed at the centre of the water cooled induction coil. The frequency of A.C magnetic field was fixed at 336 kHz and the current were kept constant.
Fig. 8 - (a) Induction heating curves of MnFe$_2$O$_4$ with concentration (2, 4, 6 and 8 mg/ml)(b) 1% (ZnS) with concentration (2, 6, 8 and 10) mg/ml (c) 3% (ZnS) with concentration (2, 4, 6, 8 and 10) mg/ml (d) 5% (ZnS) with concentration (2, 4, 6, 8 and 10) mg/ml at frequency 336 kHz, current 250 A and field amplitude H = 161G.

at two different values 250 Å and 350 Å. The magnetic field was evaluated from the relation

$$H = \frac{N I a^2}{23 \sqrt{z^2 + a^2}}$$

(1)

where N is the number of turns of the induction coil, z is the distance from the centre of the coil on z-axis, ‘a’ is the radius of the coil and I is the current.

4. Results and discussion

4.1. Structural and morphological studies

XRD patterns of MnFe$_2$O$_4$/ZnS nanocomposites at different weight percentage of ZnS (1%, 3%, 5%) are displayed in Fig. 1. All the samples shows the diffraction peaks corresponding to the lattice planes (311),(331),(511),(440) and (531), which match well with the standard JCPDS (card no.73–1964) and confirms the single phase cubic spinel structure of MnFe$_2$O$_4$. The diffraction peaks be in tune with the lattice planes (111) and (311) for the samples signify, cubic zinc blende ZnS structure JCPDS (card no.80–0020). The signature of cubic spinel structure of MnFe$_2$O$_4$ and cubic zinc blende structure of ZnS for the synthesised samples were confirms from the diffractograms. Again, MnO impurity peaks accord with the lattice plane (200) has appeared in all the spectra. The existence of impurities in the precursor material may be the possible cause for the MnO peak in the nanocomposites.

The average crystalline size and the micro strain of the samples were further calculated from Williamson–Hall (W–H) equation [43].

$$\beta \cos \theta = \frac{k \lambda}{D} + 4 \varepsilon \sin \theta$$

(2)

where \(\beta\) is the FWHM of diffraction peak, \(\theta\) is the diffraction angle, D is the average crystalline size and \(\varepsilon\) is the effective micro strain.

Table 1 shows that the crystallite size of MnFe$_2$O$_4$ nanoparticles increases from 9.53 nm to 41.2 nm after surface modification of the nanoparticles by PEG. It has been reported that the increase of crystallite size due to the more binding affinity of the organic molecules of the surfactant to the surface of nanoparticles which provides stability of the nanoparticles for further growing of crystals. The organic molecules produce a steric effect at the interface of the nanoparticles which disturbed the effective particle to particle contact and reduce the Brownian motion of the nanoparticles [44]. On the other hand crystallite size of the MnFe$_2$O$_4$ nanoparticles in MnFe$_2$O$_4$/ZnS nanocomposite decreases after incorporation of ZnS which can be ascribed as the change of morphology of synthesized nanoparticles were found to converges from irregular shaped nanoparticles to the regu-
lar nanospheres which is consistent with the result acquired by Kavas et al. [45]. As the weight percentage of the ZnS in the nanocomposites increases crystallite size of the MnFe₂O₄ nanoparticles further increases in the nanocomposites, which can be attributed to the large nucleation growth of ZnS nanoparticles on various sites of the core MnFe₂O₄ nanoparticles and multiple interfacial strain also may be the possible cause of increase of the crystallite size. On the other way crystallite size of ZnS decreases due to occurrence of large deformation of the periodic lattice of ZnS crystals, when Zn²⁺ ions of ionic radius (0.74 Å) replaced by Mn²⁺ ions of ionic radius (0.80 Å) induce lattice strain takes place in ZnS lattice [46].

The HRTEM images of 1% and 3% nanocomposites as shown in the Fig. 2 MnFe₂O₄ and ZnS nanoparticles are almost quasi spherical in shape and the average size of the MnFe₂O₄ nanoparticles are almost 6–6.5 nm whereas ZnS nanoparticles are ranges from 4.8 to 5.4 nm. The SAED pattern of 1% and 3% of ZnS in MnFe₂O₄ nanocomposites are viewed in Fig. 2(a) and 2(c) corresponds to the reflections from the crystal planes (311), (222), (440), (311) of MnFe₂O₄ and (111), (311) of cubic zinc blend structure which is match with diffraction planes indexed from the XRD diffractogram. Fig. 2(d) shows the d-spacing of (311) planes of MnFe₂O₄ and (111) planes of ZnS. The EDAX spectrum of sample 3% as shown in Fig. 3 illustrates the stoichiometric ratios of the nanoparticles in the nanocomposites. The inset shows the weight % of different elements in the nanocomposites.

4.2. FTIR analysis

The FTIR spectra of uncoated MnFe₂O₄, MnFe₂O₄/PEG, MnFe₂O₄/ ZnS @1%, 3% and 5% nanocomposites as shown in Fig. 4. The absorbance peak at 2118 cm⁻¹ assigned to C–H bending from PEG.

The broad peak 3330 cm⁻¹ due to the –OH group vibrations specify the absorption of water molecules in the surface of nanoparticles [47]. The bands stretching mode at the centered on 1186 cm⁻¹ arising from C–O, C–O–C stretches of MnFe₂O₄ nanoparticles in PEG [48]. The absorption peak at 821 attributed to C–H bending vibration and C–O stretching in PEG. The peak at 1100 cm⁻¹ signifies the characteristic stretching vibration of C–O–C from PEG and characteristic bands of SO₄²⁻ which indicate the hydrophilic group (SO₄⁻) of ZnS interact with the surface of MnFe₂O₄ nanoparticles due to the interaction of the vibrating sulphide ions, Rema Devi et al. [49] and Kuppayu et al. [50] also reported the same result. The FTIR spectra confirms the coating of PEG on the surface of MnFe₂O₄ nanoparticles and the incorporation of ZnS on the surface MnFe₂O₄ nanoparticles through surfactant PEG and form the MnFe₂O₄/ZnS nanocomposites.

Fig. 9 – (a) Induction heating curves of MnFe₂O₄ with concentration (2, 4, 6 and 8) mg/ml (b) 1% (ZnS) with concentration (2, 6, 8 and 10) mg/ml (c) 3% (ZnS) with concentration (2, 4, 6, 8 and 10) mg/ml (d) 5% (ZnS) with concentration (2, 4, 6, 8 and 10) mg/ml at frequency 336 kHz, current 350 A and field amplitude H = 262 G.
4.3. Photoluminescence study

Photoluminescence spectra of pristine ZnS and MnFe$_2$O$_4$/PEG@ZnS 1%, 3% and 5% nanocomposites at room temperature under excitation wavelength 260 nm as shown in the Fig. 5. The de-convoluted emission peaks centred 303, 351 and 360 nm for pure ZnS as shown in Fig. 5(a). The emission peak at 303 nm due to band to band transition of electrons in ZnS crystals almost remain at the same peak position in all samples.

The peaks at 351 nm attributed to the characteristics defect level (sulphur vacancy) emission of ZnS which is shifted to 343 and 348 nm (blue shift), when the amount of ZnS in the sample increases [51]. This shifting of peak towards lower wavelength region signifies the quantum size effect of ZnS nanoparticles due to decreasing of crystallite size which is consistent with our XRD result. In addition, the emission peak at 360 nm of pristine ZnS nanoparticles shifted higher wavelength region in the sample 3% and 5% when the concentration of ZnS increases, is the signature of recombination of electrons with holes in trap state arises by zinc vacancies in ZnS [46].

4.4. Optical absorption spectra analysis

The UV-Vis spectra of ZnS nanoparticles for different concentrations in MnFe$_2$O$_4$/PEG nanocomposites are illustrated in Fig. 6.

The absorption peak of ZnS nanoparticles observed within the range of 220 nm to 320 nm for all the samples. The direct band gap energy of ZnS QD was approximated from Tauc plot using the relation [52]

$$\text{Ahv} = A(h\nu-E_g)^n$$

where $\alpha$ represents the absorption coefficient, $\alpha = \frac{4 \pi k/\lambda}$ (k is the absorption index), $h\nu$ is the photon energy, A is a constant, $\lambda$ is the wavelength, and $n=2$ for the allowed direct band gap ($E_g$). The inset depicts that there is an increasing trend of direct band gap value of ZnS nanoparticles are 3.91, 4.06 and 4.10 eV, respectively, with increasing concentration of ZnS. The increase of band gap reveals the quantum confinement effect owing to decreasing of crystallite size of ZnS nanoparticles, which is a reasonable agreement with XRD analysis.

The change of band gap can be used to estimate the crystallite size ($d$) using the effective mass approximation by Brus equation, given by [53].

$$\Delta E_g = E_g(\text{nanoparticles}) - E_g(\text{bulk}) \left[ \frac{\hbar^2 \pi^2}{2m^* \lambda^2} \right] = \left[ \frac{1.8 \pi^2}{3} \right]$$

where $\mu$ is reduced electron-hole effective mass, $m^*_e$ and $m^*_h$ are the effective masses of electron and holes in ZnS, respectively ($m^*_e = 0.34m_e$ and $m^*_h = 0.23m_h$, where $m_e = 9.11 \times 10^{-19}$ kg is the free electron mass). The size of the ZnS nanoparti-

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Fig. 10 – Histogram of SAR values of sample (a) MnFe$_2$O$_4$ (b) 1% (c) 3% and (d) 5% of ZnS in nanocomposites at frequency 336 kHz, current 250 A and field amplitude 161G.
Magnetic properties of both bare MnFe₂O₄ and MnFe₂O₄/PEG with different concentration of ZnS at room temperature are shown in the Fig. 7. The magnetic parameters for all samples are listed in Table 2. The value of saturation magnetization of pure MnFe₂O₄ recorded as 0.311 emu/g which is lower than bulk MnFe₂O₄ (80 emu/g). The cause of lower magnetic saturation can be ascribed to large spin disorder of surface nanoparticles as well as surface effect of the nanoparticles [54]. It is also found that the maximum value of saturation magnetization (Ms) is 0.424 (emu/g) recorded for the sample 3%, higher than the pure MnFe₂O₄ nanoparticle. The saturation magnetization (Ms) of the nanoparticles increases as the quantity of ZnS increases. In spinel ferrite, tetrahedral sites are antiferromagnetically coupled with the octahedral sites. As the concentration of ZnS in the nanocomposites increases, an enormous amount of nonmagnetic Zn²⁺ ions of ionic radius 0.74 Å in the MnFe₂O₄/PEG/ZnS nanocomposites take over the tetrahedral site (A) of the MnFe₂O₄ nanoparticles and force the Fe³⁺ ions of ionic radius 0.60 Å to migrate from tetrahedral site to octahedral site. Thus, the magnetization of the octahedral site (B) increases than the tetrahedral site (A). Hence, the net saturation magnetization of the nanocomposites increases than the uncoated MnFe₂O₄ nanoparticles [55,56].

4.5. **Magnetic analysis**

The heat generation by the magnetic nanoparticles in A.C magnetic field for hyperthermia application can be analysed as the variation of temperature as a function of time measured. The temperature variation curves with time for the samples MnFe₂O₄, MnFe₂O₄@ZnS 1%, 3% and 5% for different concentrations (2 mg/ml, 4 mg/ml, 6 mg/ml, 8 mg/ml and 10 mg/ml) in presence of AC magnetic field at frequency 336 kHz for current 250A at an amplitude of H = 161 G as shown in the Fig. 8.

The temperature variation with time for each sample was observed for 30 min. The above graphs demonstrate that the maximum saturation temperature attain by the samples increases as the concentration increases. The maximum temperature 45 °C attain by the sample 3% of concentration 4 mg/ml, 6 mg/ml and 10 mg/ml as shown in the Fig. 8(c) which is very close to the hyperthermic threshold temperature 45.67 °C [57]. We set the safety limit as CS=Hf=6 × 10⁹ Am⁻¹s⁻¹ for all the samples in this experiments as suggested by Hergt et al. [58]. In most of the samples other than 3% with different concentration could not reach up to the threshold temperature for effective hyperthermia therapy. We observed little fluctuations in the heating curves of some samples, which...
Fig. 12 – Histogram of SAR values of sample (a) 1% (c) 3% and (d) 5% of ZnS in nanocomposites at frequency 336 kHz, current 350 A and field amplitude 262G.

may be occurred owing to the aberrant particles size distribution and the decreases of magnetic moments of each MnFe₂O₄ nanoparticles because of increasing time span in AC magnetic field with raising ambient temperature. Similar result also observed by seongate Bae et al. [59] for NiFe₂O₄ nanoparticles.

Fig. 9 illustrates the induction heating curves of pure MnFe₂O₄ and MnFe₂O₄/S/ZnS nanocomposites having different concentration of ZnS in presence of AC magnetic field at frequency 336 kHz with amplitude H = 226 G for the current of I = 350 A. In this analysis we observed that the heating curves for most of the samples reach the maximum saturation temperature of 45 °C. When the amplitude of the AC magnetic field increases, the magnetization of nanoparticles also increases linearly according to the linear response theory (LRT) hence the power dissipation of the nanoparticles also increases [60]. In addition, the power dissipation by the nanoparticles is also depends on their size. Since the Neel and Brownian relaxation losses governed by the size of the magnetic nanoparticles, which may directly affects, the heat dissipation power of the nanoparticles.

The heating efficiency of magnetic nanoparticles can be represented by specific loss power (SLP) or specific absorption rate (SAR). The SAR is measured from the initial slope of the temperature variation curve using the following equation [61].

\[
SAR = C \frac{dT}{dt} \left( \frac{m_a}{m_m} \right)
\]

where C is the volumetric specific heat capacity of the solvent, \( \frac{dT}{dt} \) is the initial slope of the temperature variation curve with time, \( m_a \) is the mass of magnetic materials in the suspension and \( m_m \) is the mass of suspension.

The variation of SAR values with concentration for different samples as shown in the Fig. 10 and Fig. 12 corresponding to the current I = 250A and 350A, respectively. In both the figures, exhibits that as the concentration increases SAR value decreases. The decreases in SAR can be explained by increasing dipole interaction among the nanoparticles. The substantial anisotropic barrier increases with increasing dipole interaction which may be the possible cause for decreasing SAR value of the samples [62]. But interestingly, it is observed that the SAR value increases as the current increases from 250A to 350A. The restraint of the SAR delineation is its dependence with \( H^2 \), which provides direct comparison of reported literature values difficult owing to variations in the applied AC field conditions. For further verification, the intrinsic loss power (ILP) can be calculated whereby the SAR is normalized to the strength of AC field and its frequency [63].

\[
ILP = \frac{SAR}{f} \cdot H^2
\]
AC magnetic field amplitude as shown in the Fig. 11 and in Fig. 13.

### 5. Conclusion

In this study, bi-functional magnetic fluorescence MnFe$_2$O$_4$/ZnS nanocomposites were successfully synthesized via co-precipitation method. The XRD studies exhibit the existence of both MnFe$_2$O$_4$ cubical spinel phase and cubic zinc blende phase of ZnS in the nanocomposites with the average crystallite size of 7.14 nm for MnFe$_2$O$_4$ and that of 4.81 nm for ZnS nanoparticles, respectively, which is relatively smaller than the pristine MnFe$_2$O$_4$ and ZnS nanoparticles. The FTIR spectra demonstrate that the peak at 1100 cm$^{-1}$ represents the incorporation of ZnS on the surface of MnFe$_2$O$_4$ nanoparticles via characteristic stretching vibration of $\text{C-O-C}$ from biocompatible surfactant PEG. The photoluminescence study illustrates the trap level defects (sulphur vacancy) emission in the ZnS nanoparticles shows the blue shift in the nanocomposites due to strong quantum confinement effect. UV-Vis absorption analysis reveal the increasing band gap with increasing concentration of ZnS in the nanocomposites with decreasing crystallite size of ZnS nanoparticles due to quantum size effect. In magnetic analysis MnFe$_2$O$_4$/ZnS nanocomposites shows near superparamagnetic properties with maximum magnetic saturation of 0.424 emu/g which is greater than pure MnFe$_2$O$_4$ nanoparticles. Magnetization increases with increasing ZnS concentration in the nanocomposites owing to the migration of Fe$^{3+}$ ions from tetrahedral site to octahedral site. The induction heating analysis shows that the heating efficiency increase as the concentration of ZnS in nanocomposites increase. The MnFe$_2$O$_4$/ZnS magnetic-fluorescent nanocomposites may provide a rousing possibility in magnetic hyperthermia application for the treatment of cancer.

### Conflicts of interest

The authors declare no conflicts of interest.

### REFERENCES
