Controlled synthesis and self-assembly of ZnFe$_2$O$_4$ nanoparticles into microspheres by solvothermal method

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Abstract

Zinc ferrite (ZnFe$_2$O$_4$) colloidal nanoparticle assemblies (CNAs) were prepared controllably by solvothermal synthesis without the assistance of a template or surfactant. The X-ray diffraction (XRD) results confirm the formation spinel structure of ZnFe$_2$O$_4$ with the grain size around 11 ± 3 nm. Scanning electronic microscope (SEM) images show that the CNAs are sub-microspheres self-assembled by nanoparticles with size about 284–346 nm changed with reaction conditions. The composition of elements Zn, Fe and O in the ZnFe$_2$O$_4$ CNAs is identified by using EDAX analysis. Room-temperature vibration magnetic measurements (VSM) demonstrates the as-obtained ZnFe$_2$O$_4$ CNAs showing superparamagnetic behavior with saturation magnetization values between 58 and 66 emu g$^{-1}$. The UV–vis diffuse reflectance (UV–vis DRS) analysis revealed that the band gap energy is increased (blue shift) with decrease of particle size. The nitrogen adsorption-desorption analysis shows that CNAs are meso and microporous with a specific surface area from 71.68 to 92.92 m$^2$g$^{-1}$. The reaction time and different amounts of anhydrous sodium acetate (NaAc) influence the crystallinity, size, magnetic property and surface area of the ZnFe$_2$O$_4$ CNAs.

1. Introduction

In recent decades, significant progress has been made in chemical synthesis of zinc ferrite nanoparticles owing to their great potential applications in the fields of magnetic materials [1], lithium–ion batteries [2], ferrofluids [3], photocatalysts [4], gas sensors [5], microwave absorption [6], catalysts [7], adsorbents [8] and catalyst supports [9]. A wide variety of applications, such as building sensors or computer chips, where the self-assembly of nanoparticles can be useful. In recent years, the self-assembly of small primary nanoparticles into microspherical structures has attracted considerable attention because of their unique properties compared to their primary building blocks [10].

Self-assembly is a powerful method for producing ensembles of inorganic nanoparticles. Ensemble of nanoparticles exhibits collective properties not present in individual nanoparticles. Assembling nanoparticles displays new electronic, magnetic and optical properties due to interactions between nanoparticles [11]. In addition, for biomedical applications such as drug delivery [12], magnetic resonance imaging (MRI) [13], hyperthermia agents [14], superparamagnetic behavior of nanoparticles would be necessity. However, superparamagnetic iron series nanoparticles have a low saturation magnetization (Ms) which limits their usage in many important applications. To increase Ms, the size of nanocrystals can be increased, but the transformation from superparamagnetic to ferromagnetic behavior occurs at a critical size. Assembling these nanoparticles into colloidal nanoparticle clusters has proved to be a way to retain superparamagnetic behavior with high saturated magnetization [15].

The synthesis and assembly of ZnFe$_2$O$_4$ nanoparticle can be carried out by using various methods including solvothermal [16], sol-gel [17], co-precipitation [18], hydrothermal [19], template [20], etc. Hu et al [21] prepared microporous zinc ferrite by a hydrothermal method using triethylamine as a template. Zhang et al [22]...
prepared ZnFe₂O₄ nanochains using a carbon nanotubes (CNTs) template. Templating methods for the synthesis of nanoparticle assemblies are tedious and time-consuming; therefore, it is important to explore template-free preparation methods which are much simpler and more cost effective. Among these methods of synthesis, the solvothermal method has attracted great attention due to excellent magnetism, high yield, simple setups, crystal stability, purity and easy-to-control morphology of the products [23]. In solvothermal synthesis, various experimental parameters such as reaction time, temperature, solvent, and electrostatic stabilizer can be easily adjusted to provide a desirable nanostructure.

Time is one of the parameters that has been studied in the synthesis of nanoparticles. Wang et al [24] showed that the size of the nickel ferrite nanoparticles increases from 90 nm to 180 nm by increasing the reaction time from 6 to 48 h. Huang et al [25] have also demonstrated that magnetite particles varied from 326 to 447 nm when the reaction time was increased from 6 to 24 h.

The amount of sodium acetate is another experimental parameter that affects the size and morphology of nanoparticles. For example, Fe₂O₄ clusters show superparamagnetic behavior with Ms between 74.3–77.4 emu g⁻¹, in which the size of clusters can be adjusted in the range of 208–381 nm by controlling the concentration of sodium acetate in reaction mixture [26]. He et al [27] showed that in the synthesis of hollow or mesoporous magnetite (Fe₃O₄) nanoparticles, anhydrous sodium acetate serves as a structure-directing agent. NaAc plays an important role in the formation of Fe₃O₄ micro-particles, serving not only as an alkaline, but also as an electrostatic stabilizing agent to prevent particle agglomeration [28]. The effect of the amount of NaAc as protecting reagent on the morphology and size of nickel ferrite nanoparticles has also been reported [24]. Solvothermal synthesis of colloidal nanocrystal clusters of about 450 nm average size and Ms of 25.4 emu g⁻¹ has been reported by Guo et al [15], in which the molar ratio of FeCl₃·6H₂O to NaAc is 2:10. Using solvothermal process, Zhu et al [29] have been synthesized porous ZnFe₂O₄ microspheres with a size of 200 nm and Ms of 37.6 emu g⁻¹. The molar ratio of FeCl₃·6H₂O to NaAc is 2:3. Through solvothermal process, Wang et al [30] could prepare ZnFe₂O₄ nanocrystal clusters with narrow size distribution of 276 nm in diameter by using polyethylene glycol as a surfactant, in which the molar ratio FeCl₃·6H₂O to sodium acetate is 2:6. These studies showed that the molar ratio of FeCl₃·6H₂O to sodium acetate affects the size and different properties of the as-prepared zinc ferrites. Until now, various surfactants, precipitating agents and solvents have been used to synthesize ZnFe₂O₄ CNAs of different sizes, but controlling the size is a challenge for their practical applications.

In our synthesis, the effects of reaction time and different amounts of anhydrous sodium acetate on the size, morphology, magnetic property and surface area of ZnFe₂O₄ CNAs have been investigated. We report that the size of ZnFe₂O₄ CNAs can be adjusted in the range of 312–346 nm by controlling the molar ratio of FeCl₃·6H₂O to NaAc (4: 20, 32, 44) in the starting systems.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate (FeCl₃·6H₂O, 99%), Zinc chloride (ZnCl₂, 99%), anhydrous sodium acetate (CH₃COONa), ethylene glycol (EG) and ethanol were purchased from Merck Company. Double distilled water was used in all the experiments, and all the chemicals were of analytical grade and were used as received.

2.2. Synthesis of ZnFe₂O₄ CNAs

4 mmol FeCl₃·6H₂O and 2 mmol ZnCl₂ were dissolved in 36 ml of EG, and then an appropriate amount of CH₃COONa (20, 32 and 44 mmol) was added to the mixture under vigorous stirring. The homogeneous mixture was sealed in a Teflon-lined autoclave (80 ml capacity) and was maintained in an oven at 200 °C for 5 h. The autoclave was then cooled to room temperature naturally. The black products were collected using a magnet and were washed several times with distilled water and ethanol. At last, the products were dried in an oven at 60 °C for 12 h. Furthermore, this experiment was carried out at 8, 12 and 24 h.

2.3. Material characterizations

The morphology and size nanoparticles were observed by a KYKY EM3900M scanning electron microscopy (company: KYKY, Beijing, China) and Mira3-XMU Field emission scanning electron microscopy (FE-SEM, Manufacturer: TESCAN). The structure and phase composition were determined by a D8 advance Bruker x-ray diffractometer (Manufacturer: Bruker AXS) equipped with Cu Kα radiation (λ = 0.15418 nm) from 10 to 80° (2θ). Magnetic measurements of samples were obtained by a vibrating sample magnetometer (VSM, Meghnatis Daghigh Kavir Co; Iran) at room temperature. The structure of ZnFe₂O₄ CNAs was confirmed by FT-IR spectroscopy. Fourier transform infrared spectra were recorded on an FT-IR JASCO 680-PLUS spectrometer in the region of 400–4000 cm⁻¹ using KBr pellets. The UV–vis diffuse reflectance spectra (UV–vis DRS) were obtained with an Avantes model of Avaspec-2048-TEC with Ava Lamp DH-S Setup (company in Apeldoorn, Netherlands).
Netherlands). BaSO₄ was used as reference material. N₂ adsorption–desorption was performed by Brunauer–Emmett–Teller (BET) measurements using a Belsorp Mini II (BEL company, Japan) surface area analyzer. The pore size distribution was derived from the adsorption branch using the Barrett–Joyner–Halenda (BJH) method.

3. Results and discussion

3.1. Effect of sodium acetate (NaAc)

In order to investigate the effect of the amount of sodium acetate on the size, morphology, surface area and magnetization of final products, three experiments with different amounts of NaAc adding (20 mmol, 32 mmol, 44 mmol) are carried out. Other experimental parameters such as the amount of reactants (4 mmol FeCl₃.6H₂O and 2 mmol ZnCl₂), reaction duration (12 h) and temperature (200 °C) are fixed.

The XRD patterns of ZnFe₂O₄ CNAs obtained with different amounts of NaAc are shown in figure 1. All the reflection peaks can be indexed as ZnFe₂O₄ CNAs in a face-centered cubic (fcc) phase (JCPDS Card Files, No. 089-1009). The average crystallite sizes of ZnFe₂O₄ primary nanoparticles were approximately 12.2, 11.1 and 10.0 nm for the samples synthesized using 20, 32 and 44 mmol of NaAc, respectively. These values were calculated by measuring the (311) peak widths of the x-ray diffraction lines according to the Debye–Scherrer equation [31]. There is only a slight decrease in crystalline size with an increase in the amount of sodium acetate, indicating that sodium acetate acts as a protecting reagent for the resulting zinc ferrite nanocrystals [24].

The SEM images of synthesized ZnFe₂O₄ CNAs are presented in figure 2. As shown in these SEM images, all samples showed well-separated spherical structures with different sizes. The average size of samples synthesized with different amounts of sodium acetate (20, 32, 44 mmol) is 345.17, 340.81 and 312.83 nm, respectively. The results indicate that the size of ZnFe₂O₄ CNAs decreases gradually as the amounts of the NaAc increase; therefore, the NaAc acts as an electrostatic stabilizing agent to prevent the agglomeration of the primary magnetic nanoparticles in the reaction system. As a result, the amount of NaAc can control the size of synthesized ZnFe₂O₄ CNAs in the reaction. The elemental composition of the samples was investigated using EDAX (figure 2(d)). It demonstrates the presence of Zn, Fe and O in the ZnFe₂O₄ CNAs synthesized using 20 mmol NaAc. The EDAX result shows that the obtained product is pure ZnFe₂O₄ CNAs. Figure 2(e) shows the FE-SEM image of product obtained by using 20 mmol NaAc. It can be seen that each ZnFe₂O₄ microsphere is constructed of a large number of ZnFe₂O₄ nanocrystals and there are voids and interspaces between the nanoparticles.

The formation of spinel ZnFe₂O₄ structure in the as-synthesized zinc ferrite CNAs is supported by FT-IR analysis. Figure 3(A) shows the FT-IR spectra of samples. The broad absorption band at about 3419–3422 cm⁻¹ and the band at 1610–1615 cm⁻¹ could be attributed to the O–H stretching and bending vibrations of H₂O and EG molecules, which remain and are attached to the surface of zinc ferrite microparticles [28]. The strong absorption band of ~579 cm⁻¹ in all samples is assigned to Fe–O stretching vibrations, indicating that there is no change in peak position with increasing sodium acetate content. Furthermore, the absorption band in around 460 cm⁻¹ is ascribed as the stretching mode of Zn–O bonds [32].

The magnetic properties of all the synthesized ZnFe₂O₄ CNAs were investigated by VSM measurement. Figure 3(B) shows magnetization curves of ZnFe₂O₄ CNAs at room temperature. Samples exhibit negligible coercivity and remanence, suggesting superparamagnetic behavior.
All magnetic parameters such as saturation magnetization \(\text{Ms} \), coercivity \(\text{Hc} \), retentivity \(\text{Mr} \) and squareness ratio \(\text{Mr}/\text{Ms} \) values are listed in table 1. The values of saturation magnetization \(\text{Ms} \) were measured to be 66.71, 58.46 and 66.52 emu g\(^{-1}\) for samples obtained using NaAc 20, 32 and 44 mmol, respectively. The large value of magnetization observed in this work shows that the cation distribution changed from normal to mixed spinel type. Therefore, some of Fe\(^{3+}\) ions occupy both A- and B-sites, leading to the formation of two magnetic sub-lattices. Super-exchange interaction between Fe\(^{3+}\) ions on two sub-lattices is much longer than Fe\(^{3+}\) ions interaction in the B-site \[33\]. The values of \(\text{Mr}/\text{Ms} \) of all the samples are significantly lower than 0.5. Therefore, the particles interact by magneto-static interactions \[34\].

In order to study the optical absorption properties of ZnFe\(_2\)O\(_4\) CNAs, UV–vis diffuse reflectance spectroscopy (UV–vis DRS) is performed. The optical band gap energy of samples is also determined by UV–vis DRS analysis. Figure 4(A) shows the UV–vis diffuse reflectance of the ZnFe\(_2\)O\(_4\) CNAs synthesized with different amounts of sodium acetate (20, 32 mmol).
The diffuse reflectance values were converted to absorbance by applying the Kubelka–Munk function,

\[ F(R_\infty) = \left( 1 - R_\infty \right)^2 / 2R_\infty, \]

where \( R_\infty \) is the diffuse reflectance of the examined samples. \( R_\infty = R_{\text{sample}} / R_{\tan \text{ data}} \). The \( F(R) \) curves of the samples are also shown in figure 4(B). As seen from the spectra, a broad peak in the around 400–450 nm is observed for both the samples. Guo et al. [35] have reported that in ZnFe\(_2\)O\(_4\) the valance bands are mainly composed of O 2p, Zn 3d and Fe 3d states, while the conduction bands are dominated by Fe 3d states. Zn\(^{2+}\) has completely filled 3d\(^{10}\) configuration and Fe\(^{3+}\) is d\(^5\) high spin. Thus, this absorption band might be due to the photoexcited electron transition from O 2p level as the valence band into Fe 3d level as the conduction band [36].

To calculate the bandgap, Tauc plots and the Kubelka-Munk (K-M) function were used. The Tauc plot is a method that is widely used for the determination of band gap. The absorption coefficient (\( \alpha \)) in the Tauc equation is substituted with \( F(R_\infty) \). Thus, for allowed direct transitions, the relational expression becomes:

\[ (F(R_\infty)h\nu)^2 = A(h\nu - E_g) \]

Where \( A \) is a constant, \( E_g \) is the band-gap energy in eV, \( h\nu \) is the photon energy in eV. Then, the direct band gap of samples were obtained from a plot of the \( (F(R_\infty) \ h\nu)^2 \) versus \( h\nu \) extrapolating the linear portion of the curve to the x-axis [37]. The computational results of Yao et al. [38] show that ZnFe\(_2\)O\(_4\) acts as a direct band gap semiconductor. The direct band gap of ZnFe\(_2\)O\(_4\) CNAs are shown in figure 4(C). The direct band gap energies for the samples are found to be 2.05 and 2.15 eV for the samples synthesized with different amounts of sodium acetate 20 and 32 mmol, respectively, which are blue shifted when compared with the bulk band gap value of 1.9 eV. Furthermore, the results show that the band gap energy (\( E_g \)) increases with decrease in the particle size of ZnFe\(_2\)O\(_4\) CNAs, which can be attributed to the quantum size effect [39]. The quantum size effect is known as the blue shift of the band gap energy with decrease of particle size. Moreover, additional sub band gap might be ascribed to the abundant surface and interface defects in the agglomerated nanoparticles [40]. The synthesized

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**Table 1.** Effect different amounts of NaAc on the magnetic properties of the as-prepared zinc ferrite.

| NaAc mmol | Ms emu.g\(^{-1}\) | Mr emu.g\(^{-1}\) | Mr/Ms | Hc Oe |
|-----------|-----------------|-----------------|-------|-----|
| 20        | 66.71           | 0.42            | 0.0048| 3.67|
| 32        | 58.46           | 0.30            | 0.0043| 3.15|
| 44        | 66.52           | 0.38            | 0.0059| 3.32|

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**Figure 3.** FT-IR spectra (A) and magnetization hysteresis curves (B) of ZnFe\(_2\)O\(_4\) CNAs prepared with different amounts of NaAc (a) 20 mmol, (b) 32 mmol, and (c) 44 mmol.

**Figure 4.** (A) Diffuse reflectance (%R) spectra, (B) Kubelka-Munk absorption curves and (C) band gap of ZnFe\(_2\)O\(_4\) CNAs prepared with different amounts of NaAc (a) 20 mmol and (b) 32 mmol.
products have good absorption in the visible region. Therefore, these are potential candidates for photocatalytic activities or photodegradation.

To further investigate the porous structure and surface area of ZnFe$_2$O$_4$ CNAs, N$_2$ adsorption–desorption analysis was performed. As plotted in figures 5(a), (b), the recorded isotherms are a combination of type I and IV isotherms according to the IUPAC classification. Such a type of isotherm may indicate the presence of both mesopores and micropores. The measured specific surface areas were 71.68, 72.79 and 77.95 m$^2$ g$^{-1}$ for the ZnFe$_2$O$_4$ CNAs synthesized using 20, 32, 44 mmol NaAc, respectively. These data suggest that the BET surface area of ZnFe$_2$O$_4$ CNAs slightly increased with an increase in anhydrous sodium acetate. Furthermore, the pore size distribution analysis was performed by using the Barrette-Joynere-Halenda (BJH) method as shown in the insets of figures 5(a), (b). From the figures, it can be seen that the samples have mesopores of 2 to 10 nm radius. Moreover, they have a distribution peak at 1.29 nm suggesting the microporous nature. Therefore, the gas adsorption behavior of samples shows a combination of microporous and mesoporous.

The t-plot method is commonly used to determine the external surface area and micropore volume of microporous materials. In t-plot of ZnFe$_2$O$_4$ CNAs (figures 5(c), (d)), two different slopes are observed. One of which is a sharp slope passing the original point and the other is a more gradual slope, meaning that the adsorbent has homogeneous sized micropores [41]. The classical way to determine the microporous volume is to extrapolate line S$_2$ in figures 5(c)–(d) and to take the intercept as the microporous volume. In the figures, there is a red circle around this point. The specific surface area (a$_1$) can be obtained using the slope of straight line S$_2$. Moreover, using the slope of straight line S$_1$, the external surface area (a$_2$) can be calculated. Pore surface area can be calculated by subtracting a$_2$ from a$_1$. Volume and area of micropores are given in table 2. These results indicate that with an increase in sodium acetate content, the volume and area of micropores have increased. Moreover, the BET surface area increases with an increase in volume and area of micropores. This increase in surface area and pore volume amount can be attributed to the fact that smaller grain assembly possesses more channels.

### 3.2. Effect of reaction time

In order to investigate the effect of the reaction time on the products, four experiments under different reaction times (5, 8, 12 and 24 h) are carried out. Other experimental parameters such as the amount of reactants (4 mmol FeCl$_3$·6H$_2$O, 2 mmol ZnCl$_2$ and 20 mmol NaAc) and temperature (200 °C) are fixed.
The XRD patterns of ZnFe$_2$O$_4$ CNAs at different times (5, 8, 12 and 24 h) are presented in figure 6. Distinct diffraction peaks of all the samples matched well with the cubic spinel structure of ZnFe$_2$O$_4$ (JCPDS No. 089-1009). Using the Scherrer equation, the crystallite sizes were calculated from the (311) peaks to be about 8.3 nm, 13.9 nm, 12.9 nm, and 13.2 nm for synthesized samples at reaction times 5, 8, 12 and 24 h, respectively. The results show that the size of crystallites increased as the reaction time increased from 5 to 8 h, but by increasing the time from 8 to 24 h, the crystallite size was not significantly altered because the part of the product is still amorphous at 5 h and completely crystalline after 8 h. Moreover, during the reaction, some glycol and its oligomer can be absorbed into the surface of the crystallites and form an organic layer that prevents the growth of crystallites. Therefore, the crystallite size does not increase significantly [42]. Furthermore, the diffraction peaks become sharper with reaction time extended from 5 to 24 h, indicating enhanced crystallinity.

The shape and size of the synthesized ZnFe$_2$O$_4$ CNAs were determined by SEM measurement. The SEM images of samples obtained at reaction time 5, 8 and 12 h are presented in figures 7(a)–(c), respectively. The SEM images reveal that all CNAs exhibited monodispersed spherical structures with different sizes. Figure 7(d) shows the surface morphology of the ZnFe$_2$O$_4$ CNAs obtained at 24 h investigated by FESEM. As shown in figure 7(d), the sample has a spherical structure with a diameter of 284.23 nm. The FESEM image of a single microsphere (figure 7(e)) demonstrated that the microspheres are self-assembled by numerous interconnected nanoparticles. The thermodynamic driving force for self-assembly of nanoparticles can be attributed to electrostatic interactions and van der Waals forces [43]. In addition, attachments among the primary nanoparticles reduces their high surface energy.

The energy dispersive x-ray spectroscopy (EDAX) measurement was performed to determine the elemental composition of synthesized CNAs. The result of EDAX analysis with color mapping is presented in figure 8 for the sample obtained at 24 h, indicating the presence of Zn, Fe and O elements.

The average colloidal particle sizes at various reaction times of 5, 8, 12 and 24 h are summarized in table 3. It is seen in the table that the size of particles increased with the elongation synthesis time from 5 to 12 h (due to Ostwald ripening) [44]. Ostwald ripening refers to the solution process in which smaller particles are dissolved and deposited on the larger ones. However, when the reaction time increased to 24 h, their sizes decreased to 284.24.

The FT-IR spectra were recorded to identify the functional groups available on the surface of ZnFe$_2$O$_4$ CNAs. Figure 9 shows the FT-IR spectra of samples. The broad band in the range 3401–3434 cm$^{-1}$ and the band at 1610–1619 cm$^{-1}$ were attributed to O–H stretching and bending vibrations of molecular water and ethylene glycol on the surface of zinc ferrite microparticles. The peaks at ~1073 and ~885 cm$^{-1}$ are related to C–O stretching vibrations and –CH$_2$ rocking vibrations of ethylene glycol molecules, respectively [45]. The weak bands around at 2986, 2862 and 1416 cm$^{-1}$ are attributed to the stretching and bending vibrations of C–H bond; and the strong and broad absorption bands in the range 579–587 cm$^{-1}$ are assigned to the Fe–O stretching vibrations. Furthermore, the absorption band in around 460 cm$^{-1}$ is ascribed as the stretching modes of Zn–O bonds. In our study, the absorption bands for Fe–O were observed at ~587, ~584, ~579 cm$^{-1}$ for nanoparticles.

| Sodium acetate dosage (mmol) | BET surface area (m$^2$g$^{-1}$) | Micropores volume (cm$^3$g$^{-1}$) | Micropore area (m$^2$g$^{-1}$) |
|-----------------------------|---------------------------------|---------------------------------|-------------------------------|
| 20                          | 71.68                           | 28.265                          | 54.45                         |
| 32                          | 72.80                           | 28.160                          | 55.73                         |
| 44                          | 77.96                           | 34.588                          | 70.83                         |

Figure 6. XRD patterns of ZnFe$_2$O$_4$ CNAs obtained at synthetic times of 5, 8, 12 and 24 h.
synthesized at 5, 8 and 12 h, respectively. According to previous results, particle size is increasing from \( \sim 294 \) nm to \( \sim 345 \) nm with an increase in the reaction time from 5 to 12 h. Hence, as the particle size increases, the decrease in frequency can be observed [46].

The magnetic properties of ZnFe₂O₄ CNAs obtained at the times of 12 and 24 h are studied by VSM. Figure 10(A) shows hysteresis loops of samples at the full scale measured at room temperature. In the partial enlarged drawing of the full scale (figure 10(B)), samples show very small coercivity at this temperature, confirming the superparamagnetic behavior of samples. The values of saturation magnetization (Ms) were measured to be 66.71 and 63.45 emu g⁻¹ for ZnFe₂O₄ CNAs obtained at synthesis time 12 and 24 h, respectively. This magnetization value is good and higher than the reported values for ZnFe₂O₄ CNCs (25.4 emu g⁻¹) at room temperature [15].
All magnetic parameters such as saturation magnetization ($M_s$), remanence magnetization ($M_r$), coercivity ($H_c$) and squareness ratio ($R = M_r/M_s$) values are listed in table 4. We can see that saturation magnetization decreases as the sizes of particles become smaller. The decrease in the saturation magnetization is most likely attributed to the surface distortion, magneto-crystalline anisotropy and defects within the lattice.
Diffuse reflectance spectra of samples synthesized at reaction times of 5 and 12 h are shown in figure 11(A). The F(R) curves of the samples are also shown in figure 11(B). As seen from the spectra, a peak at 400–450 nm is observed for both the samples. This broad band may be ascribed to charge transfer transition from O 2p level as the valence band into Fe 3d level as the conduction band in ZnFe2O4 spinel.

The direct band gap energies for the samples are found to be 2.22 and 2.10 eV for the samples synthesized at times of 5 and 12 h, respectively (figure 11(C)). The results show that the band gap energy decreases with increase of reaction time due to increase in the particle size of ZnFe2O4 CNAs. It can be attributed to the quantum size effect in ZnFe2O4 nanoparticles.

The as-prepared ZnFe2O4 CNAs exhibit a porous nature, which has been examined by N2 adsorption-desorption technique. Figure 12 shows the adsorption-desorption isotherms of the ZnFe2O4 CNAs prepared at 200 °C by using 20 mmol NaAc at 12 and 24 h. According to the IUPAC classification, the recorded isotherms are intermediate between the type I and IV, which indicate the presence of both mesopores and micropores [47]. At relatively high pressures a narrow hysteresis loop appears that is attributed to the mesoporous structure.

The results of BET surface area, volume and area of micropores of synthesized zinc ferrite are listed in table 5. It can be clearly seen that the sample obtained at time 24 h shows a higher surface area than other samples. This increase in specific surface area may come from the small size of CNAs [48].

In addition, the corresponding Barrett–Joyner–Halenda (BJH) analyses show that the cumulative pore volumes are 0.1132 and 0.124 cm3 g⁻¹ for samples obtained using times 12 and 24 h. From the insets of figures 12(a), (b), it can be seen that these samples have mesopores of 2 to 10 nm radius.

In t-plot of ZnFe2O4 CNAs (figure 12(c), (d)) two different slopes are observed, meaning that the adsorbent has homogeneous sized micropores [41]. Hence, the gas adsorption behavior of samples shows a combination of
microporous and mesoporous. The experimental results are shown in Table 5, indicating that the BET surface area increases with an increase in volume and area of micropores.

3.3. Possible formation mechanism of ZnFe$_2$O$_4$ microspheres with tunable sizes

To investigate the formation process of the ZnFe$_2$O$_4$ microspheres, time-dependent experiments were carried out. The experimental results show that after 2 h of solvothermal treatment, the product was a light brown suspension with no black precipitate, indicating that the reaction rate was slow. When the synthesis time was increased to 5 h, the black precipitate was obtained. In SEM image (Figure 7(a)), it can be clearly seen that spherical particles, with diameters of 294.99 nm, were fabricated. Energy dispersive x-ray (EDX) analysis confirms that only Fe, Zn and O elements were contained in these spheres. The XRD pattern of this black precipitate belongs to spinel ZnFe$_2$O$_4$. As the synthesis time is increased to 8 and 12 h, the spherical structures are grown. The FE-SEM image (Figure 7(e)) shows that each ZnFe$_2$O$_4$ microsphere was composed of many ZnFe$_2$O$_4$ nanocrystals. In addition, XRD analysis (Figure 6) shows that as the reaction progresses, the diffraction peaks become sharper, indicating that the crystallinity of the products has increased.

On the basis of the experimental results, the formation mechanism of the ZnFe$_2$O$_4$ microspheres can be proposed in two stages. In the first stage, ZnFe$_2$O$_4$ nanocrystals were synthesized and aggregated to spherical particles by a dominant oriented attachment process. But, in the following stage, the growth of ZnFe$_2$O$_4$ microparticles is dominated by the Ostwald ripening process.

The first stage of growth, which involves the formation of microspheres, may have the following reactions.

Nucleation is the first step of the formation process where the small ZnFe$_2$O$_4$ nanocrystals are formed. In the next stage, the growth of the microspheres occurs through the Ostwald ripening process. This process involves the diffusion of ions from larger particles to smaller particles, leading to the formation of larger, more stable microspheres. The growth of the microspheres is controlled by the diffusion rate of the ions, which is influenced by factors such as temperature, concentration, and surface tension. A high concentration of ions leads to faster growth rates, while a low surface tension facilitates the diffusion of ions, resulting in faster growth rates.

### Table 5. BET surface area, volume and area of micropores of synthesized zinc ferrite.

| Time (h) | BET surface area (m$^2$ g$^{-1}$) | Micropores volume (cm$^3$ g$^{-1}$) | Micropore area (m$^2$ g$^{-1}$) |
|----------|----------------------------------|-----------------------------------|-------------------------------|
| 12       | 71.68                            | 28.265                            | 54.45                         |
| 24       | 92.92                            | 39.461                            | 82.25                         |

Figure 12. Nitrogen adsorption/desorption isotherms (a), (b), pore size distribution (inset of (a), (b)) and t-plot (c), (d) of ZnFe$_2$O$_4$ CNAs synthesized by using 20 mmol NaAc at 12 h (a), (c), and 24 h (b), (d).
synthesis of ZnFe$_2$O$_4$ CNAS, it has been suggested that the presence of crystalline water in the FeCl$_3$.6H$_2$O causes the hydrolysis of sodium acetate. Hydrolysis of sodium acetate creates an alkaline environment in the solution. The alkaline condition leads to the formation of Fe(OH)$_3$ and Zn(OH)$_2$ due to the hydrolysis of Fe$^{3+}$ and Zn$^{2+}$ ions, which will be transformed into ZnFe$_2$O$_4$ primary nanocrystals via dehydration process under high temperature [28]. Moreover, Zhong et al [49] have been reported that ethylene glycol might coordinate with metal ions to produce metal alkoxide, which precipitated to become the nuclei and quickly grew into the primary particles. On the other hand, the thermal decomposition of the chelates might produce water into the system, which led to increasing hydrolysis of metal ions. Secondly, with the elongation of synthesis time, the large ZnFe$_2$O$_4$ nanocrystals were gradually formed and assembled to porous microspheres by self-assemble, as shown in figure 7(e). At this stage, oriented attachment is considered as the main mechanism. In the oriented attachment growth, the primary crystal particles with the common crystallographic orientation collide and directly combine together to form larger secondary crystals [50]. Finally, the microspheres continued to grow. At this stage the growth of ZnFe$_2$O$_4$ microparticles is dominated by the Ostwald ripening process. Furthermore, based on the Oswald mechanism, smaller inner crystallites dissolve and recrystallize on the exterior of the spheres, which can be confirmed by increasing particle size. The findings suggest that the mass transfer is due to the pores in the microspheres (confirmed by the BET analysis), which are the communication channels between the interior of the microsphere and the outer space of solution.

In addition, the XRD measurements confirm the secondary structure of ZnFe$_2$O$_4$ CNAs. Figure 6 shows XRD patterns with almost identical broadenings for ZnFe$_2$O$_4$ CNAs of different sizes. The average grain sizes of primary nanoparticles are 8.3, 13.9, 12.9 and 13.2 nm for CNAs with sizes of 294.99, 314.03, 345.17 and 284.24 nm, respectively, this indicates that the primary nanocrystals do not grow significantly with increasing size of ZnFe$_2$O$_4$ CNAs.

4. Conclusions

In summary, the ZnFe$_2$O$_4$ self-assembled submicrospheres were synthesized with different sizes in a controlled manner using a solvothermal method. Different amounts of sodium acetate and reaction time affect the size, surface area and magnetic properties of as-obtained ZnFe$_2$O$_4$ CNAs. By varying the amount of sodium acetate, the size of the ZnFe$_2$O$_4$ CNAs can be controlled between 312 and 345 nm. Experimental data show that these ZnFe$_2$O$_4$ CNAs are formed from the \textit{in situ} self-assembly of small primary nanoparticles. The results of UV–vis diffuse reflectance of the ZnFe$_2$O$_4$ CNAs synthesized with different amounts of sodium acetate show that the band gap energy ($E_g$) increases as particle size of the ZnFe$_2$O$_4$ CNAs decreases, which can be attributed to the quantum size effect. VSM results demonstrated the superparamagnetic behavior of the synthesized samples at room temperature, which might be potentially applied in biomedical fields such as targeted drug delivery, magnetic resonance imaging, cancer diagnosis, and treatment. A possible formation process of the ZnFe$_2$O$_4$ CNAs microparticles was discussed.

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