Sunlight photocatalytic performance of Mg-doped nickel ferrite synthesized by a green sol-gel route

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Original Article

5. Introduction

Environmental contaminants in water and atmosphere are severe threats to the ecosystem. Only 10–15% of the total organic pollutants produced all over the world remains as waste in the environment. Since synthetic dyes contain complex aromatic structures, they are chemically stable and cannot be biodegraded easily. Managing and processing of these pollutants from contaminated water is critical for the environmental safety. Nanomaterials (NM’s) are considered to be the key element in photocatalytic studies to remove organic pollutants. Metal oxides or sulfides are generally considered to be the most proficient and environmentally friendly photocatalysts due to their meticulous optical, electric and catalytic properties [1].

Recently, magnetically separable nanosized catalysts are widely studied. Among nanocatalysts, nanoferrites with an innate magnetic character are in major demand, increasing elementary and applied research because of their brilliant reactivity, economic and facile recovery mode. These ferrite nanoparticles (NPs) are used in different research fields of catalysis, electronics, photonics, sensors as well as in biomedical sciences [2]. The catalytic activity of ferrite NPs relies on their particle size, surface area, morphology, red-ox
properties of metal ions, the distribution of metal ions among the lattice sites and the doping of guest ions into the ferrite lattice. Bhukal et al. performed the decomposition of the methyl orange dye using Manganese (Mn) substituted cobalt zinc ferrite systems [3]. Sharma et al. prepared magnetic bi-metallic nanosystems (MFe2O4; M = Cu, Zn, Ni and Co) and investigated their heterogeneous Photo-Fenton catalytic activity under the visible light for the decomposition of organic pollutants [4]. The catalytic results proved that the rate of reaction depends upon the nature of dopant metal ions. The superior capability of electron-donating, stability of alkaline-earth metal ions and economic aspects of these materials created interests in the research community. This study demonstrated the MgFe2O4-RGO nanocomposite sample for PL studies in white Light Emitting Diodes (WLED) applications as well as the photoluminescence properties of ferrite NPs [5].

The characteristics and the activity of NiFe2O4 NPs are influenced by the composition and the morphology of the sample which is dependent on the preparation technique adopted. Several techniques were used to synthesize NiFe2O4 NPs including the co-precipitation, the sol-gel technique, the hydrothermal synthesis, the citrate reduction method, the plasma assisted deposition technique, the high energy ball milling, the mechanical alloying, the pulsed wire technique and the microwave assisted processing technique [6]. Of all the existing chemical synthesis techniques, eco-friendly green sol–gel technique is the best method to synthesize NPs with high purity. This method exhibited advantages such as simple preparation, cost effective and gentle chemistry route resulting in ultra-fine and homogeneous powder [7]. By adopting the green modified sol–gel technique, it is possible to stoichiometrically control the growth and produce ultrafine particles with a narrow size distribution, in comparatively lesser time [8]. In order to achieve the green sol-gel route, Aloe vera is used. It acts as a complexing and also as a capping agent. Since there is a possibility of agglomeration of NPs during synthesis, the capping agent is needed. Our previous study had already reported the potential application of Euphorbia tirucalli phyto-mediated route for the synthesis of Eu³⁺ doped Gd₂O₃ NPs and A. vera gel bio-mediated route for the synthesis of Eu doped Y₂O₃ nanostructures [9,10].

Herein, for the first time we reported a novel modified green sol–gel method for the synthesis of pure and NiFe₂O₄: Mg²⁺ NPs. In this work, we not only demonstrate the significantly enhanced photocatalytic activity towards organic pollutants of the NiFe₂O₄: Mg²⁺ (1 mol %) NPs, but also reveal the implication of the photoluminescence property towards white LED applications. The characteristics of prepared samples were studied by transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) images, selective area electron diffraction (SAED), X-ray diffraction (XRD), UV–Vis diffuse reflectance spectroscopy (DRS), and photoluminescence (PL) spectra. This project opens new window to use this simple greener route to synthesize bi-functional NPs in the area of photocatalysis particularly waste water treatment and display applications.

2. Experimental

The chemicals used in this investigation were of analytical grade procured from Merck (≥98%) India. They were utilized as such without any further purification. IC dye and Phenol were purchased from S. D. Fine chemicals, Bombay, India, and also used without any further purification. The A. vera leaves were obtained from Dayananda Sagar College of Engineering, Bengaluru, Karnataka state, India-560078. The fresh Aloe Vera leaves were cleaned using distilled water to remove the mud particles or dirt adhering to them. Then, A. vera plant extracted solution can be prepared from a 3 g section of A. vera leaves which were carefully chopped to obtain the gel, then dissolved in 20 mL of de-ionized water and stirred for 30 min till a clear solution was formed. The obtained clear solution had been used as an A. vera plant extract.

NiFe₂O₄: Mg (1 mol %) NPs were synthesized by the modified sol–gel green route using 5 mL A. vera extract as chelating agent, reducing agent and natural template for the first time. In this modified green sol–gel route, stoichiometric quantities of the nickel nitrate and the ferric nitrate were mixed with a Mn²⁺/Mg²⁺ molar ratio of 2:1 and dissolved in 30 mL of the double distilled water. Then, a solution containing A. vera extract was added dropwise into above mentioned solution, and the calculated amount of Mg dopant in the form of nitrate salt was added. After that the mixture was continuously stirred for 1 h to form a gel at 80 °C. The aq. Ammonia (25%) was further added to maintain the pH at 6. The obtained viscous gel was again heated for drying in an autoclave at 200 °C until the auto ignition starts. Finally, to accomplish NiFe₂O₄: Mg²⁺ (1 mol %) NPs, the obtained samples were calcined at 350 °C for 1 h. The same method could be adopted for the preparation of NiFe₂O₄: Mg²⁺ (5 mol %) and for pure NiFe₂O₄ nanomaterials. The modified green sol-gel route is illustrated in Fig. S1.

At an accelerating voltage of 300 kV, the HRTEM studies were carried out on a Tecnai G2 S- twin high resolution transmission electron microscope to know the internal morphology and crystalline size. In addition, with the help of the SEM, Hitachi-3000, the surface morphology of synthesized samples was observed. The FT-IR was performed in the range of 4000–400 cm⁻¹ using the Perkin Elmer FTIR (Spectrum1000) spectrometer in order to identify the functional groups presented in the sample. The UV–Vis absorption spectrum was recorded using the SL 159 ELICO UV–Visible spectrophotometer. The X-ray powder diffraction patterns were well characterized by means of the Shimadzu Powder X-ray diffractometer at room temperature (Cu-Kα radiation) with nickel filter at a scan rate of 2 min⁻¹. The PL emission spectra for the synthesized NPs were recorded using the Horiba Fluorolog Spectrofluorometer at room temperature.

The synthesized NPs (pure and NiFe₂O₄:Mg²⁺ (1 and 5 mol %)), graphite powder and silicone oil were blended by hand mixing with a mortar and pestle for the preparation of the carbon paste. The resulting paste was then introduced from the bottom of a Teflon tube. The electrical connection was established by inserting a copper wire into the Teflon tube. A fresh electrode surface was generated rapidly by extruding a small plug of the paste with a stainless steel rod and smoothing the resulting surface on wax paper until a smooth shiny glassy surface was observed.

3. Results and discussion

3.1. Crystal structure analysis

Fig. 1a depicts the X-ray diffraction patterns of the NiFe₂O₄ and NiFe₂O₄: Mg²⁺ (1 and 5 mol %) NPs calcined at 350 °C. The XRD peaks of all the samples were identified with the Face Centered Cubic structure (JCPDS card No. 44-1485). In this case, a lattice parameter of a = 8.337 Å was obtained [11]. The diffraction peaks obtained at 30.28, 35.67, 37.22, 43.55, 53.72, 57.53 and 63.05° can be indexed corresponding to the planes (220), (311), (222), (400), (422), (511) and (440) of the cubic spinel lattice respectively. The absence of diffraction lines corresponding to Fe₂O₃, NiO and Mg₂O₃ ions clearly suggests that the phyto extract (Aloe Vera gel) was very efficient to insert the slightly bulky cation into the spinel matrix. For the material doped with Mg²⁺, the diffraction lines attributing to the iron oxide were disappeared. This fact confirms the formation of the pure spinel phase.
The quantitative information concerning the preferential crystal orientation can be obtained from the texture coefficient (Tc), which is defined as in Eq. (1) given by Ilican et al. [12].

\[
Tc(hkl) = \frac{I(hkl)}{\frac{1}{n}\sum I(hkl)} / \frac{I_0(hkl)}{I_0(hkl)} 
\]

[1]

where Tc (hkl) is the texture coefficient, I (hkl) is the XRD intensity, \(n\) is the number of diffraction peaks considered and \(I_0\) (hkl) is the standard intensity of the plane which is taken from JCPDS data.

If Tc (hkl) = 1 for all the considered (hkl) planes, then the particles are randomly oriented crystallites which is similar to the JCPDS references. If the values of Tc (hkl) is greater than 1, it indicates that the abundance of the grain is formed in a given (hkl) direction. If 0 < Tc (hkl) < 1 it indicates that there is a lack of grains in that given direction [13]. This is shown in Table 1. In the present sample the Tc value is less than 1 which clearly indicates the lack of grain in that (hkl) plane direction. The experimental d-values and JCPDS d-values are approximately equal thereby, suggesting the face centered cubic spinel structure.

The relative percentage errors for all the particles which are shown in Table 1 have been evaluated by Eq. (2) and JCPDS standard d-values using the following equation:

\[
\text{Relative percentage error} = \left( \frac{Z_H - Z}{Z} \right) \times 100\%
\]

[2]

where \(Z_H\) is the obtained actual d-value in XRD pattern, \(Z\) is the standard d-value in JCPDS data. The values of 2\(\theta\), d-values, and d % error for the crystalline NiFe\(_2\)O\(_4\) are given in Table 1. The relative percentage error is found to be 6.56, 7.33, 5.31, 4.18, 2.12, 0.46 and 0.15% respectively.

The average crystallite size of NiFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\): Mg\(^{2+}\) (1, 5 mol %) NPs were estimated from Debye-Scherrer formula [14]. The average crystallite size was found to be ~14 nm for undoped sample. For Mg\(^{2+}\) doped samples, it was found to be ranging between 9 and 11 nm. Hence, we can conclude that Aloe Vera extract has played a profound role in controlling the particle size. Further structural parameters such as dislocation density and stacking fault can be calculated by the following equations [15,16].

\[
\delta = \frac{1}{D^2}
\]

[3]

\[
SF = \left[ \frac{2\pi^2}{45 (3\tan\theta)^{1/2}} \right]
\]

[4]

The estimated crystallite size, dislocation density, stacking fault and lattice parameter were determined and tabulated in Table 2.

The doping with Mg\(^{2+}\) cations generates a slight decrease of lattice parameter and interplanar distance values from 8.337 to 8.327  

\[\text{Fig. 1. a) PXRD patterns of NiFe}_2\text{O}_4\text{ and NiFe}_2\text{O}_4\text{: Mg}^{2+}\text{ (1 and 5 mol %) NPs and SEM image of b) pure NiFe}_2\text{O}_4\text{; c) NiFe}_2\text{O}_4\text{: Mg}^{2+}\text{ (1 mol %) and d) NiFe}_2\text{O}_4\text{: Mg}^{2+}\text{ (5 mol %) NPs.} }\]
The smaller ionic radii of Fe\(^{3+}\) therefore, the octahedral strain relaxation takes place, because of the number of iron cations from tetrahedral to octahedral lattices. Tetrahedral sites accompanied by the migration of equivalent nickel cations from octahedral to generates a partial migration of nickel cations from octahedral to expected that the dopant cations to be distributed in the octahedral sites\[19\]. Normally, while doping spinel ferrites, the dopant may replace atoms in both sites, if the ionic radii are adequate. Nevertheless, in the particular case of the Mg\(^{2+}\) (ionic radii = 0.86 Å) doped ferrite, because of the higher ionic radii it is expected that the dopant cations to be distributed in the octahedral sites, which are larger compared to the tetrahedral ones. This fact generates a partial migration of nickel cations from octahedral to tetrahedral sites accompanied by the migration of equivalent number of iron cations from tetrahedral to octahedral lattices. Therefore, the octahedral strain relaxation takes place, because of the smaller ionic radii of Fe\(^{3+}\) (0.645 Å) compared to Ni\(^{2+}\) (0.69 Å) [20]. The variation of lattice parameter and interplanar distances depends on the phase purity.

### 3.2. Morphological studies

Fig. 1b–d illustrates the SEM micrographs of pure NiFe\(_2\)O\(_4\) (b), NiFe\(_2\)O\(_4\): Mg (1 mol %) (c) and NiFe\(_2\)O\(_4\): Mg (5 mol %) (d) NPs respectively. The SEM images show that the particles have irregular porous flake like morphology. The auto combustion of the Aloe Vera gel during drying process would result in such a porous morphology due to the escaping gases. As the gas evades with high pressure, pores are created along with the resulting small particles close to the pores. The crystal flakes of the host matrix are observed in the form of dumped dry leaves on the ground (inset of Fig. 1b). These non-uniform flakes are less dense at the 1 mol % Mg\(^{2+}\) concentration. At 5 mol %, these flakes more porous and assembled in the form of cauliflower and looks like a germ infected Cauliflower (inset Fig. 1d).

The SEM image is often used to qualitatively characterize the pore size of the NPs. The resolution depends on the image size and the observation range. The image size in Fig. 1b is 1280 × 1040 pixels, and the observation range is 200 μm. The numbers of the horizon pixels within the observation range was calculated and divided by 200 μm and then the resolution was determined. In the pure sample, the pore size is varying between 62.2 and 9.28 μm whereas in the 5 mol % doped sample, the size is varying between 0.46 and 8.33 μm.

To provide an insight on the morphology of NPs, TEM, HRTEM and SAED studies were carried out for NiFe\(_2\)O\(_4\): Mg\(^{2+}\) (1 mol %) NPs. Fig. 2 The agglomerated and irregular particles can be clearly observed from the TEM micrographs (Fig. 2a, b). Some particles are bigger (46.50 nm) and some particles are smaller (16.32 nm). The lattice fringes with inter planar spacing of 0.2698 nm corresponding to the (311) plane of the spinel cubic NiFe\(_2\)O\(_4\): Mg\(^{2+}\) NPs are clearly analyzed with the HRTEM image. They signify ultrafine quality cubic nanocrystals (Fig. 2c, d). Moreover, the crystalline structure of the materials, observed from XRD patterns, is confirmed by the fringe pattern. As an example, the fringe pattern observed for NiFe\(_2\)O\(_4\): Mg\(^{2+}\) (1 mol %) NPs is typical for the spinel ferrite system and clearly proves that the particle is single crystalline with no defect according to the related literature. In the SAED pattern the spots were identified as (220), (311), (222), (400), (422), (511) and (440) planes of the cubic arrangement of NiFe\(_2\)O\(_4\): Mg\(^{2+}\) NPs (Fig. 2e). All these observations along with PXRD results verify that Mg\(^{2+}\) ion has been successfully lying into the NiFe\(_2\)O\(_4\) host material.

### 3.3. Functional group analysis

The FTIR pattern of the pure and NiFe\(_2\)O\(_4\): Mg\(^{2+}\) (1 and 5 mol %) NPs are in the range of 400–4000 cm\(^{-1}\) as shown in Fig. 3. Commonly, the infrared spectra of spinel ferrites consists of two strong absorption bands in the range 400–600 cm\(^{-1}\): v1 (~600 cm\(^{-1}\)) is attributed to the stretching vibration of the tetrahedral metal – oxygen bond and v2 (~400 cm\(^{-1}\)) is attributed to the octahedral metal – oxygen bond respectively [11]. Thus, the two major absorption peaks at ~546 and ~417 cm\(^{-1}\) correspond to metal-oxygen bond due to the vibrations in the tetrahedral and the octahedral sites. In addition, the bond observed at ~546 cm\(^{-1}\) can be associated with the vibrations at the tetrahedral site between Ni\(^{2+}\) – O\(^{2-}\) and the bond identified at ~417 cm\(^{-1}\) could be associated with the octahedral group Fe\(^{3+}\) – O\(^{2-}\) vibrations [21]. Further, the absorption peak attributed to carbon-hydrogen bond bending,

| Table 1 | Comparison of X-ray diffraction peak intensities, 2θ, d-values, and d % error of the JCPDS data in comparison with the observed data. |
|----------------|---------------------------------------------------------------|
| XRD peak (hkl) observed | JCPDS | Intensity observed | Intensity observed from JCPDS | D spacing observed (Z0) | D spacing from JCPDS (Z) | Texture Coefficient | Relative percentage error |
| (220) | 30.28 | 31 | 320 | 299 | 3.141 | 2.9476 | 0.1387 | 6.56 |
| (311) | 35.67 | 35 | 1020 | 999 | 2.698 | 2.5117 | 0.1323 | 7.33 |
| (222) | 37.22 | 37 | 85 | 72 | 2.279 | 2.4057 | 0.153 | 5.31 |
| (400) | 43.55 | 43 | 243 | 203 | 1.997 | 2.0842 | 0.155 | 4.18 |
| (422) | 53.72 | 53 | 95 | 80 | 1.738 | 1.7018 | 0.153 | 2.12 |
| (511) | 57.55 | 57 | 262 | 258 | 1.597 | 1.6045 | 0.132 | 0.46 |
| (440) | 63.05 | 63 | 346 | 332 | 1.476 | 1.4738 | 0.135 | 0.15 |

| Table 2 | Estimated crystalline size, other structural parameters of NiFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\): Mg\(^{2+}\) (1 and 5 mol %) NPs. |
|----------------|---------------------------------------------------------------|
| Samples | Interplanar spacing (Å) | Crystallite Size (nm) | Dislocation density (10\(^{15}\) lin m\(^{-2}\)) | Stacking Fault X 10\(^{-3}\) | Lattice parameter (Å) |
| NiFe\(_2\)O\(_4\) | 2.698 | 14 | 5.337 | 0.4466 | 8.337 |
| NiFe\(_2\)O\(_4\): Mg\(^{2+}\) 1 mol % | 2.692 | 18 | 5.385 | 0.4472 | 8.334 |
| NiFe\(_2\)O\(_4\): Mg\(^{2+}\) 5 mol % | 2.688 | 22 | 5.392 | 0.4476 | 8.329 |
O–H bending vibration and (O–H) hydroxyl group were observed and are listed in Table 3.

3.4. Bandgap analysis

The optical behavior of a NP is vital while selecting the NP for an explicit application. So the band gap energy ($E_g$) of NiFe$_2$O$_4$ and NiFe$_2$O$_4$: Mg$^{2+}$ (1 and 5 mol %) NPs were evaluated.

Fig. 2. (a & b) TEM images; (c & d) HRTEM images and (e) SAED analysis of NiFe$_2$O$_4$: Mg$^{2+}$ (1 mol %) NPs.

Fig. S3(a) shows the UV-Vis absorption band investigated NPs. The absorbance varies according to the varying of factors such as particle size, oxygen deficiency, defects in grain structure [22]. Every sample exhibits its particular absorption spectra with an extreme alteration in the visible range of the spectra which are due to the alteration of the band gap in the different composition. The $E_g$ can be calculated using the following equation:
3.5. Photoluminescence and electrochemical studies

Mg2+ of the pure, NiFe2O4:Mg2+ [24]. The values of Eg were found by extending the linear segment of the graph \( \frac{1}{2}, 2, 3/2, 3 \) for the direct acceptable, indirect acceptable, direct prohibited and indirect prohibited transitions correspondingly [24]. The values of Eg were found by extending the linear segment \( \frac{1}{2}, 2, 3/2, 3 \) for the direct acceptable, indirect acceptable, direct prohibited and indirect prohibited transitions correspondingly [24]. The values of Eg were found by extending the linear segment \( \frac{1}{2}, 2, 3/2, 3 \) for the direct acceptable, indirect acceptable, direct prohibited and indirect prohibited transitions correspondingly [24]. The values of Eg were found by extending the linear segment \( \frac{1}{2}, 2, 3/2, 3 \) for the direct acceptable, indirect acceptable, direct prohibited and indirect prohibited transitions correspondingly [24]. The values of Eg were found by extending the linear segment \( \frac{1}{2}, 2, 3/2, 3 \) for the direct acceptable, indirect acceptable, direct prohibited and indirect prohibited transitions correspondingly [24].

It is beneficial to study the PL patterns of the NPs as it helps to explain the phenomenon of the charge migration, exchange and recombination of the photo-induced electron–hole pairs within the NPs. The room temperature photoluminescence emission plots of pure and NiFe2O4: Mg2+ (1 and 5 mol %) NPs are recorded at the excitation wavelength of 329 nm and are shown in Fig. 4a. An emission peak was observed in the visible region between 420 and 630 nm for all samples. The RT PL emission signatures were observed at 423, 450, 530, 590, 610 and 626 nm (Fig. 4b). It was found that there the positions of PL peaks are reserved for all samples whereas their intensities are slightly changed. The Ni2+ (with F2+ ground state) and Fe3+ (with sextet S0 ground position) ions possess the electronic configuration 3d3 and 3d6 respectively. The PL indicates the presence of Ni2+ and Fe3+ in the octahedral and tetrahedral complexes which is assigned based on the Tanabe–Sugano diagrams. The signature indexed at 423 nm in the plot can be attributed to the transitions from 3A2 (3P) \( \rightarrow \) 3T1 (3P) of the Ni2+ ion in the octahedral group [26]. The peaks identified at 456 and 530 nm, however, were ascribed to the transition from \( \frac{3d5}{2} \rightarrow \frac{3d4}{2} \) 4s of Fe3+ ions due to the electron excitation from the localized \( \frac{3d5}{2} \) state of Fe3+ to the 4s orbital of Fe3+ [27]. The wide spectrum from 590 to 620 nm could be attributed to several transitions of Ni2+ and Fe3+ ions. On the other hand, the peaks at 610 and 626 nm corresponds to the transitions from \( \frac{3T1}{2} (3P) \rightarrow \frac{3T1}{2} (3P) \) of Ni2+, in the tetrahedral locations, where all are in the visible luminescence region. The transition of excited optical centers at the depth level may lead to the emission in the visible region. While comparing the intensities of the transition peaks of Ni2+ in the octahedral and tetrahedral locations, it can be concluded that the octahedral transitions are superior in comparison to that of tetrahedral transitions.

The transitions at octahedral sites were due to the static or dynamic defects compared to the standard octahedral alignment. The PL plot demonstrates the occupancy of Ni2+ ions on octahedral and tetrahedral positions, obtaining mixed spinel geometry [28]. The PL emission varies as a function of Mg-doping level and the maximum PL emission has been obtained for 5 mol % Mg and no appreciable emission was observed for doping 1 mol % Mg ion. The visible emissions decrease in the following order: pure NiFe2O4 > NiFe2O4: Mg2+ (5 mol %) > NiFe2O4:Mg2+ (1 mol %). It is observed that the emission of NiFe2O4:Mg2+ (1 mol %) was suppressed compared to other NPs, which can be justified by the inhibition of the recombination of photo-induced electrons and holes in this composition. This ability of the material can be ascribed to the formation of novel electronic bands between the conduction and the valence band attributing to moderate raise in intrinsic faults [29]. This argument was consistent with the band gap analysis. The presence of a large number of oxygen vacancies in NiFe2O4 induces the formation of the energy level in the forbidden gap of the ferrite which lies below the conduction band edge. The most common defects are oxygen vacancies which serve as radiative centers in the luminescence phenomenon. As the ferrite NPs have relatively wide band gap, electrons of the oxygen vacancies easily get excited in the conduction band (CB) rather than from the valence band (VB). Thus, the existence of the peak at 530 nm is ascribed to the point defect levels those are related with oxygen vacancies [30]. The nanoferrites are expected to be effective centers in the luminescence phenomenon.

### Table 3

The wavenumber corresponding to functional groups of NiFe2O4 and NiFe2O4: Mg2+ (1 and 5 mol %) NPs.

| Samples      | Functional Groups | \( v_1 \) (cm\(^{-1}\)) | \( v_2 \) (cm\(^{-1}\)) | Carbon-hydrogen bond (cm\(^{-1}\)) | O–H bending vibration (cm\(^{-1}\)) | (O–H) hydroxylgroup (cm\(^{-1}\)) |
|--------------|-------------------|--------------------------|--------------------------|---------------------------------|-----------------------------------|----------------------------------|
| NiFe2O4      |                   | 542                      | 417                      | 3375                            | 1420                              | 1638                             |
| NiFe2O4:Mg2+ 1 mol% |             | 542                      | 417                      | 3407                            | 1356                              | 1642                             |
| NiFe2O4:Mg2+ 5 mol% |             | 542                      | 417                      | 3399                            | 1363                              | 1646                             |
to the emit longer wavelength that arises from impurity levels and/or various defects within the band gap. Also the band-to-band transitions leads to the intrinsic emission in nanoferrites. Furthermore, the resulted peak at 623 nm may be due to the recombination of the trapped electrons in the oxygen vacancies with the presence of deep holes in the VB (1.79 eV) [31]. It has also been predicted that, for the at 1 mol% composition, the suppressed PL intensity may be due to the dissipation of the light in the form of the absorption by ferrite NPs which is a critical part for the photocatalytic performance.

When Mg$^{2+}$ ions were doped into the pure NiFe$_2$O$_4$ matrix, ions could possibly engage the octahedral and tetrahedral locations. Oxygen vacancies were created to compensate the difference in cation charges. The Mg would possibly occupy the grain boundaries or surface of the host matrix so as to attain the maximum strain relief. The defect reaction can be given by the relation:

$$(1 - x)\text{NiFe}_2\text{O}_4 + 0.5x\text{Mg} \rightarrow x\text{Mg}_{6k} + 0.5x\text{V}_o + (1 - x)\text{Ni}^{2+}_{5Ni}$$

$$+ (2 - 0.5x)\text{O}^{2-}_o$$

where ‘Mg$_6k$’ means Mg residing in the position usually resided by a Ni$^{2+}$ as a result of replacement by Mg. ‘V’$_o$ represents oxygen vacancy, ‘Ni$^{2+}_{5Ni}$’ is the number of remaining nickel in the matrix of NiFe$_2$O$_4$, and ‘O$^{2-}_o$’ represents the oxygen in the matrix of NiFe$_2$O$_4$.

The Commission International De l’Eclairage (CIE) values for NiFe$_2$O$_4$:Mg$^{2+}$ (1 and 5 mol %) phosphors were obtained with respect to Mg$^{2+}$ doping level (Fig. 4c) [32]. The CIE coordinates corresponding to white light of Mg$^{2+}$ ions depend on the higher energy emission concentrations as well as on the asymmetric ratio. It is observed that the CIE co-ordinates for each concentration of Mg$^{2+}$ ions shift the NiFe$_2$O$_4$ phosphor closer to the white region. The correlated color temperature (CCT) can be obtained by Planckian locus, which is a minor part of the (x, y) chromaticity plot representation and several operating points may be present exterior to the Planckian locus. The CCT is used to define the color temperature of the light source when coordinates of a light source fall somewhere away from Planckian locus. The CCT of 4150 K was found by converting the corresponding (x, y) values of the light resource to (U', V') with the help of the mentioned equations and by identifying the color temperature of the nearest point of Planckian locus to the light source on the (U', V') uniform chromaticity diagram (Fig. 4d) [33].

$$U = \frac{4x}{-2x + 12y + 3}$$

$$V = \frac{9y}{-2x + 12y + 3}$$

The calculated CCT values for the NPs were identified to differ from 4135 to 4170. Normally, the correlated color temperature values lesser than 5000 K correspond to the warm white emission which can be applied in commercial lighting lamps and values above 5000 K correspond to the cool white light used in household applications [34]. Moreover, the purity of white light with respect to the color correlated temperature was represented by Mc Camy empirical formula

$$\text{CCT} = -437 n^3 + 3601 n^2 - 6861 n + 5514.31$$

where, $n = (x - x_c)/(y - y_c)$ and chromaticity epicenter is at $x_c = 0.3320$ and $y_c = 0.1858$. So that, it was calculated to be 4215 K.
which is closest to the value 4150 K as obtained by the graph. The calculated CCT values were found to be lesser than 5000 K, signifying that the synthesized phosphors can be utilized well for cool white LED applications.

The electrochemical impedance spectroscopy (EIS) was conducted for the samples under investigation to examine the charge transfer inhibition as well as charge separation efficiency of the photo-induced electrons and holes since the charge separation ability of photo-induced holes and electrons is a critical aspect for the photocatalysis performance [35]. EIS was carried out on pure NiFe$_2$O$_4$ and NiFe$_2$O$_4$:Mg$^{2+}$ (1 and 5 mol %) with an AC bias voltage of 5 mV for the frequency region from 1 Hz to 0.1 MHz. The corresponding obtained spectrums are shown in Fig. 5a (inset Fig. 5a shows the enlarged portion of the spectrum). The EIS were performed with standard three electrode system in 0.1M KNO$_3$ electrolyte. The semicircle portion in the impedance plot indicates higher frequency element and the linear portion indicates a low-frequency element. The semicircle diameter represents the charge transfer resistance ($R_{ct}$) and was found to be 53, 75, 89 Ω for NiFe$_2$O$_4$:Mg$^{2+}$ (1 mol%), NiFe$_2$O$_4$:Mg$^{2+}$ (5 mol%) and NiFe$_2$O$_4$ respectively. The charge transfer resistances ($R_{ct}$) of samples are of the order: NiFe$_2$O$_4$:Mg$^{2+}$ (1 mol %) <NiFe$_2$O$_4$:Mg$^{2+}$ (5 mol%) < pure NiFe$_2$O$_4$. Smaller values of $R_{ct}$ inhibit the charge recombination and improve the photocatalytic performance. Thus, NiFe$_2$O$_4$:Mg$^{2+}$ (1 mol %) with smaller diameter has been anticipated to show improved photo catalytic performance. This result can be well justified by the PL studies where NiFe$_2$O$_4$:Mg$^{2+}$ (1 mol %) had given rise to minor emission spectra relative to various NPs that could be ascribed to a low recombination rate [36]. The impedance curve can be explained by an equivalent Randles circuit that contains solution resistance ($R_s$), capacitance (C), charge transfer resistance ($R_{ct}$), and Warburg impedance (W) [37]. The equivalent circuit for the NiFe$_2$O$_4$:Mg$^{2+}$ (1 mol%) NPs is shown in Fig. 5a. At the higher frequency region, the circuit consists of only resistive effect whereas the lower frequency region it comprises of both capacitive and resistive effect. The circuit consists of resistance and capacitance in parallel acquiring a semicircle at higher frequency region in Nyquist plot whereas Warburg impedance (W) contributes to slant in the line at the lower frequency region.

3.6. Photocatalytic studies

The photocatalysis was experimented on sunny days between 11 am and 2 pm in the month of May at Bangalore, India. The entire method has already been discussed in our previous research article [38]. The test was done by dispersing 40 mg of photocatalyst in 250 ml of 20 ppm IC and phenol solution. This reaction mixture was uniformly mixed using a magnetic stirrer for the entire time span of the experiment. The adsorption/desorption equilibrium can be achieved by stirring the reaction mixture for 30 min before irradiation. The degree of adsorption can be determined from the equation $Q = \frac{(C_0 - C)}{V}$, where $Q$ - amount of adsorption, $C_0$ and $C$ - concentrations after and before adsorption, $V$ - volume of the reaction mixture and $W$ - amount of catalyst present in grams. The unit of $Q$ is ppm ml mg$^{-1}$. Then 5 ml aliquots were obtained at regular time intervals, immediately centrifuged and filtered through 0.45 μm Millipore filter to remove the catalyst particles. This becomes essential for the spectrophotometric analysis and in resolving residual concentration of IC and Phenol. The photocatalytic performance of these catalysts was estimated by using the measurement of absorbance of the aqueous organic pollutant.
solution as a function of the illumination time using an UV–vis spectrophotometer (SHIMADZU, UV-3150). Similar kind of control experiments was carried out with or without catalysts (blank) in dark conditions.

The plot of % D as a function of time and in C/C_0 versus time for the decomposition of hazardous IC dye and Phenol in the presence of pure NiFe_2O_4, NiFe_2O_4: Mg_2^+ (1 and 5 mol %) NPs and commercial P25 for comparison purpose under sunlight for the period of 120 min is shown in Fig. 5b−e respectively. The percentage decomposition either with the presence of photocatalyst in dark or in the absence of photocatalyst (blank) was negligible. The photocatalytic activity of the photocatalysts for the decomposition of organic pollutants can be ranked in the order of: NiFe_2O_4: Mg_2^+ (1 mol %) + H_2O_2 < NiFe_2O_4: Mg_2^+ (1 mol %) < P25 < NiFe_2O_4: Mg_2^+ (5 mol %) < pure NiFe_2O_4 with the rate constant of 58, 40.2, 37.6, 32.4 and 18.6 × 10^{-3} min^{-1} for the decomposition of IC. For the decomposition phenol, it was found to be 43, 38.2, 34.5, 30.3 and 16.9 × 10^{-3} min^{-1} respectively. It can be stated that in the beginning, the photocatalysis performance of NiFe_2O_4 is improved with the addition of the Mg_2^+. and when Mg_2^+ doping content was 5 mol % it gets diminished. The decomposition rate of IC and Phenol in the presence of NiFe_2O_4: Mg_2^+ (1 mol %) was 84.6 and 79.4% respectively and with the addition of H_2O_2 (6 mM for IC and 5 mM for Phenol) it reached up to 99.4 and 94% under sunlight irradiation for 120 min. Fig. 5f represents the spectral absorbance graph for the decomposition of IC dye in attendance of NiFe_2O_4: Mg_2^+ (1 mol %). Fig. 5f inset displays the aliquots containing the IC solution collected in every 30 min.

This study implies that when the energy level is just on top of the valence band, the Mg_2^+ ion within the NiFe_2O_4 matrix can make h^+ as trappers and when the energy level is just below the conduction band it makes h^+ as e^- trappers. The trapping of electrons by Mg_2^+ leads to its reduction to the Mg^+. The e^- trappers are shifted to the O_2 molecule promoting the formation of O_2 and OH^- radicals. Here Fe_3^+ gets oxidized to Fe_3^+, if Fe_3^+ ions were expected to act as hole trap. The hydroxyl radical is formed due to the transportation of trapped holes to OH^- ion on the surface of the catalyst. This phenomenon stimulates the production of efficient oxidative species like O_2 and OH^- radicals.

\[
e^- + Mg_2^{2+} \rightarrow Mg^+ \quad (10)
\]
\[
O_{2ads} + Mg^+ \rightarrow Mg_2^{2+} + O_2^{-} \quad (11)
\]
\[
2H^+ + O_2^- \rightarrow 2OH^* \quad (12)
\]
\[
h^+ + Fe_3^{3+} \rightarrow Fe_3^{4+} \quad (13)
\]
\[
OH^- + Fe_4^{4+} \rightarrow Fe_3^{3+} + OH^* \quad (14)
\]

Also, the addition of Mg_2^{2+} ions at the lattice location of Ni^{3+}/Fe^{3+} raises the defect levels in the lattice structure and which traps the electron/hole pair thereby encouraging the charge transfer. In addition, at higher dopant concentration (5 mol %) trapped hole (Fe^{4+}) and trapped electron (Mg^{2+}) at Ni^{2+}/Fe^{3+} lattice location can also recombine with free electrons and holes to reduce the photocatalytic performance of NiFe_2O_4:Mg_2^{2+}.

\[
h^+ + Fe_2^{2+} \rightarrow Fe_3^{3+} \quad (15)
\]
\[
e^- + Fe_4^{4+} \rightarrow Fe_3^{3+} \quad (16)
\]

\[
h^+ + Ni_2^{2+} \rightarrow Ni_3^{3+} \quad (17)
\]
\[
e^- + Ni_3^{3+} \rightarrow Ni_2^{2+} \quad (18)
\]

Hence, by increasing the concentration of dopant the trap distance could be reduced. The recombination rate K_r is found to be related to the distance between the trap [39].

\[
K_r \approx \exp \left(-\frac{2R}{a_0}\right) \quad (19)
\]

where a_0 = the radius of the hydrogenic wave function of the trapped carriers, r = the distance between traps. As there is a decrease in the average distance between trap sites, the recombination rate was found to enhance exponentially with the concentration of the doping material. Additionally, if the doping concentration goes beyond the optimal concentration, the number of traps gets greater than before and these traps operates as new recombination center of charge carriers. This implies that the excess of the doping concentration has a negative impact on the photocatalytic activity and with the proper doping concentration of Mg_2^{2+} the photocatalysis of catalysts can be enhanced, which is in good agreement with the other experiments.

In general, the Photo-Fenton activity involves a number of possible mechanisms as shown in Fig. 5S(a). When a photon incidents the photocatalyst, electron-hole pairs are generated on the surface. The photo-excited electron reacts with oxygen and holes with the water molecule to generate the superoxide and OH radicals respectively. In this reaction, H_2O is produced as an intermediate compound, which reacts with Fe_3^{3+} (on the surface of photocatalyst) to generate Fenton reagent (Fe_2^{2+}). The Fe_2^{2+}, in its turn, reacts with added H_2O_2 to generate *OH radical. Addition of H_2O_2 drastically enhances the generation of hydroxyl radical for the decomposition process. These radicals participate in weakening of the organic bonds existed in the organic pollutant. The addition of Mg_2^{2+} ions introduces oxygen vacancies, intermediate energy levels in NiFe_2O_4 thereby increasing the charge carrier separation and producing more radicals to take part in the decomposition of the organic pollutant. Due to combined facets of the photocatalysis and Fenton activity, the Mg doped NiFe_2O_4 (1 mol%) is a better photocatalyst than NiFe_2O_4.

The photocatalysis reaction can be summarized as follows,

\[
\text{Photo – excited e}^- + O_2 = *O_2^- \quad (20)
\]
\[
h^+ + H_2O = *OH + H^+ \quad (21)
\]
\[
*O_2^- + H^+ = HO_2^- \quad (22)
\]
\[
HO_2^- + H^+ + \text{Photo – excited e}^- = H_2O_2 \quad (23)
\]
\[
Fe_3^{3+} + H_2O_2 = Fe_2^{2+} + HOO^* + H^+ \quad (24)
\]
\[
Fe_2^{2+} + H_2O_2 = Fe_3^{3+} + OH^* + OH^- \quad (25)
\]

Organic pollutant + *O_2^- + OH^* = Decomposition of organic pollutants \quad (26)

Based on the experimental results, it is obvious that the different content of Mg in NiFe_2O_4 exhibits a major role in the improvement of the photocatalytic process. More Mg_2^{2+} cations were
accommodated by reducing particle size at 1 mol%, which leads to the deterioration of crystallinity as demonstrated by PXRD. Additionally, the dopant ion such as Mg$^{2+}$ with ionic radius (0.72 Å) larger than Ni$^{2+}$ (0.69 Å), but smaller than O$_2$ (1.31 Å) can either isomorphously substituted or interstitially introduced into the matrix of NiFe$_2$O$_4$. It produces oxygen vacancies that accelerate the transition of NiFe$_2$O$_4$. Consequently, the entry of 1 mol% Mg$^{2+}$ in the NiFe$_2$O$_4$ lattices restrains the growth of the particle and accordingly diminishes the band gap values of NiFe$_2$O$_4$ that reduces the recombination of hole and electron during the photocatalytic decomposition of organic pollutants. The morphology studies by SEM and HRTEM indicate the particles are non uniform flakes and less dense with cubic structure, signifying that the (311) planes proficiently housed Mg$^{2+}$ cations. The absorbance change was improved extensively with the Mg dopant concentration. Strong responses to an excitation indicate a large electron population and hence, a restricted recombination of hole-electron. Several transitions of Ni$^{2+}$ and Fe$^{3+}$ as demonstrated by PL could suppress electron–hole recombination. Further, the suppressed PL intensity at 1 mol% Mg may be due to dissipation of light in the form of absorption by NiFe$_2$O$_4$ due to defects inside the band gap which is consistent with the band gap analysis and electrochemical impedance studies. The defects can inhibit the recombination of the electron–hole pairs and eventually enhance the activity. Hence, it can be accomplished that optimum dopant concentration, efficient crystallite size, smaller charge transfer resistance, proficient electron–hole separation and reduced band gap values were responsible factors for the enhanced sunlight driven photocatalysis of NiFe$_2$O$_4$: Mg$^{2+}$ (1 mol %).

3.7. Factors influencing the photocatalytic decomposition

3.7.1. Effect of the catalyst dosage, dye concentration, pH and H$_2$O$_2$ on the decomposition of the recalcitrant pollutants IC and phenol

It was evident that as the amount of NiFe$_2$O$_4$: Mg$^{2+}$ (1 mol %) catalyst was increased, there is an improved photocatalytic decomposition. Based on these experimental outcomes, the decomposition of organic pollutants increased with increase in the catalyst amount. As the photocatalyst dose increases from 20 to 50 mg, the decomposition rate differed [Fig. S4(a, b)]. This result may be attributed to the fact that the higher the number of photons absorbed by NiFe$_2$O$_4$: Mg$^{2+}$ (1 mol %) photocatalysts, the available active sites and the adsorption of organic pollutant get increased. But when the catalyst amount was raised to 50 mg, there was no noticeable increment in the decomposition rate. The turbidity increase in the solution could be the reason behind this result, which reduced the light penetration through the solution and decreased the availability of photocatalyst surface. Therefore, the optimal dosage of NiFe$_2$O$_4$: Mg$^{2+}$ (1 mol %) was determined to be 40 mg.

As shown in Fig. S4(c, d), the decomposition efficiencies for both recalcitrant pollutants were found to strongly depend on the initial dye concentration. Initial concentrations of both recalcitrant pollutants were increased in the range of 10–40 ppm at 40 mg catalyst loadings. At 20 ppm the photodecomposition was high and further decreased. This may be attributed to the fact that as the initial concentration increases, a large number of pollutants were adsorbed on the photocatalyst surface leading to the reduction of OH$^-$ and O$_2$ radicals generation. The number of active sites is less for the adsorption of hydroxyl ions to generate hydroxyl radicals. The other possibility could be demonstrated by using the Beer–Lambert law. In this case, when the concentration of both organic pollutants and solution increases, the photons get interrupted before they reach the catalyst surface. Hence, the absorption of photons by the catalyst decreases, and thereby the decomposition percent gets reduced. These results indicate that the organic pollutant removal is concentration dependent.

The pH value of the aqueous solution is a key parameter in the Photo-Fenton decomposition of pollutants. Fig. S4(e) illustrates the pH effect (range from 2–6) on the IC decomposition, highest decomposition efficiency occurred at pH = 3 and decreased as the pH increases. This is due to the Fenton’s reagent formation at acidic condition to generate *OH which plays a major role to decompose IC. Therefore, the optimum value of pH was adjusted to 3.

As shown in Fig. S4(f), the highest decomposition efficiency for phenol occurred at pH = 3. This was attributed to the fact that, in addition to *OH radicals produced by photo Fenton activity. At lower pH, hydrogen ions react to generate *OH radicals to decompose phenol. In alkaline conditions there was an increase in the concentration of *OH radicals and negatively charged phenolate species. This increase may be due to the greater decomposition of phenol at neutral pH in comparison with alkaline pH. But as the hydroxyl ions are highly concentrated in the solution, Sunlight does not reach the photocatalyst surface and hence reduces the decomposition rate.

3.7.2. Effect of H$_2$O$_2$ in improving and retarding the photocatalysis process

To investigate the effect of H$_2$O$_2$ on photocatalysis for both organic pollutants, experiments were conducted by varying H$_2$O$_2$ dosage from 5 to 20 mM in the presence of NiFe$_2$O$_4$: Mg$^{2+}$ (1 mol %) and sunlight, the results were shown in Fig. S4(g, h). The decomposition rate gradually increased up to 6 mM for IC and thereafter it decreased with increase in the dosage. For the phenol, the decomposition rate increased up to 5 mM and thereafter it decreased with increase in the dosage.

At the optimum dosage of oxidant, H$_2$O$_2$ reacts with NiFe$_2$O$_4$: Mg$^{2+}$ (1 mol %) to produce hydroxyl radicals and thereby enhancing the photocatalytic process for the decomposition of IC and phenol. The decomposition rate of IC and phenol decreases with the addition of excess of oxidant which enhances the hydroxyl radical scavenging, thereby decreasing the reaction rate as well as resulting in the H$_2$O$_2$ wastage [40]. Hence to achieve the highest photocatalytic decomposition of organic pollutants, the concentration of H$_2$O$_2$ was optimized at 6 mM for IC and 5 mM for phenol.

The photocatalyst NiFe$_2$O$_4$: Mg$^{2+}$ (1 mol %) was tested for different types of dyes including Methylene Blue (MB), Malachite Green (MG), Rhodamine B (RB) and Metanil Yellow (MY) under sunlight illumination for about 120 min. The initial concentration of dye was kept constant and the same procedure used for decomposition of IC dye and phenol was adopted for all the dyes. The results were shown in Fig. S5(d), that all the dyes have showed decomposition above 74%, which proves that the synthesized photocatalysts would be potential candidates in waste water treatment.

To examine the stability and efficiency of photocatalyst the NPs were reused for 5 consecutive runs. In each test, the photocatalyst was filtered and washed with ethanol, dried at 70 °C. The irradiation-separating–washing process can be repeated multiple times, while retaining high photocatalytic activity to decompose organic pollutants. No obvious loss of the photocatalytic activity for the decomposition of IC and phenol was observed [Fig. S5(b, c)] respectively. Hence, its use can be greatly supportive in industrial applications for the elimination of organic pollutants from wastewater.

4. Conclusion

The present work demonstrates an eco-friendly, green route based and simple approach for the NiFe$_2$O$_4$ and NiFe$_2$O$_4$: Mg$^{2+}$ (1 &
5 mols% synthesis using the modified green sol-gel method. The structural and morphological behaviors of all samples were carefully investigated with the variation of the Mg-doped concentration. The electrochemical and photoluminescence property were also examined to understand the influential factors on the enhanced photocatalytic activity. The process of decomposition of recalcitrant organic pollutants is found to be optimum in an acidic pH 3. The NiFe2O4: Mg5+ (1 mol %) photocatalyst revealed an excellent photocatalytic activity due to the influence of some parameters like particle size, more oxygen vacancies and narrow energy band gap. This photocatalytic system can be estimated to be competent as a useful sunlight responsive photocatalyst in practical applications. The photocatalyst was found to be stable even after five cyclic runs indicating its high reusability for several practical applications. In addition, the PL emission properties, the estimated CIE chromaticity co-ordinates (x = 0.366, y = 0.341) and the CCT value of 4150 K of the present photocatalyst exhibited its potential to be used for cool white light emitting display applications.

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Appendix A Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jsamd.2018.12.002.

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