Synthesis and characterization of $\text{Co}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles by anionic, cationic, and non-ionic surfactant templates via co-precipitation

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The cobalt ferrite nanoparticles ($\text{Co}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4$) were synthesized by the surfactant templated co-precipitation method using various surfactants namely sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium bromide (CTAB), and Tween20. Under the substitution, the $\text{Co}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4$ particles were synthesized at various $\text{Co}^{2+}$ and $\text{Fe}^{2+}$ mole ratios ($x = 1, 0.6, 0.2, \text{and } 0$) with the SDS. The cobalt ferrite nanoparticles were characterized for their morphology, structure, magnetic, and electrical properties. All $\text{Co}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles showed the nanoparticle sizes varying from 16 to 43 nm. In the synthesis of $\text{CoFe}_2\text{O}_4$, the SDS template provided the smallest particle size, whereas the saturated magnetization ($M_s$) of $\text{CoFe}_2\text{O}_4$ was reduced by using CTAB, SDS, and Tween20. For the $\text{Co}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4$ as synthesized by the SDS template at 1.2 CMC, the $M_s$ increased with increasing $\text{Fe}^{2+}$ mole ratio. The highest $M_s$ of 100.4 emu/g was obtained from the $\text{Fe}_3\text{O}_4$ using the SDS template. The $\text{Fe}_3\text{O}_4$ nanoparticle is potential to be used in various actuator and biomedical devices.

Magnetic nanoparticles have been widely investigated for many applications such as magnetic fluid1, catalysis2, magnetic resonance imaging (MRI)3, proton exchange membrane4, actuator5, hyperthermia6, and drug delivery7. Substitution of various divalent cations ($\text{M}^{2+}$) namely $\text{Co}^{2+}$, $\text{Mn}^{2+}$, $\text{Zn}^{2+}$, $\text{Mg}^{2+}$, and $\text{Ni}^{2+}$ into ferrite nanoparticles can significantly alter their magnetic properties8. Among the ferrites magnetic nanoparticles with the spinel structures, $\text{CoFe}_2\text{O}_4$ provides the notable properties namely: chemical stability, high coercivity ($H_c$), and high Curie temperature9. Moreover, $\text{CoFe}_2\text{O}_4$ possesses a good anisotropic property as the $\text{Co}^{2+}$ substitution provides a higher degree of anisotropy relative to $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$10. However, the bulk saturated magnetization ($M_s$) of $\text{CoFe}_2\text{O}_4$ (80 emu/g) obtained so far is still lower than $\text{Fe}_3\text{O}_4$ (presently at ~89 emu/g)11.

The shape, size, and properties of magnetic particles are generally dictated by the synthesis method12–14. There are various methods to synthesize magnetic nanoparticles such as hydrothermal15, sol-gel16, micro-emulsion17, thermal decomposition18, and co-precipitation19. Among these techniques, the co-precipitation is a simple method as it is inexpensive, with a short reaction time and a lower reaction temperature. The important factors namely the reaction temperature, stirring speed, and pH of the reactant are essential in controlling the particle shape and size as related to the particle nucleation and growth rates. Ideally, the nucleation rate should be higher than the growth rate to obtain smaller particles.

Alternatively, the particle shape and size can be manipulated by using surface-active agents, namely surfactants, because of their electrostatic repulsion and steric hindrance properties. In particular, the surfactant could reduce the agglomeration of the magnetic nanoparticles from the magnetic interaction and with high surface reactivity. Vadivel et al. used sodium dodecyl sulfate (SDS) as the surfactant for the co-precipitation synthesis of $\text{CoFe}_2\text{O}_4$ under various SDS concentrations. SDS improved the particles size distribution and magnetic property of $\text{CoFe}_2\text{O}_4$20.

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Nanomagnetic particles (NMPs) have been utilized in various applications, in particular actuators and biomedical devices. The important and required features of NMP for these applications are the high magnetization, superparamagnetic behavior, and non-toxicity towards humans.

In this work, the effect of surfactant types, namely sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium bromide (CTAB), and Tween 20 as anionic, cationic, and non-ionic surfactants, were investigated on the synthesis of \( \text{Co}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4 \) with \( 0 \leq x \leq 1 \) and on the resultant magnetic properties. It will be shown that SDS was the most suitable surfactant for the synthesis of \( \text{CoFe}_2\text{O}_4 \) with the nanoparticle size of 16 ± 3 nm, whereas the highest magnetization as obtained from the \( \text{Fe}_3\text{O}_4 \) by the SDS template was as high as 100.41 emu/g with the superparamagnetic behavior. The synthesized \( \text{Fe}_3\text{O}_4 \) particle possesses magnetic properties which are potential to be used in various actuator and biomedical devices.

**Methods**

**Materials.** Iron (III) chloride (99% purity, Sigma Aldrich), cobalt (II) chloride (AR grade, Merck), and iron (II) sulfate heptahydrate (99% purity, Univar) were used as the precursors. Sodium dodecyl sulfate, SDS, (98.5% purity, Sigma Aldrich), hexadecyltrimethylammonium bromide, CTAB, (96% purity, Sigma Aldrich), and Tween 20 (AR grade, Sigma Aldrich) were the surfactants used. Sodium hydroxide, NaOH (AR grade, Univar) was utilized as a precipitating agent.

**Synthesis of \( \text{CoFe}_2\text{O}_4 \) magnetic nanoparticles by surfactant assisted co-precipitation under various surfactant types.** Metal precursors including iron (III) chloride (Fe(III)), and cobalt (II) chloride (Co(II)) with the Fe(iii):Co(ii) molar ratio of 0.10: 0.05 (0.81 g: 0.33 g) were put in 25 ml deionized water. The metal ion solution was separately mixed with 25 ml of various surfactant solutions namely: SDS (8.2 mM), CTAB (0.92 mM, 0.033 g), and Tween 20 (0.06 mM, 0.02 g) at their critical micelle concentrations (CMC). To obtain the CMC data, the surfactant solution in water was tested at 25 °C. Each surfactant was dissolved in the deionized water and was stirred for 30 min to form micelles before adding the metal ions at room temperature. The mixture solution was continuously stirred at room temperature for 30 min. After that, 3 M NaOH solution (15 ml) was added dropwise and then continuously stirred for 4 h at 80 °C. The obtained dark precipitate was washed with water and ethanol to eliminate the remaining surfactant, and then dried at 80 °C for 24 h. The synthesized \( \text{CoFe}_2\text{O}_4 \) by SDS, CTAB, and Tween20 as the surfactants and no surfactant are coded as \( \text{CoFe}_2\text{O}_4_{-\text{SDS}_-1\text{CMC}}, \text{CoFe}_2\text{O}_4_{-\text{CTAB}_-1\text{CMC}}, \text{CoFe}_2\text{O}_4_{-\text{Tween20}_-1\text{CMC}}, \text{and CoFe}_2\text{O}_4_{-\text{Bare}} \), respectively.

**Synthesis of \( \text{Co}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4 \) magnetic nanoparticles by surfactant assisted co-precipitation under various molar ratio of \( \text{Co}^{2+} \) and \( \text{Fe}^{3+} \).** \( \text{CoFe}_2\text{O}_4, \text{Co}_{0.6}\text{Fe}_{0.4}\text{Fe}_2\text{O}_4, \text{Co}_{0.2}\text{Fe}_{0.8}\text{Fe}_2\text{O}_4, \text{and Fe}_3\text{O}_4 \) were synthesized with the metal precursors including iron (III) chloride (Fe(III)), cobalt (II) chloride (Co(II)), and iron (II) sulfate (Fe(II)) at the Fe(iii):Co(ii):Fe(ii) molar ratios of 0.10: 0.05: 0.00 (0.81 g: 0.33 g: –), 0.10: 0.03: 0.02 (0.81 g: 0.26 g: 0.14 g), 0.10: 0.01: 0.04 (0.81 g: 0.07 g: 0.56 g), and 0.10: 0.00: 0.05 (0.81 g: –: 0.70 g), where they were dissolved in 25 ml deionized water. The SDS (10 mM, 0.14 g) was dissolved in 25 ml deionized water for 30 min and then each metal precursor solution was put in the SDS solution and stirred at room temperature for 30 min to obtain a homogeneous solution. After that, 3 M NaOH solution (15 ml) was added and then continuously stirred for 4 h at 80 °C. The obtained dark precipitate was washed with water and ethanol to eliminate the remaining surfactant and then dried at 80 °C for 24 h. The synthesized \( \text{CoFe}_2\text{O}_4 \) by SDS, CTAB, and Tween20 as the surfactants and no surfactant are coded as \( \text{CoFe}_x\text{O}_y_{-\text{SDS}_-1.2\text{CMC}_x}, \text{CoFe}_x\text{O}_y_{-\text{CTAB}_-1.2\text{CMC}_x}, \text{CoFe}_x\text{O}_y_{-\text{Tween20}_-1.2\text{CMC}_x}, \text{and CoFe}_x\text{O}_y_{-\text{Bare}} \), respectively.

**Cobalt ferrite nanoparticles characterization.** A wide angle X-ray diffractometer, XRD, (Rigaku, SmartLab) was utilized to investigate the crystalline structures of the magnetic nanoparticles. The CuK-alpha radiation source was employed at 40 kV/30 mA using the K-beta filter to eliminate interference peaks. The XRD device was fitted with the Bragg-Brentano geometry, the graphite monochromator and the diffracted radiation source was employed at 40 kV/30 mA using the K-beta filter to eliminate interference peaks. Each sample was distributed on a carbon tape on the sample holder, and a copper grid was used as the reference for the elemental analysis.

A Fourier transform infrared spectrometer, FT-IR, (Nicolet, iS5) was employed to measure spectra of the magnetic nanoparticles using potassium bromide (KBr) as the background material. To prepare a sample, a small amount of sample powder was mixed and grinded with KBr. The mixture powder was put into a mold and then compressed by a hydraulic machine.

A scanning electron microscopy, SEM, (Hitachi, S-4800) was used to determine the atomic percentages of the cobalt ferrite nanoparticles. Each sample was coated with a thin layer of platinum. The images were obtained at the acceleration voltage of 5 kV and at the magnifications of 100,000 and 150,000.

An electron dispersive spectrometer, EDS, (FE-SEM Hitachi, S-4800) was used to determine the atomic percentages of the cobalt ferrite nanoparticles. Each sample was coated with a thin layer of platinum.

An X-ray photoelectron spectrometer, XPS, (Kratos, Axis Ultra DLD) was employed to determine the atomic percentages of \( \text{Co}_{0.6}\text{Fe}_{0.4}\text{Fe}_2\text{O}_4 \) using the monochromatized Al K. Each sample was distributed on a carbon tape on the sample holder, and a copper grid was used as the reference for the elemental analysis.

A vibrating sample magnetometer, VSM, (LakeShore, Series 7400 model 7404) was employed to measure the saturated magnetization (M_s) and coercivity (H_c) of the cobalt ferrite nanoparticles. The measurements were taken under a magnetic field strength of 10,000 Gauss at room temperature, with 80 points/loop and with a scan speed of 10 s/point.
Results and discussion

Cobalt ferrite synthesis and characterization. The synthesis scheme is shown in Fig. 1. After the complete micelle formation at equal or above the critical micelle concentration (CMC), the metal ions (Fe³⁺, Fe²⁺, and Co²⁺) were added into the surfactant solution. The metal ions were stabilized with the spherical micelles of surfactant by the interaction between the polar groups of the surfactants and the metal cation precursors. The synthesis reaction was carried out by adding NaOH (at the pH of 13) for 4 h under the nitrogen atmosphere to prevent the oxidation of ferrous ions (Fe²⁺) to ferric ions (Fe³⁺) by the oxygen atmosphere. In the case of SDS as an anionic surfactant, it could stabilize the metal cations by the micelle formation via the interaction between the polar group of SO₄⁻ and the metal cations. After the adding NaOH to precipitate the ferrite particle, the OH⁻ from NaOH interacted with the metal cations to form the hydroxide precipitant and the SDS interacted with the hydroxide precipitant on the surface. The co-precipitation reaction is shown in Eq. (1).

\[
\begin{align*}
2\text{Fe}^{3+} + 6\text{OH}^- & \rightarrow 2\text{Fe(OH)}_3 \\
x\text{Co}^{2+} + 2\text{OH}^- & \rightarrow x\text{Co(OH)}_2 \\
(1-x)\text{Fe}^{3+} + 2\text{OH}^- & \rightarrow (1-x)\text{Fe(OH)}_2 \\
x\text{Co(OH)}_2 + (1-x)\text{Fe(OH)}_2 + 2\text{Fe(OH)}_3 & \rightarrow \text{Co}_x\text{Fe}_{1-x}\text{O}_4 + 4\text{H}_2\text{O}
\end{align*}
\]

The crystalline structure of cobalt ferrite nanoparticles was characterized by the x-ray diffraction technique. Normally, magnetite nanoparticles are of a cubic spinel structure (AB₂X) which consists of a divalent cation (A), a trivalent cation (B), and a divalent anion (X). The cations A and B occupy the octahedral or tetrahedral site of the spinel structure. Nevertheless, the ferrite nanoparticles can also form a reverse spinel structure, where the tetrahedral site is occupied by a trivalent cation and the octahedral site is occupied by a divalent cation and the remaining trivalent cation. The XRD patterns of the CoFe₂O₄ as synthesized by SDS, CTAB, Tween20 and without surfactant are shown in Fig. 2a. The patterns of CoFe₂O₄ synthesized by all surfactants show the major characteristic peaks at (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) which reflect a cubic spinel structure. Table 1 lists the calculated average crystallite sizes. The average crystallite size was calculated by using the (3 1 1) peak and Eq. (2):

\[
t = \frac{k\lambda}{\beta \cos \theta}
\]
where $k$ is the dimensionless shape factor ($k = 0.9$), $\lambda$ is the X-ray wavelength (CuKα = 1.5405 Å), $\beta$ is the full width at the half maximum of diffraction peak (3 1 1), and $\theta$ is the angle of diffraction (2θ/2). The lattice constant ($a$) was calculated by using the (3 1 1) peak and Eq. (3):

$$a = d\sqrt{h^2 + k^2 + l^2}$$

(3)

where $d$ is the interplanar spacing, and $(h l k)$ are the Miller indices. The volume unit cell was calculated by Eq. (4):

$$V_{\text{cell}} = a^3$$

(4)

The hopping lengths for the tetrahedral site ($L_A$) and octahedral site ($L_B$) were calculated by Eqs. (5–6)39:

$$L_A = a\sqrt{\frac{3}{4}}$$

(5)

and

$$L_B = a\sqrt{\frac{2}{4}}$$

(6)

Table 1 also lists the calculated average crystallite sizes ($t_{311}$), lattice constants ($a$), volumes ($V_{\text{cell}}$), hopping lengths for tetrahedral site ($L_A$), hopping lengths for octahedral site ($L_B$), particle sizes, and the Co: Fe atomic ratios from EDS and XPS of cobalt ferrite nanoparticles.

| Sample            | Co: Fe mole ratio | XRD Average crystallite size ($t_{311}$) (nm) | Lattice constant ($a$) (Å) | Volume ($V_{\text{cell}}$) | $L_A$ (nm) | $L_B$ (nm) | Particle size (nm) | Co: Fe atomic ratio | Co: Fe atomic ratio |
|-------------------|-------------------|---------------------------------------------|-----------------------------|----------------------------|------------|------------|-------------------|-------------------|-------------------|
| CoFe$_2$O$_4$ _Bare_ | –                 | 10.9                                       | 8.32                        | 596.22                     | 3.60       | 2.94       | 42 ± 8            | –                 | –                 |
| CoFe$_2$O$_4$ _SDS_1CMC_ | –                 | 15.9                                       | 8.34                        | 579.05                     | 3.61       | 2.95       | 16 ± 3            | –                 | –                 |
| CoFe$_2$O$_4$ _CTAB_1CMC_ | –                 | 12.5                                       | 8.34                        | 579.68                     | 3.61       | 2.95       | 20 ± 3            | –                 | –                 |
| CoFe$_2$O$_4$ _Tween20_1CMC_ | –                 | 9.21                                       | 8.32                        | 597.60                     | 3.60       | 2.94       | 21 ± 3            | –                 | –                 |
| CoFe$_2$O$_4$ _SDS_1.2CMC_ | 1:2               | 16.8                                       | 8.35                        | 581.96                     | 3.62       | 2.95       | 22 ± 3            | 1:1.8             | 1:1.9             |
| Co$_0.6$Fe$_{0.4}$O$_3$ _SDS_1CMC_ | 1:4               | 18.7                                       | 8.41                        | 596.18                     | 3.64       | 2.98       | 24 ± 3            | 1:3.5             | 1:3.9             |
| Co$_0.2$Fe$_{0.8}$O$_3$ _SDS_1.2CMC_ | 1:14              | 11.7                                       | 8.36                        | 585.51                     | 3.62       | 2.96       | 32 ± 4            | 1:12              | 1:14              |
| Fe$_3$O$_4$ _SDS_1.2CMC_ | 0:1               | 9.81                                       | 8.35                        | 583.11                     | 3.62       | 2.95       | 43 ± 8            | 0:1               | 0:1               |

Table 1. Co: Fe mole ratios, average crystallite sizes ($t_{311}$), lattice constants ($a$), unit volume cells ($V_{\text{cell}}$), hopping lengths for tetrahedral site ($L_A$), hopping lengths for octahedral site ($L_B$), particle sizes, and the Co: Fe atomic ratios from EDS and XPS of cobalt ferrite nanoparticles.
respectively. The calculated synthesis values of Co: Fe mole ratios are 1: 2, 1: 4, 1: 14, and 0: 1 respectively; thus, the EDS experimental values are quite close to the theoretical values.

The XPS technique was also used to confirm the Co: Fe mole ratio and the XPS spectra are shown in Fig. 5. The visible peaks can be observed at 778.3 eV, 706.7 eV, and 529.2 eV corresponding to the Co 2p, Fe 2p and O 1s respectively. The corresponding Co: Fe mole ratios of Co\textsubscript{x}Fe\textsubscript{1−x}Fe\textsubscript{2}O\textsubscript{4} are 1: 1.9, 1: 3.9, 1: 14, and 0: 1, respectively. These mole ratio values from the EDS and XPS techniques are quite close thus confirming that the synthesized Co\textsubscript{x}Fe\textsubscript{1−x}Fe\textsubscript{2}O\textsubscript{4} mole ratios match their theoretical stoichiometric values.

Morphology of the cobalt ferrite nanoparticles was investigated by the scanning electron microscope. In the case of CoFe\textsubscript{2}O\textsubscript{4} under various surfactant types, the nearly spherical shapes of CoFe\textsubscript{2}O\textsubscript{4} were obtained from all surfactants as shown in Fig. 6. The particle sizes of CoFe\textsubscript{2}O\textsubscript{4} synthesized without surfactant, and with SDS, CTAB, and Tween20 are 42 nm, 16 nm, 20 nm, and 21 nm and, respectively. It appears that the particle size of cobalt ferrite nanoparticles as synthesized by the co-precipitation method was reduced by employing a surfactant because of the steric hindrance effect from the surfactant contributing to a slower nucleation and growth rate. Interestingly, SDS as an anionic surfactant provides the smaller particle size of 16 nm along with a narrow size distribution as the anion from SDS could stabilize the metal cations and the cobalt ferrite nanoparticles. For cases of CTAB and Tween20, the particle sizes are 20 nm and 21 nm, respectively, thus their sizes are comparable. However, the CoFe\textsubscript{2}O\textsubscript{4} particle as synthesized by CTAB (cationic surfactant) tended to agglomerate and formed a larger flake, as shown in Fig. 6b. Figure 7 shows the nearly spherical shapes of CoFe\textsubscript{2}O\textsubscript{4}, Co\textsubscript{0.6}Fe\textsubscript{0.4}Fe\textsubscript{2}O\textsubscript{4}, Co\textsubscript{0.2}Fe\textsubscript{0.8}Fe\textsubscript{2}O\textsubscript{4}, and Fe\textsubscript{3}O\textsubscript{4} with SDS at the surfactant concentration of 1.2 times the critical micelle concentration. The particle sizes are 22 nm, 24 nm, 32 nm, and 43 nm, respectively. For the different particle sizes of the Co\textsubscript{x}Fe\textsubscript{1−x}Fe\textsubscript{2}O\textsubscript{4} ferrite particles, the particle sizes increased with increasing the Fe\textsuperscript{2+} substitution, indicating that
the addition of Fe\(^{2+}\) effectively increases the crystal growth rate of Co\(_{x}\)Fe\(_{1-x}\)O\(_4\) with a larger particle size\(^{43}\). The smaller particles can be obtained when the nucleation rate is higher than the growth rate\(^{44}\).

**Magnetic property of cobalt ferrite nanoparticles.** The magnetic properties of cobalt ferrite nanoparticles were measured by the VSM at room temperature (300 K). The saturated magnetization (M\(_s\)) and coercivity (H\(_c\)) values were obtained from the hysteresis curves in Fig. 8a,b, and are tabulated in Table 2. The hysteresis curves show the large loops of cobalt ferrite nanoparticles with the presence of cobalt atoms namely: CoFe\(_2\)O\(_4\), Co\(_{0.6}\)Fe\(_{0.4}\)Fe\(_2\)O\(_4\), and Co\(_{0.2}\)Fe\(_{0.8}\)Fe\(_2\)O\(_4\) with the high H\(_c\) and M\(_s\) values; thus, the synthesized cobalt ferrite nanoparticles are hard or ferromagnetic materials\(^{45}\). On the other hand, the Fe\(_3\)O\(_4\) hysteresis curve shows the superparamagnetic behavior where the H\(_c\) and M\(_r\) values were close to zero\(^{46}\).

Figure 8a shows the hysteresis curves of CoFe\(_2\)O\(_4\) as synthesized by various surfactant types. The M\(_s\) values are 13.30 emu/g, 28.06 emu/g, 31.25 emu/g, and 15.15 emu/g, for the CoFe\(_2\)O\(_4\) synthesized by using no surfactant, SDS, CTAB and Tween20 with the particle sizes of 42 nm, 16 nm, 20 nm, and 21 nm, respectively. For the CoFe\(_2\)O\(_4\) as synthesized by SDS and CTAB, it appears that the M\(_s\) value depends on the particle size, it increases slightly with increasing particle size; a smaller particle has a weaker coordination of surface atoms resulting in a disorder in the surface spins\(^{47}\). However, the CoFe\(_2\)O\(_4\) as synthesized by Tween20 and no surfactant show the lower M\(_s\) values due to the lower crystallinity\(^{48}\), which can be observed from the (311) plane of the XRD patterns in Fig. 2a. The XRD patterns of CoFe\(_2\)O\(_4\) as synthesized by Tween20 and no surfactant show the weak and broad peaks due to the lower crystallinity relative to the XRD patterns of CoFe\(_2\)O\(_4\) as synthesized by SDS and CTAB as shown in Fig. 2a.

In the case of Co\(_x\)Fe\(_{1-x}\)O\(_4\) as shown in Fig. 8b, the M\(_s\) values are 46.19 emu/g, 74.19 emu/g, 80.62 emu/g, and 100.41 emu/g for the CoFe\(_2\)O\(_4\), Co\(_{0.6}\)Fe\(_{0.4}\)Fe\(_2\)O\(_4\), and Co\(_{0.2}\)Fe\(_{0.8}\)Fe\(_2\)O\(_4\), and Fe\(_3\)O\(_4\), respectively. On comparing with the previous M\(_s\) values of the bulk CoFe\(_2\)O\(_4\) (80 emu/g)\(^{49}\) and Fe\(_3\)O\(_4\) (90 emu/g)\(^{47}\), the present M\(_s\) value of Co\(_x\)Fe\(_{1-x}\)O\(_4\) increases with increasing Fe\(^{2+}\) substitution due to fact that Fe\(^{2+}\) provides more unpaired electrons in the 3d orbital leading to the higher number of magnetic moments in the metal ion of the magnetic nanoparticles\(^{50,51}\). On comparing the Fe\(^{2+}\) and Co\(^{2+}\) 3d orbitals, Fe\(^{2+}\) has a higher number of unpaired electrons in the 3d orbital resulting in a higher magnetic moment and Bohr magneton which can be approximately by Eq. (7)\(^{45}\).

\[
\mu_s = g \sqrt{S(S+1)}
\]
where \( \mu_s \) is the magnetic moment (Bohr magneton), \( g \) is the gyromagnetic ratio or the ratio of the magnetic moment to the angular momentum. For a free electron, \( g = 2 \), and \( S \) is the sum of the spin quantum numbers where each electron contributes \( \pm 1/2 \). The \( S \) values of \( \text{Co}^{2+} \) and \( \text{Fe}^{2+} \) are \( 3/2 \) and \( 4/2 \), respectively. Thus, the calculated magnetic moments of \( \text{Co}^{2+} \) and \( \text{Fe}^{2+} \) are 3.87 magnetons and 4.90 magnetons, respectively. Other previous works also showed the increase of \( M_s \) values under the substitution of increasing \( \text{Fe}^{2+} \) in the \( \text{Co}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4 \) \( x = 0 \) to 1.11.

The \( H_c \) values of the cobalt ferrite nanoparticles are 263.02 Oe, 877.76 Oe, 190.76 Oe, and 43.03 Oe for \( \text{CoFe}_2\text{O}_4 \), \( \text{Co}_{0.6}\text{Fe}_{0.4}\text{Fe}_2\text{O}_4 \), and \( \text{Co}_{0.2}\text{Fe}_{0.8}\text{Fe}_2\text{O}_4 \), and \( \text{Fe}_3\text{O}_4 \), respectively. Comparing with previous work as shown in Table 2, the \( H_c \) values of the synthesized \( \text{CoFe}_2\text{O}_4 \) and \( \text{Fe}_3\text{O}_4 \) are comparable to the previous work. It can be noted that the \( H_c \) value increases with decreasing \( x \) values from 1 to 0.4, along with the increase of the \( \text{Fe}^{2+} \) mole ratio. Below \( x \) value of 0.4, the \( H_c \) value decreases to the lowest value for \( \text{Fe}_3\text{O}_4 \) (\( x = 0 \)). The result is consistent with the previous work as the highest \( H_c \) value was found in the case of \( \text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4 \) (\( x = 0.5 \)).

Lastly, it may be noted that the \( M_s \) values of \( \text{Fe}_3\text{O}_4 \) from previous works\(^ {43,57-59} \) as tabulated in Table 2 were 63.36, 61.92, and 78.00 emu/g, respectively. The presently obtained \( M_s \) value of \( \text{Fe}_3\text{O}_4_{\text{SDS}_1.2\text{CMC}} \) is 100.41 emu/g which is relatively higher.

**Electrical conductivity of cobalt ferrite nanoparticles.** Electrical conductivity of cobalt ferrite nanoparticles was investigated by using a two-point probe meter. The electrical conductivity values of cobalt ferrite nanoparticles are shown in Table 2. For the \( \text{CoFe}_2\text{O}_4 \) under various surfactant types, the electrical conductivity values are \( 1.11 \times 10^{-2} \) S/cm, \( 1.41 \times 10^{-2} \) S/cm, \( 1.33 \times 10^{-2} \) S/cm, and \( 1.13 \times 10^{-2} \) S/cm for the \( \text{CoFe}_2\text{O}_4 \) synthesized by using no surfactant, SDS, CTAB, and Tween20, respectively. Comparing with previous work results, \( \text{CoFe}_2\text{O}_4 \) can be categorized as a semiconducting material\(^ {53} \). Under various \( \text{Fe}^{2+} \) and \( \text{Co}^{2+} \) substitution, the electrical conductivities are \( 2.06 \times 10^{-2} \) S/cm, \( 3.94 \times 10^{-2} \) S/cm, \( 5.33 \times 10^{-2} \) S/cm, and \( 1.18 \times 10^{-1} \) S/cm for the \( \text{CoFe}_2\text{O}_4 \), \( \text{Co}_{0.6}\text{Fe}_{0.4}\text{Fe}_2\text{O}_4 \), \( \text{Co}_{0.2}\text{Fe}_{0.8}\text{Fe}_2\text{O}_4 \), and \( \text{Fe}_3\text{O}_4 \), respectively. Thus, the electrical conductivity increases with increasing \( \text{Fe}^{2+} \) mole ratio as shown in Table 2. The electrical conductivity of \( \text{Fe}_3\text{O}_4 \) can be attributed to the electron hopping between \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) in the octahedral site of the inverse spinel structure. With the substitution of \( \text{Fe}^{2+} \) by \( \text{Co}^{2+} \), the electrical conductivity decreases due to the loss of closed-neighbor pairs (\( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \)).

**Conclusions**

The cobalt ferrite nanoparticles were successfully synthesized by the simple surfactant templated co-precipitation method. The cobalt ferrite nanoparticles show the cubic spinel structure with the nano-sizes varying between 16 and 43 nm with the nearly spherical shapes. The most suitable surfactant for the synthesis of \( \text{CoFe}_2\text{O}_4 \) was SDS with the smallest particle size of 16 ± 3 nm. The experimental stoichiometry of cobalt ferrite nanoparticles was...
as obtained by EDS and XPS agreed with the theoretical stoichiometry. The magnetization of cobalt ferrite nanoparticles depended on the size of the nanoparticles and the Fe²⁺ and Co²⁺ ratio. The currently highest magnetization value, \( M_s \), was obtained from the synthesized \( \text{Fe}_3\text{O}_4 \) using the SDS template at 100.41 emu/g. The synthesized \( \text{Fe}_3\text{O}_4 \) nanoparticle with high \( M_s \) is potential to be utilized in various actuator devices and biomedical applications.

Figure 7. SEM images of \( \text{Co}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4 \): (a) \( \text{CoFe}_2\text{O}_4 \_\text{SDS}_\_1.2\text{CMC} \); (b) \( \text{Co}_0.6\text{Fe}_0.4\text{Fe}_2\text{O}_4 \_\text{SDS}_\_1.2\text{CMC} \); (c) \( \text{Co}_0.2\text{Fe}_0.8\text{Fe}_2\text{O}_4 \_\text{SDS}_\_1.2\text{CMC} \); and (d) \( \text{Fe}_3\text{O}_4 \_\text{SDS}_\_1.2\text{CMC} \).

Figure 8. Hysteresis loops of \( \text{CoFe}_2\text{O}_4 \) and \( \text{Co}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4 \): (a) under various surfactant types; (b) under various Fe²⁺ contents.
Table 2. Magnetic and electrical properties of CoFe$_{1-x}$Fe$_{2}$O$_4$ nanoparticles.

| Sample               | VSM M$_a$ (emu/g) | H$_c$ (Oe) | M$_r$ (emu/g) | Electrical conductivity (S/cm) | Ref |
|----------------------|------------------|------------|---------------|-------------------------------|-----|
| CoFe$_2$O$_4$ Bare   | 13.30            | 786.66     | 4.31          | 1.11 x 10$^{-2}$ ± 9.16 x 10$^{-4}$ |     |
| CoFe$_2$O$_4$ SDS 1CMC | 28.06            | 448.58     | 8.18          | 1.41 x 10$^{-2}$ ± 1.48 x 10$^{-3}$ |     |
| CoFe$_2$O$_4$ CTA6 1CMC | 31.26            | 232.52     | 7.48          | 1.33 x 10$^{-2}$ ± 1.41 x 10$^{-3}$ |     |
| CoFe$_2$O$_4$ Tween20 1CMC | 15.15            | 53.52      | 1.01          | 1.13 x 10$^{-2}$ ± 7.07 x 10$^{-4}$ |     |
| CoFe$_2$O$_4$ SDS 1.2CMC | 46.19            | 263.02     | 11.83         | 2.06 x 10$^{-2}$ ± 9.44 x 10$^{-3}$ |     |
| Co$_{0.2}$Fe$_{0.8}$Fe$_2$O$_4$ SDS 1.2CMC | 74.19            | 877.76     | 24.78         | 3.94 x 10$^{-2}$ ± 3.03 x 10$^{-3}$ |     |
| Co$_{0.6}$Fe$_{0.4}$Fe$_2$O$_4$ SDS 1.2CMC | 80.62            | 190.76     | 13.56         | 5.33 x 10$^{-2}$ ± 8.64 x 10$^{-4}$ | 56  |
| Co$_{0.2}$Fe$_{0.8}$Fe$_2$O$_4$ SDS 1CMC | 100.41           | 43.03      | 4.37          | 1.8 x 10$^{-2}$ ± 1.82 x 10$^{-2}$ | 55  |
| Fe$_3$O$_4$          | 74.08            | 527.97     | 23.81         | –                             | 54  |
| Fe$_3$O$_4$          | 58.40            | 286.00     | 12.45         | –                             | 55  |
| Fe$_3$O$_4$          | 34.70            | 233.00     | 47.20         | –                             | 55  |
| Fe$_3$O$_4$          | 63.36            | –          | –             | –                             | 56  |
| Fe$_3$O$_4$          | 61.92            | –          | –             | –                             | 56  |
| Fe$_3$O$_4$          | 78.00            | –          | –             | –                             | 56  |
| Fe$_3$O$_4$          | 87.00            | 31.00      | 4.60          | 9.68 x 10$^{-3}$             | 57  |

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Competing interests
The authors declare no competing interests.

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