Sol–Gel Synthesis of Ce_{4−x}Sr_{1+x}Fe_{5−x}Zn_{x}O_{14+δ} [0 ≤ x ≤ 0.45] Superparamagnetic Oxide Systems and Its Magnetic, Dielectric, and Drug Delivery Properties

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Supporting Information

ABSTRACT: In this work, we have successfully synthesized superparamagnetic nanocomposites, Ce_{4−x}Sr_{1+x}Fe_{5−x}Zn_{x}O_{14+δ} (0 ≤ x ≤ 0.45) (CSFZ) (TA1−TA4: x = 0, 0.15, 0.30, and 0.45) via the Nitrate–citrate sol–gel method. X-ray diffraction studies show the formation of single-phase nanocomposites (NCs) and the average crystallite size is found to be 18 nm. Energy-dispersive X-ray spectroscopy analysis supports the formation of the desired product with the expected composition. The scanning electron microscopy image shows that the prepared samples are in spherical shape and highly porous in nature. Most of the particle sizes present in the image are in the range of 5–20 nm. The optical studies show an intense peak at 583 nm corresponding to the instantaneous existence of both Fe^{3+} and Fe^{3+} intervalence electronic charge transition bands. X-ray photoelectron spectra analysis confirms the presence of elements with their preferred oxidation state. The superparamagnetic nature of the prepared sample was confirmed by vibrating sample magnetometer analysis. Synthesized materials show a low saturate magnetic moment ranging from 0.3400 to 0.1075 emu/g. The coercivity and retentivity value of the synthesized NC is zero. The NCs show high encapsulation efficiency toward ciprofloxacin hydrochloride because of their unique structure and release the loaded drug molecules in a sustained manner up to 10 h at pH 7.4. Such NCs have high potential for use as multifunctional material in various fields such as optical properties, conductivity studies, dielectric, sensor, and drug delivery properties.

1. INTRODUCTION

In the last few decades, the word starts with “nano” have been hurried into the scientific research field such as, nanomaterial, nanocomposites, nanoclusters, nanoparticle, nanocluster, nanoreactor and etc.1−2 The increased interest to research the nano objects corresponds to the innovation of chemical and physical properties of prepared nanomaterials and also relates to their quantum-size effects. Currently, exclusive physical properties of the NCs are under concentrated research. There is a wide difference in the magnetic properties between the bulk material and nanomaterials. Magnetization and the magnetic anisotropy properties of the nanomaterials are always higher than that of bulk molecules, especially at Curie (TC) or Neel (TN) temperatures.3 Including this, nanomaterials possess some other properties such as large magnetoresistance, abnormally high magnetocaloric effect, and so on. Nanoparticle magnetic properties are influenced by chemical composition, particle size, structure, morphology, type, and the degree of the defectiveness in the crystal lattice. By changing the characteristics of the nanoparticle, one can control to an extent the magnetic properties of the material concerned. However, it is difficult to synthesize nanomaterials having the same properties by controlling the reaction alone, and therefore, the nanomaterial shows distinctly different properties. Most of the particles are not similar in size because of their different proportions.

In recent years, there has been increasing emphasis on materials that are applicable in biomedical areas. Biomaterials are synthetic materials used to replace parts of a living system from a biological material. Bioactive materials have specific

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biological responses at the interface of the material with the biological tissue, which results in the formation of a bond between the living part and the material. NC materials with nanoscale separation of phases improve the macroscopic properties of the products. Multilayer NCs which possess magnetic property are used in the storage media. They are either multilayer structures or inorganic/organic composites. Gas phase deposition produces multilayer structures or monolayer self-assembly. In general, organic or inorganic NCs are easily prepared by the sol-gel manner.

Rare-earth elements and their compounds are used for a wide variety of applications in chemistry and materials science. The rare-earth compounds with elements exhibiting several oxidation states find uses as catalysts, laser, and other optical materials that make use of their magnetic properties. Considering the wide variety of applications and potentialities of the rare earth-doped transition metals, it is our desire to understand their structure and physical properties. Cerium oxide-based systems are used in photosensitive glass as a catalyst to polish glass and stone. Also, Fe2O3-containing systems exhibit interesting electrical conductivity. Combining these two interesting properties together in a single platform may yield materials with excellent activities in electrical, conductivity, and magnetic properties. Herein, we report the structure-property relations of CSFZ oxide systems and their drug-releasing behaviors.

2. RESULTS AND DISCUSSION

Four combinations of metal oxide (TA1–TA4) were prepared by a sol–gel procedure. The prepared metal oxides were characterized by various analytical techniques.

2.1. Crystal Structure. Figure 1 shows the X-ray diffraction (XRD) patterns of the samples TA1–TA4. The powder XRD pattern confirms the formation of a single-phase material. The XRD patterns for all the compositions (TA1–TA4) are similar, and the predominant peaks appeared with the same diffraction angle. This indicates that the crystalline phases of all the prepared composites are of similar type. XRD peaks of all the samples produced appreciable diffraction broadening, and it is reasonably assumed that this arises from the crystallite size. The crystallite size (D) of the samples is calculated using the Debye–Scherrer formula (eq 1)

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

where \( K \) is the shape factor, \( \beta \) is the full line width at the half-maximum, and \( \theta \) is the Bragg angle. Crystallites sizes were calculated using the above equation for all intense peaks, and the average crystallite size is found to be in the range of 5–20 nm. The crystallite size (D) and micro strain (\( \varepsilon \)) were also confirmed by the Williamson–Hall plot (uniform deformation model) (Figure S1), and the average crystallite size is calculated by using eq 2.

\[ W–H plot (D + \varepsilon) = \frac{K \lambda}{\beta \cos \theta} + \frac{\beta}{4 \tan \theta} \] 

The average crystallite size is found to be 18 nm. The unit cell parameter is obtained using XRD data by Treor90 software, and the data are given in Table 1.

2.2. Structural and Morphological Studies. Scanning electron microscopy (SEM) images (Figure 2) of the CSFZ composite at 5 \( \mu m \) magnification show that the metal oxides exist as NCs. Furthermore, the SEM image shows that the

| s. no | unit cell | \( a \) (nm) | \( b \) (nm) | \( c \) (nm) | \( \alpha \) | \( \beta \) | \( \gamma \) | unit cell volume (nm\(^3\)) |
|-------|-----------|-------------|-------------|-------------|-----------|-----------|-----------|-----------------|
| TA1   | tetragonal| 6.7402      | 6.7402      | 15.3785     | 90        | 90        | 90        | 698.64          |
| TA2   | tetragonal| 9.3275      | 9.3275      | 6.4239      | 90        | 90        | 90        | 558.90          |
| TA3   | tetragonal| 7.4489      | 7.4489      | 7.9387      | 90        | 90        | 90        | 440.49          |
| TA4   | tetragonal| 7.6486      | 7.6486      | 3.2489      | 90        | 90        | 90        | 190.07          |
prepared samples are in spherical shape and highly porous in nature. However, in some places, the prepared composites have shown the particles with irregular shapes like nanoflakes (TA2 and TA3) and nanoclusters (TA4). Most of the particles present in the image are in the range of 5–20 nm. Also, the average particle size of the CSFZ NC is found to be nearly 9 nm. Because of unavoidable agglomeration that occurred during the synthetic procedure by various methodologies, the prepared materials are not formed with a uniform structure. These different morphological structures and particle sizes of prepared NCs are useful for enhanced activity in electric and magnetic properties.

To confirm the presence of Ce, Sr, Zn, Fe, and O in the prepared NCs, energy-dispersive X-ray spectroscopy (EDX) study is carried out. Figure 3 shows the EDX spectrum of a selected area of the prepared CSFZ NC. From the Figure 3a–d, it is confirmed that the CSFZ contains elements like oxygen, cerium, strontium, iron, and zinc. The absence of any other elements in the EDX spectrum indicates the purity of the CSFZ NC which is prepared by the sol–gel method.

Further, the internal structure of the prepared CSFZ was examined closely by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) analysis. The TEM images of the NC TA2 (as a representative of the synthesized series) at different magnifications are presented in Figure 4. From Figure 4a–c, it is confirmed that the TEM images of the CSFZ NC have shown the spherical structure, and most of the particles have sizes below 10 nm. Also, the TEM images of CSFZ (Figure 4d,e) show a clear two-dimensional lattice fringe image with the interlattice spacing of 0.258 and 0.436 nm which correspond to the crystalline space (102) and (202), respectively. From this, it is confirmed that the prepared NCs have a pure tetragonal phase structure. The selected area electron diffraction pattern (SAED) was recorded, and it appeared as a set of sharp diffraction spots (Figure 4f). The appeared pattern of intermittent bright dots with concentric rings indicates that the material exists in a high crystalline nature with a particle size of below 10 nm which is related to the super paramagnetic nature of the system.

X-ray photoelectron spectra (XPS) analysis is a main tool to determine oxidation states of elements with comparison of their binding energies (BEs). Figure 5a shows the survey spectrum for TA2 of the CSFZ composite, and it proves that the elements iron, zinc, strontium, cerium, and oxygen are present in the synthesized composite. The BEs were confirmed
by the standard carbon 1s peak at a BE of 285.2 eV. Iron appeared in the valence states of Fe$^{3+}$ and the peak positions of 2p$_{3/2}$ and 2p$_{5/2}$ (Figure 5b) spin orbit doublet components of Fe$^{3+}$ appeared in the BEs of 710 and 724.8 eV, respectively.14 Figure 5c shows the XPS spectrum of zinc, and it is present in the oxidation states of Zn$^{2+}$, and the peak positions of 2p$_{1/2}$ and Zn 2p$_{3/2}$ are located at 1045.6 and 1021.4 eV, respectively.10 From Figure 5d, it has been proved that strontium is present in the 3d valance state with the BE of 133.2 and 135.0 eV for 3d$_{5/2}$ and 3d$_{3/2}$, respectively. It is also confirmed that strontium is present in the Sr$^{2+}$ oxidation state.15 BEs at 882.5 and 897.8 eVs (Figure 5e) correspond to the signals of Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$, which confirms that the cerium is present as the Ce$^{3+}$ oxidation state in the synthesized CSFZ composite.24 Two kinds of oxygen species, $\alpha$ and $\beta$, are located at 529.6 and 531.8 eV (Figure 5f).19 The intensity of the peak is related to the concentration of oxygen vacancies. Therefore, the concentration of oxygen vacancies will change the intensity of the prepared components.

2.3. Optical Properties. Figure 6 shows the calculated and the experimental optical absorption spectra of samples TA1−TA4, respectively. An intense absorption peak, which appears at 231 nm may be attributed to the change of charge-transfer transitions. The peak at 582 nm is due to the instantaneous presence of both Fe$^{3+}$ and Fe$^{2+}$ intervalence charge-transfer
The peak at 754 nm is assigned to the transition of \( ^6A_{1g}(S) \) to \( ^4T_{1g}(G) \) and \( ^6A_{1g}(S) \) to \( ^4T_{2g}(G) \) state of the Fe\(^{3+}\) ion.\(^{25}\) The other bands observed at 231, 324, and 348 nm are assigned to the transition from \( ^4f_{1}(2F_{5/2}) \) to \( ^5d_{1}(2D_{3/2}) \) of the Ce\(^{3+}\) ion.\(^{26}\)

2.4. Magnetic Properties. The magnetic properties of the CSFZ NCs are calculated by Langevin eq 3

\[
M = M_s (\text{Coth} - 1), \quad Y = mH/kT
\]

where “\(M_s\)” is the saturation magnetization of NCs, “\(m\)” is the average magnetic moment of the individual nanoparticle in the sample, and \(k\) is the Boltzmann constant.\(^{27}\) Figure 7 shows the magnetization curves obtained for CSFZ NCs. All vibrating sample magnetometer (VSM) curves (Figure 7) showed a hysteresis loop with zero coercivity and retentivity values.

Figure 7. VSM pictures of Ce\(_{1-x}\)Sr\(_{1+x}\)Fe\(_{5-x}\)Zn\(_x\)O\(_{14+d}\) (0 \(\leq x \leq 0.45\)) (TA1–TA4).

Figure 8. TGA−DTA curves of Ce\(_{1-x}\)Sr\(_{1+x}\)Fe\(_{5-x}\)Zn\(_x\)O\(_{14+d}\) (0 \(\leq x \leq 0.45\)).
which exhibit the super paramagnetic behavior to the synthesized CSFZ nanoparticles. On increasing the applied field from $-15\,000$ to $15\,000$ Oe, the magnetization $M$ increases sharply, and it becomes nearly saturated at $10\,000$ Oe. The VSM data also confirm that all the prepared samples have strong magnetic responses to different magnetic fields. The hysteresis loops showed a smooth change of magnetization with the applied field. The VSM curves also showed gradual decreases which are due to the decreasing Fe$^{3+}$ ion concentrations in the prepared samples TA1–TA4. In addition to these magnetic properties of the CSFZ NCs confirmed by VSM analysis, the VSM data show that the magnetic property is dependent on the composition and the particle size of the nanoparticles. As we change the composition and particle size of the nanoparticles, they also change the surface area to ratio volume which in turn influences magnetization. The CSFZ NCs possess saturation magnetization $M_s$ at 0.5534, 0.3491, 0.3400, and 0.1075 emu/g, for TA1, TA2, TA3, and TA4, respectively.

2.5. Thermal Analysis. To know the thermal stability, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are performed on CSFZ NCs (Figure 8). The CSFZ were annealed with the temperature of 50–1050 °C at 10 °C/min under nitrogen atmosphere. Figure 8 shows the TGA and DTA curves of samples TA1–TA4. All the samples showed a similar type of TGA curve, with the total weight loss at 1000 °C being 8.30, 9.60, 10.32, and 11.25% for TA1, TA2, TA3, and TA4, respectively. The first weight loss is observed from ambient temperature to 190 °C, which is associated with the loss of water absorbed in the solid NCs. However, after that point, the TGA curve does not show any appreciable changes in the weight loss up to 1000 °C. From the TGA curves, it is shown that the thermal stability of the samples decreases from TA1 to TA4. In order to understand the thermal transitions which can occur during the heat treatment of the sample, differential scanning calorimetry (DSC) is performed on the synthesized NCs. The DSC curve of the sample is presented in Figure S2. The two endotherm peaks are observed in the ranges of 185–195 and 330–375 °C, which is due to the loss of water which occurs in two steps.

2.6. Infrared, Raman, and Photoluminescence Studies. The Fourier transform infrared (FT-IR) spectrum of the prepared CSFZ nanoparticles is shown in Figure S3. From the IR spectrum, it is confirmed that the peak that appears at 515 cm$^{-1}$ is due to Zn–O and the peak at 445 cm$^{-1}$ is due to Ce–O bond stretching. The weak absorbance at 570 and 415 cm$^{-1}$ is due to the Fe–O and Sr–O bond stretching, respectively. From this IR result, it is evident that the prepared NC is in the form of corresponding metal oxides. The Raman spectrum of the CSFZ NC is shown in Figure S4. The spectrum consists of a strong band at 465 cm$^{-1}$ which corresponds to the Fe$^{3+}$ vibrational mode of the Ce–O$_2$ bond. In the case of Fe$_2$O$_3$, totally, seven modes ($\Gamma = 2A_{1g} + 5E_g$) of vibrations are expected, 225 and 498 cm$^{-1}$ band due to $2A_{1g}$ mode, band at 247, 293, 299, 412, and 613 cm$^{-1}$ due to $E_g$ modes of vibration, but the $1A_{1g}$ mode of vibration observed in the region of 223–225 cm$^{-1}$ and $1E_g$ mode of vibration observed in the region of 610–614 cm$^{-1}$. For Zn–O, totally eight modes of vibration ($\Gamma = 2A_{1g} + 2B_1 + 2E_1 + 2E_2$) are possible; from this, six remain active ($2A_{1g} + 2E_1 + 2E_2$) and $2B_1$ is Raman inactive. The additional weak peak is observed because of $A_{1g} + E_g + T_{2g}$ vibration modes of SrO. The sharp band 620 cm$^{-1}$ is due to the $A_{1g}$ mode of SrO vibration, and very weak band 707 cm$^{-1}$ (TO + LO) is due to $E_{2g}^{\text{low}} + E_{2g}^{\text{high}}$ modes of SrO. $T_{2g}$ modes are not observed because of the very low intensity. The intensity of the peak at 465 cm$^{-1}$ in the Raman spectrum decreases with the decrease in the concentration of Ce$_2$O$_3$. Similarly, the Fe$_2$O$_3$ peak intensity decreases from TA4 to TA1 because of the decrease in the concentration of Fe$_2$O$_3$, and also the peak showed a red shift in

![Figure 9. Dielectric curves of Ce$_{x-}$Sr$_{x}$Fe$_{3-}Zn$_{2}$O$_{14+\delta}$ (0 ≤ x ≤ 0.45).](image)
the Raman spectrum. Further, the observed Raman band value confirms that the formed NCs are in the form of monoclinic symmetry.

A photoluminescence (PL) study was carried out to measure the light emission property of the NCs TA1–TA4. Figure S5 displays the PL spectra of TA1–TA4. The decrease in the PL emission intensity is due to the low recombination rate of electrons and holes under the light irradiation. The highest PL emission intensity may indicate the highest recombination of electrons and holes. The characteristic PL strong peaks observed at 376 nm are due to 5d–4f transition of Ce3+ ions. Another strong peak observed at 412 nm is due to the transition of 6A1−→4T1(G4) Fe3+ ions. The low intensity broad-band peak observed is due to the double excitation process of strongly coupled Fe3+ ions rather than the single Fe3+ ions as stated by the transition [6A1 + 6A1]−→[4T1(G4) + 4T1(G4)].

The graph shows a high dielectric constant value at the frequency. The dielectric constant becomes a constant value. The dielectric constant of the samples are listed in Table 2. The size of the system. The values of the dielectric loss and the compound decreases with increase in the average particle size. As frequency increases, the dielectric constant decreases, which can be explained on the basis of the space-charge polarization effect. The dielectric constant is found to be constant at elevated frequency because of the electronic polarizability.

### 2.8. Drug Encapsulation and Release Experiments.

The encapsulated amount was measured by using UV–visible spectroscopy at the absorbance of 276 nm (Figure 10). The quantity of encapsulation was found to be 45% (4.14 mg/10 mg of particles). Ciprofloxacin hydrochloride (CFH) has a pKa value of 6.09 for carboxylic acid groups and a pKb value of 8.74 for nitrogen on the piperazinyl ring. Because the synthesized NCs have a positive surface potential of about +100 mV, we believe that the major driving force for encapsulation is physical adsorption (i.e., surface adsorption and loading into the core via pore diffusion). The rate of drug release is significantly influenced by the particle size as the encapsulated drug from the interior has to move to the surface, and then to the liquid. As a result, the drug release from smaller-sized NCs, which have a small core and high surface area to volume ratio, is at a faster rate than that of larger-sized NCs. As the larger-sized NCs have large cores, it allows more drugs to be encapsulated per particle and gives the ability to control the release in a sustained manner. Thus, the control of particle size provides a method of tuning drug release rates from the NCs.

The drug release profiles for different systems (TA1, TA2, TA3, and TA4) were estimated in water at pH 7.4. In general, the following two factors are mainly responsible in releasing the drug molecules from the NPs: (a) normal pore diffusion via surface pores due to concentration gradient and (b) charge screening in drug–NP interactions (e.g., ionic interactions). Because there is no involvement of ionic interactions, we believe that only the diffusion process controls the release process. Drug release occurs in two stages; (i) diffusion of surface-adsorbed drug molecules (burst release) and (ii) diffusion of drug molecules that are loaded in the inner core of the NPs (sustained release). In all the cases, the drug release was found to occur in two phases, first disintegrate release and then persistent release over a period of 10 h. The burst release in the first 1 h occurs because of the release of the drug present on the surface of the NPs. The burst drug release behavior is often observed for the spherically symmetrical systems and is inevitable. From 2 h onward, the release was observed in a sustained manner and continued up to 10 h. The total release was found to be 99% (i.e., 50% via burst release and 49% via sustained release).
3. CONCLUSIONS

NCs of the formula Ce$_{x}$Sr$_{1+x}$Fe$_{5-x}$Zn$_x$O$_{14+δ}$ ($0 \leq x \leq 0.45$) (TA1–TA4: $x = 0, 0.15, 0.30$, and 0.45) are prepared by the nitrate–citrate gel route. XRD analysis shows that the prepared nanomaterial exists as a single-phase material. SEM images show that the prepared NC has the particles with irregular shapes of nanoflakes and nanoclusters. Most of the particle size present in the image is in the range of 5–10 nm. EDX analysis results confirmed that the prepared material contains Ce, Sr, Fe, Zn, and O with appropriate ratios expected from the experiment. The optical studies confirm the simultaneous presence of both Fe$^3+$ and Fe$^{2+}$ inter-valence electronic charge transition band. The peak at 753 nm may be assigned to the transition state $^4$A$_{ig}$($S$) to $^4$T$_{ig}$($G$) state of the Fe$^{3+}$ ion. Preliminary VSM spectra show that the CSFZ NC is in a single domain and perfectly super paramagnetic in nature at room temperature. From the TGA curves, it is confirmed that the prepared sample has lower photoemission property which leads to NCs should have higher photocatalytic property. The drug encapsulation in CSFZ NCs was found to be 45%. The release was observed in two phases and continued up to 10 h. Thus, the NPs reported here have high potential for use as drug delivery carriers.

4. MATERIALS AND METHODS

4.1. Materials. Hydrated cerium nitrate [Ce(NO$_3$)$_3$$\cdot$6H$_2$O], hydrated strontium nitrate [Sr(NO$_3$)$_2$$\cdot$3H$_2$O], hydrated ferric nitrate [Fe(NO$_3$)$_3$$\cdot$9H$_2$O], and hydrated zinc nitrate [Zn(NO$_3$)$_2$$\cdot$6H$_2$O] are bought from Sigma-Aldrich and used as such. Citric acid was purchased from Merk Chemicals and used without further purification. CFH was purchased from Sigma-Aldrich Chemicals. Triple-distilled water was freshly prepared and used as a solvent throughout the experiment.

4.2. Characterization. Particle size and crystallinity of the synthesized CSFZ composites are estimated using the powder XRD method (Siemens D5005 diffractometer) using Cu Kα ($\lambda = 0.154178$ nm) radiation in the range 10$^\circ$–80$^\circ$ in 2θ. Microstructure studies are carried out using SEM model Hitachi-S3400. EDX analysis is done with a super Dryer-II model analyzer. The presence of element and its oxidation state is determined by an XPS ESCA-3 Mark II spectrometer (VG Scientific Ltd, England) using Al Kα (1486.6 eV) radiation as the source. The room temperature of optical absorption spectra is measured in the region of 200–800 nm using a UV–visible spectrometer (LAB INDIA model UV 320). An ALPHA Bruker FT-IR spectrophotometer is used to find the metal oxide bonding interaction by the KBr pellet method. The thermal response of the synthesized CSFZ composites is done by using DTA and TGA recorded at Q600 SDT instruments. DSC is recorded using Q20 DSC instruments with the operating temperature range of 50–1050 °C. VSM is recorded by using the VSM model Lake Shore’s new 7400 series instrument. The internal structure of prepared CSFZ composites is analyzed by TEM analysis (HRTEM, JEOL JEM-2010, Japan). The scattering property of the prepared CSFZ composites is measured by Raman spectra (Renishaw micro-Raman system). Dielectric properties of the CSFZ composites are recorded by using Solartron electrochemical impedance spectroscopy (SI model no. 1260, 100 mV; 0.01 Hz to 7 MHz). The PL analysis is carried out using a UV-spectrophotometer model Fluorolog-3 (HORIBA Jobin Yvon, Japan).

4.3. Synthesis of Ce$_{4-x}$Sr$_{1+x}$Fe$_{5-x}$Zn$_x$O$_{14+δ}$ ($0 \leq x \leq 0.45$) Composite. The CSFZ composite is prepared using the procedure which is available in the literature, and the flow chart of the synthetic strategy is presented in Scheme 1. There are four combinations (TA1–TA4) of metals used in the synthesis of nano metal oxide, and the details about the synthesized different combinations of NCs are presented in Table 3. The required amount of hydrated ceriumnitrate

![Scheme 1: Synthesis of Ce$_{4-x}$Sr$_{1+x}$Fe$_{5-x}$Zn$_x$O$_{14+δ}$ NC](image-url)

| Table 3. Composition Calculation of Ce$_{4-x}$Sr$_{1+x}$Fe$_{5-x}$Zn$_x$O$_{14+δ}$ ($0 \leq x \leq 0.45$) |
|---|---|---|
| sample code | X | composition of Ce$_{4-x}$Sr$_{1+x}$Fe$_{5-x}$Zn$_x$O$_{14+δ}$ |
| TA1 | 0.0 | Ce$_6$Sr$_{2}$Fe$_{5}$O$_{14+δ}$ |
| TA2 | 0.15 | Ce$_{5.85}$Sr$_{1.15}$Fe$_{4.85}$Zn$_{0.15}$O$_{14+δ}$ |
| TA3 | 0.30 | Ce$_{5.6}$Sr$_{1.4}$Fe$_{4.6}$Zn$_{0.4}$O$_{14+δ}$ |
| TA4 | 0.45 | Ce$_{5.35}$Sr$_{1.65}$Fe$_{4.35}$Zn$_{0.65}$O$_{14+δ}$ |

4.4. Encapsulation of CFH into the NCs. NC powder (10 mg) is dispersed in 2 mL of water in centrifuge tubes and ultrasonicated for 2 min to obtain uniformly dispersed nanoparticle suspension. The suspension is then centrifuged...
at 7500 rpm for 10 min and triple washed with water. CFH solution (2 mL, 5 mg/mL) is added to the CSFZ composites at acidic conditions (pH 5) and incubated for 1 h at ordinary temperature. After incubation, the suspension was centrifuged at 7500 rpm for 10 min, and supernatant absorbance is measured at 276 nm using a ND-2000c UV spectrophotometer (NanoDrop Technologies, USA). The actual amount of drug loading is calculated by subtracting the amount of drugs present in the supernatant from the original amount used for the encapsulation process. After the encapsulation process, the drug-loaded NC powder is washed twice with water and used for release experiments. The encapsulation efficiency (EE) is calculated by using eq 4

\[
EE = \frac{\text{amount of drug loaded in composite NPs}}{\text{initial amount of drug}} \times 100
\]

4.5. In Vitro Drug Release Experiments. The in vitro drug release study for the systems TA1, TA2, TA3, and TA4 is analyzed by incubating drug-loaded NCs in 2 mL of triple distilled water at 37 °C. Drug-loaded NCs (10 mg) are dispersed in 2 mL of water in a centrifuge and placed in an incubator shaker at 37 °C. At a particular time period, 1.4 mL of the sample is extracted from the centrifuge tube and charged with an equal quantity of prewarmed water in such a way that the mechanism equilibrium does not get disturbed during the evaluation process. The amount of CFH released is calculated by measuring the increase in absorbance values at 276 nm using UV spectroscopy.

ASSOCIATED CONTENT
Supporting Information
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Notes
The authors declare no competing financial interest.

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