



International Journal of Engineering, Business and Enterprise Applications (IJEBA)

(Open Access, Double Blind Peer-reviewed, Refereed and Indexed Journal)

www.iasir.net

Investigation on Morphologies, Forming Mechanism, Photocatalytic and electronic Properties of Co-Zn ferrite Nanostructure grown on the reduced graphene oxide support

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Abstract: Graphene sheets are promising nanoscale building blocks as a support material for the dispersion of nanoparticles. In this work, a solvothermal method employed to directly grow $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite nanospheres on graphene oxide support that is subsequently reduced to graphene. The samples morphology, structure and crystallography were investigated using field-emission scanning electron microscopy (FE-SEM) and powder X-ray diffraction (XRD). The influences of the Zn^{2+} content on photocatalytic activity, electrical conductivity and magnetic property of the samples are also investigated. The results showed that $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles are dispersed on graphene sheets and obtained nanocomposites are soft magnetic materials. In addition the samples showed excellent photocatalytic activity under visible light irradiation.

Keywords: reduced graphene oxide; ferrite; magnetic nanocomposite; photocatalytic activity; solvothermal method

I. Introduction

One of the most exciting classes of nanomaterial is represented by the graphene. Graphene by the definition is a two dimensional sheet of sp^2 bonded carbon atoms arranged in a honeycomb lattice [1, 2]. Although, graphene by the definition is a single layered structure samples with two or more but less than ten layers are also desirable [3]. Based on its excellent performances, graphene and its products have been regarded as a promising component for synthesizing various composites [3-7]. In particular, its large surface area and tuneable surface properties allocate graphene to be a competitive host substrate for the heterogeneous growth of desired active guest materials [4,7]. This is because of the presence of functional groups such as hydroxyl and epoxide groups on the surface of graphene and especially graphene oxide (GO) [8] which acts as favourable nucleation sites for guest materials. Iron containing metal oxide phases has been subjected of extensive investigations due to their unique magnetic, magneto optical, magneto resistive, thermal and electrical properties [9]. Ferrimagnetic cubic spinels namely ferrites are large class of metal oxide with remarkable magnetic properties which have investigated during the last 50 years [10,11]. Among spinel ferrites, cobalt ferrites ferrite has attracted many attentions due to its large magnetic multi axial anisotropy, moderate saturation magnetizations, high Curie temperature and remarkable chemical stability [12,13,14]. The magnetic and electrical properties of spinel ferrites could be easily tuned by suitable additions of divalent or trivalent cations in the spinel structure. Substitution of non - magnetic ions at either sites alters the A-A or B-B and A-B interactions, which can lead to a significant change in their physical properties. It is well known that Zn substitution in a spinel type of ferrite increase its saturation magnetization and decreases its coercivity [15]. Incorporation of a certain amount of Zn^{2+} ions in the spinel structure of cobalt ferrites make a new structure that is called Co-Zn spinel ferrites ($\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$) (fig.1d). $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ have attracted considerable attention because of its high sensibility of magnetization to temperature, magneto-optical properties and broad applications in diagnostic and cancer therapy, magnetic drug delivery, microwave devices, photonics crystal and high density information storage systems [16-21]. Recently, the photocatalytic activity of $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ nano particles under visible light irradiation was investigated [21]. It was revealed that, compared to conventional photocatalysts such as TiO_2 and ZnO , $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ samples exhibited appreciable photocatalytic activity in the degradation of methylene blue under visible light irradiation. The little band gap of $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ (1.73-1.9 eV) allows it to be photocatalytically active in the visible light region, while photocatalytic activity of TiO_2 and ZnO is limited to wavelengths below the visible light region due to their relatively large band gap (3.2 eV). In addition, $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles have a magnetic property, which makes themselves magnetically separable in a suspension system. With considering this fact that the solar energy is a renewable resource and UV region occupies only around 4% of the sunlight, while

45% of the solar energy belongs to visible light[22], it is necessary to develop high-performance visible light photocatalysts. Since, high electrical conductivity of the graphene is valuable for promoting electron transfer in photocatalytic reactions, the magnetically functionalized graphene composites attracted tremendous attention in recent years. Y. Fu et al. [23] made graphene/MnFe₂O₄ composite via a solvothermal method in ethanol solution. This composite showed the significant enhancement in photocatalytic activity under visible light irradiation. Y. Fu et al [22] reported that graphene/ZnFe₂O₄ composite serves a dual function as the catalyst for photoelectrochemical degradation of MB and the generator of a strong oxidant hydroxyl radical via photoelectrochemical decomposition of H₂O₂ under visible light irradiation.

In this work rGO/Zn_xCo_{1-x}Fe₂O₄ magnetic nanocomposites with tunable magnetic, electrical and photocatalytic properties are prepared via a solvothermal method. Therefore, four samples of thermally reduced graphene oxide (TrGO)/Zn_xCo_{1-x}Fe₂O₄ with different composition ($x=0.3, 0.4, 0.5, 0.6$) were prepared and the influence of Zn²⁺ content on the structure, magnetic and electrical property and also photocatalytic activity of the samples were investigated.

II. EXPERIMENTAL

A. Materials

All the chemical reagents: ferric chloride hexa hydrate FeCl₃·6(H₂O), cobalt nitrate hexa hydrate Co(NO₃)₂·6(H₂O), zinc nitrate tetra hydrate Zn(NO₃)₂·4(H₂O), ethylene glycol (EG), polyethylene glycol (PEG), hydrogen peroxide H₂O₂, graphite powder, anhydrous sodium acetate, ortho-phosphoric acid H₃PO₄, sulphuric acid H₂SO₄, potassium permanganate KMnO₄, hydrochloric acid HCl were purchased from Merck and used as received without further purification.

B. Preparation of graphene oxide

Graphite oxide was synthesized according to the modified Hummer's method [24] that is claimed to produce GO flakes with lower C/O but less structural defects compared with the ordinary Hummer's method. A mixture of concentrated H₂SO₄:H₃PO₄ (240:26.7 ml) was added to a mixture of graphite powder: KMnO₄ (2:12 g). Then, the reaction was heated to 50°C and stirred for 14 hr. later, the reaction was cooled to ambient temperature and poured on to 270 mL ice along with 30% H₂O₂ (2 mL). For work up, the mixture was centrifuged and the supernatant was decanted away. The remaining solid material washed for three times in 200 mL of water, 200 mL of 10% HCl and 200 mL of ethanol, respectively. Finally, the product was washed with deionized water until the pH reached to 7, then dried in the vacuum to give a brown solid(fig.1a)

C. Growth of Co_xZn_{1-x}Fe₂O₄ on graphene support

Four rGO/Co_xZn_{1-x}Fe₂O₄ samples with different stoichiometry ($x=0.4, 0.5, 0.6$ and 0.7) are prepared through a solvothermal method with the same initial weight ratio of GO: Co_{1-x}Zn_xFe₂O₄ ferrite (1:1). The ferrite weight is considered as the maximum theoretical weight of ferrite that could be from the initial solution.

The typical procedure for preparation of TRGO/Co_{0.4}Zn_{0.6}Fe₂O₄ sample is as follows: 340 mg FeCl₃·6(H₂O), 73 mg Co (NO₃)₂·6(H₂O) and 112 mg Zn (NO₃)₂·4(H₂O) were added to 75 ml EG and stirred to form a transparent solution, then 2 g Na (Ac) as the alkaline agent was added and the solution stirred for an extra hour. Simultaneously, 0.15 g GO was added to 75 ml EG and ultrasonicated for 1 hr to give a stable suspension(fig.1b,c,d).

These two solutions were added to each other and stirred for 1 hr. The resulting solution was poured into a 200 mL stainless steel autoclave and maintained at 200°C for 12 hr. The mixture was cooled to ambient temperature and 100 mL of distilled water was added, then the black precipitate was magnetically separated. It was observed that during the magnetic separation procedure, the precipitate become separated into two distinguishable parts (fig. 2). A part of precipitate was easily gathered via the magnetic separation and remained at the bottom of the container, while the other part showed high tendency to float and rise in the suspension (fig.2) These two parts of precipitate were separated and washed several times with distilled water, ethanol and acetone, respectively. Finally, the products was dried at 70°C for 24 hrs to give a black powder. In order to elucidate the effect of solvothermal reaction time on the growth of Zn_xCo_{1-x}Fe₂O₄ nanoparticles on the graphene support, the above procedure was repeated by 6 and 18 hr of heating time. Also, the same method was used to synthesize rGO without adding metallic salts to initial solution.

III. Result and Discussion

A. Structural Characterization of rGO/Co_{1-x}Zn_xFe₂O₄ samples

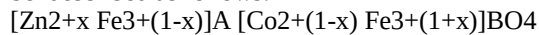
The size and morphology of rGO/Co_{1-x}Zn_xFe₂O₄ samples was observed by FE-SEM(VEGA II TESCAN). The representative FE-SEM images of as-obtained GO, TrGO and rGO/Co_{1-x}Zn_xFe₂O₄ samples are displayed in Fig. 3 and 4. It is obvious that transparent graphene flakes are exfoliated and decorated with Co_{1-x}Zn_xFe₂O₄ nano-spheres. The crystal growth of Co_{1-x}Zn_xFe₂O₄ between the GO layers lead to an increase in the interlayer

distance and consequently, the exfoliation of rGO. While, rGO sheets are highly aggregated in the absence of Co_{1-x}Zn_xFe₂O₄ ferrite nanoparticles (fig.4a,b-fig.3a).

In addition, the Co_{1-x}Zn_xFe₂O₄ particle size increased as the solvothermal reaction time increased from 12 (89-160 nm) to 18 hr (116-220 nm) (fig.3b,c). But in the case of samples that were prepared during a 6 hr solvothermal reaction, Co-Zn particles were not detectable in the FE-SEM images. Furthermore, their magnetic property was so weak. It can be seen that the floated part of precipitate is formed by the small rGO sheets and contains less amount of Co_{1-x}Zn_xFe₂O₄ ferrite particles compared with the sedimented part (fig.4c,d-fig.3d). Indeed, the magnetic property and higher density of Co_{1-x}Zn_xFe₂O₄ ferrite compared to rGO sheets is the main reason for the separation of ferrite rich part from the graphene rich part of the precipitate.

The XRD patterns of the as-prepared GO, rGO and rGO/Co_{1-x}Zn_xFe₂O₄ samples were characterized by X-ray Diffraction (Siemens D5000) and are shown in Fig. 5. Almost all the diffraction peaks of rGO/Co_{1-x}Zn_xFe₂O₄ can be assigned to spinel-type Co_{1-x}Zn_xFe₂O₄ [25, 26]. The peaks at 2θ values of 18.3, 30.1, 35.3, 43.0, 53.5, 56.3, and 62.4 can be indexed to (1 1 1), (2 2 0), (2 2 2), (3 1 1), (4 0 0), (4 2 2), (4 4 0), (5 1 1), (5 3 3) and (6 2 0) crystal planes of Co_{1-x}Zn_xFe₂O₄ phase. Peaks are assigned to (001) and (002) planes of the GO and graphene at 2θ values of 10 and 25 [25], indicating that the GO was partially reduced to graphene through the solvothermal reaction. However, no typical pattern of graphene (002) was observed in rGO/Co_{1-x}Zn_xFe₂O₄. This may be due to the fact that rGO flakes were exfoliated by the intercalated Co_{1-x}Zn_xFe₂O₄ nano particles, leading to disappearance of the diffraction peaks of graphene (002). The XRD data were used to determine lattice constant and crystallite size of the rGO/Co_{1-x}Zn_xFe₂O₄ samples.

The values of lattice constant and crystallite size are given in Table 1. The lattice constant (*a*) was calculated using inter-planar spacing (*d_{hkl}*) values and Miller indices (*h k l*) values. The lattice constant increases with rising Zn content. This may be due to the larger ionic radius of Zn²⁺ (82 pm) as compared to Co²⁺ (79 pm) and Fe³⁺ (67 pm) [26]. It is well known that zinc ions have a strong tendency to occupy A sites. The addition of Zn²⁺ ions in the reverse spinel structure of CoFe₂O₄, force Fe³⁺ ions to migrate from the A sites to the B sites that can be described as follows:



As a result, the lattice will be expanded. In order to calculate the crystallite size, the Debye-Scherrer's method was applied [27]. According to this method, the average crystallite size (*D_{hkl}*) can be determined from the half-width of the most intense peak (311).

It can be seen that increase in the zinc content leads to a gradual decrease in the crystallite size. The crystal growth of Co_{1-x}Zn_xFe₂O₄ ferrite on the rGO sheet depends on various parameters such as temperature, reaction time and composition of initial solution. In order to avoid complexities, only the effect of reaction time and Zn content are investigated in the present work.

B. Effect of Zn content and reaction time on crystal growth of Co_{1-x}Zn_xFe₂O₄

In order to investigate the effect of Zn content on crystal growth of Co_{1-x}Zn_xFe₂O₄ ferrite, four samples of rGO/Co-Zn ferrite were prepared while the only difference between the preparation conditions was the variation of Zn content in the initial solutions. During the formation of ferrite particles, near the growing crystals, temperature becomes a little higher than solution [28, 29].

This phenomenon can be explained by the liberation of latent heat at the surface of growing crystals. Since, the formation of both Co and Zn ferrite are exothermic, increasing the temperature is not thermodynamically favorable. Therefore, a little increase in the local temperature can slightly obstruct the crystal growth of ferrites. In the other hand, the formation of Zn ferrite is more exothermic as compared to Co ferrite [30]. Hence, formation of crystals that contains more amount of Zn lead to more increase in the local temperature. As a result, grain size decreases by increasing the Zn concentration. Furthermore, a rise in the local temperature will correspond to depletion the concentration of cations approaching the surface of growing crystals, hence obstructing the grain growth. The obtained results from the XRD analysis showed that the grain size slightly decreases with increasing the Zn concentration. Also, FE-SEM analyses revealed that the size distribution of ferrite particles decreases with increasing the Zn content.

In order to elucidate the effect of reaction time on crystal growth of Co_{1-x}Zn_xFe₂O₄ particles, three samples of rGO/Co_{1-x}Zn_xFe₂O₄ with the same composition, were prepared by keeping the three initial solutions at the same temperature for the various times (6, 12 and 18 hr). The solvothermal reaction slowly takes place and follows in the reaction time would provide more chance for the particles to grow. Therefore, it's expected that the size distribution of the particles increases during the reaction time. FE-SEM analyses revealed that the particle size distribution obviously improved with rising the reaction time.

C. Electrical conductivity of compacted rGO/Co_{1-x}Zn_xFe₂O₄ samples

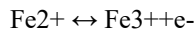
Generally, the interface between the particles offers extra resistance to charge transport, thus electrical conductivity of the individual particles is higher than bulk powders [31]. In compacted rGO sheets which have a layered structure similar to graphite, electron transport is highly anisotropic. Parallel to the basal planes, rGO sheet is a mediocre conductor due to its low free carrier concentration. But normal to the basal planes, it is a relatively good electric insulator [32]. Thus, there are two key factors that define overall electrical conductivity of compacted rGO/Co_{1-x}Zn_xFe₂O₄ samples: (1) interlayer electron transport (electron tunneling) (2) intralayer electron transport.

GO can be described as a random distribution of oxidized areas combined with non-oxidized regions. Oxidized areas are heavily decorated by the oxygen-containing functional groups, including tetrahedrally bonded sp^3 carbon atoms and non-oxidized regions that consist of trigonally bonded sp^2 carbon atoms [33].

The presence of oxygen-containing functional groups breaks the conjugated structure, which results in a decrease of both carrier mobility and carrier concentration. Though, there are conductive areas in GO, they are heavily surrounded by the non-conductive regions which leads to blocking the electron percolating pathways. As a result, synthesized GO sheets or films are typically insulating [34]. By a thermal treatment or a chemical reduction, oxidized areas could be reduced to restore the hybridized structure and their conductive properties. During the reduction process, oxygen-containing functional groups remove from the GO sheets and oxidized area collapses. Hence, the blockages against electron transport decreasing and the electrical conductivity significantly increases. Although solvothermal reduction is an effective way for the reduction of GO, large numbers of oxygen-containing functional groups still exist on the GO surface that are difficult to reduce [33-35]. This defects can limiting the electrical conductivity of rGO. Temperature, time and processing environment are the three determinant parameters in the solvothermal reduction of GO. In the present work, the only difference between the preparation conditions of samples is the variation of zinc content in the initial solutions which can lead to the formation of ferrite particles with different compositions. Overall, interlayer electron transport is unlikely to be importantly affected by such a poor electrical conductor as like as $Co_{1-x}Zn_xFe_2O_4$ ferrite.

If a non-insulator compound is intercalated between the graphene layers, the carrier concentration of the crystal is raised by charge transfer from the intercalant particles to the surrounding graphene sheets. Therefore, the higher electrical conductivity of rGO/ $Co_{1-x}Zn_xFe_2O_4$ samples compared to rGO is not unexpected. The electron transport between the graphene sheets is controlled by the two parameters: (1) Electrical conductivity of the $Co_{1-x}Zn_xFe_2O_4$ particles (2) distance between the layers.

The electrical conductivity in ferrites can be explained by the Verwey mechanism in which electron exchange between ions of the same element present in more than one valence state takes place [36]. In the case of spinel ferrites, the electronic hopping between Fe^{2+} and Fe^{3+} ions located on the octahedral sites, is the primary mechanism which allows electrical transport. This mechanism can be explained by the following process:



The energy required for this hopping is so low that it is thermally activated at room temperature [37]. The distribution of the divalent and trivalent ions over the B sites is random, and both electrical conductivity and magnetic properties of spinel ferrites are highly influenced by this disorder [38]. If Fe^{2+} is replaced by another divalent Me^{2+} , the interchange of electrons is no longer possible between the trivalent Fe^{3+} and the divalent Me^{2+} ions at the B-sites without having the final state differ from the initial one [37].

Therefore, substitution of Fe^{2+} by a divalent ion like Co^{2+} , significantly reduces the electrical conductivity of $CoFe_2O_4$ compared to Fe_3O_4 . In the case of Co ferrite, Co^{2+} and Co^{3+} ions are available for hopping. Hence the main contribution of conductivity may be due to the hole hopping.

On the other hand, introducing the Zn^{2+} ions in the reverse spinel structure of cobalt ferrite can easily alter the distribution of Fe^{3+} ions,. Because Zn^{2+} have a strong preference for the A sites which is occupied by Fe^{3+} ions. Increase in the zinc concentration diminishes the hole hopping by increasing Fe^{3+} and decreasing the Co^{2+} and Co^{3+} ions on the B sites. Thus electron hopping become predominant and the electrical conductivity increases [39]. It must be noted that, electrical conductivity can be also affected by grain size and the formation of grain boundaries. It was mentioned that, the grain size decreases with increase of Zn concentration. When grain size decreases, the grain boundary increases and as a consequence, the possibility of formation of oxygen rich layers on the surface of the grains increases [40]. The non-conducting layer which is formed by oxygen ions decreasing the electrical conductivity of $Co_{1-x}Zn_xFe_2O_4$ ferrite particles.

Previous reports about the electrical conductivity of spinel ferrites showed that the electrical conductivity of Zn ferrite is higher than Co ferrite [41-43]. Moreover, there are several reports about the variation of conductivity of mixed ferrites containing Zn with composition, in some cases the electrical conductivity increased with increase in the Zn content [44] and in some cases the variation of electrical conductivity followed dissimilar trends at the different content of Zn [39].

The electron transport between the graphene sheets can be also affected by the distance between the layers [45], which depends on the compression and the size of $Co_{1-x}Zn_xFe_2O_4$ particles. The presence of $Co_{1-x}Zn_xFe_2O_4$ particles improves the electrical conductivity due to facilitating the electron transport by providing the channels between the graphene sheets. But, the enhancement in electrical conductivity can be weakened by the larger particles. With considering this fact that the $Co_{1-x}Zn_xFe_2O_4$ ferrite is a very weak conductive ceramic, electron transport through the larger particles become more difficult than the smaller one.

In addition, direct electron transfer between the layers can be diminished by the large particles. Because, the graphene sheets can be more separated by the larger particles (fig.2b,c). It was previously mentioned that, increase in the Zn concentration leads to formation of smaller particles between the graphene sheets. Therefore, it can be expected that electrical conductivity of the samples increases by mounting in the Zn concentration. The obtained results are in good agreement with these suggestions and electrical conductivity of the samples increased by increasing the Zn concentration (Fig.6).

D. Magnetic property

Magnetic properties of samples were measured by using a vibrating sample magnetometer (VSM 7400 Lake Shore). A surprising fact about mixed ferrites containing zinc is that the addition of the non-magnetic Zn^{2+} ion increases their saturation magnetization. Fig.7a, b shows the dependence of saturation magnetization (M_s) and coercivity (H_c) of the $\text{rGO/Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples on Zn content.

The saturation magnetization value of the $\text{rGO/Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ composites (x : 0.4, 0.5, 0.6, 0.7) were 28.46, 32.34, 32.41, 22.36 emu/g, respectively. In a cubic system of spinel ferrites, the magnetic order is mainly constructed due to the super exchange interaction between metal ions of sub lattices A and B. The saturation magnetization first increased when zinc content in the initial solution was lower than 0.6 and then decreased for the higher zinc content (fig.7a,b). The increase in the saturation magnetization value with increase in the Zn content is due to the migration of Fe^{3+} ions from A sites to B sites. Therefore, the magnetic moment of a sites (M_A) decreases and the net magnetization ($M_B - M_A$) improves. Nevertheless, there is still a problem. The decrease in the magnetization saturation with increasing the Zn content cannot be justified in this way. As mentioned, the saturation magnetization of the obtained samples at the first, increased and then decreased by increasing the Zn content. The replacement of Co^{2+} by Zn^{2+} ions weakens the A–B superexchange interactions which cause the B-B interaction to geting stronger and becoming the main exchange. As a result, the magnetization saturation of the ferrite decreases. More detailed informations about this phenomena are available in the ref. [46]. According to the Fig.7C the magnetic coercivity decreases with increasing the Zn content. Decreasing in coercivity maybe affect on Saturation magnetization in other words base on Brown's relation which is presented by:

$$H_c \geq 2 \kappa \frac{1}{M_s} \quad (1)$$

Reduction of the magnetic coercivity can be justified according to the relation between magnetic anisotropic and coercivity forces. H_c is inversely proportional to M_s which we have detected experimentally as shown in fig.7C. reduces the anisotropy energy constant influence on Reduction of H_c .

E. Photocatalytic Properties

The photocatalytic activities of the $\text{rGO/Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples were evaluated by the degradation of methylene blue (MB) under visible-light irradiation at room temperature. Experiments were performed in a 100 mL cylindrical reactor. 50 mg of photocatalyst was added to 50 mL of a 10 mg/L MB aqueous solution. In order to reach the adsorption-desorption equilibrium between the dye and the catalyst, the reaction mixture was stirred for 60 min in the dark and then, the resulting suspension was transferred into the reactor vessel. The reactor was containing this suspension with air bubbling continuously at a certain flow rate (about 50 mL/min) by a feed pump from the bottom of the reactor and a 110-W xenon lamp was employed as the photoirradiation source. The concentrations of the remnant dye were spectrophotometrically monitored by measuring the absorbance of solutions during the photodegradation process.

According to Fig. 8, for all the samples, concentration of the remnant dye continuously decreased with respect to the irradiation time.. It is clear that the photocatalytic activity of the $\text{rGO/Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples improved by increasing Zn content, which can be due to this fact that, more efficient electron transport between the semiconductor and the carbon-based material, would enhance the photoelectronic response.

High electrical conductivity and unique electron mobility of the graphene make it an excellent electron-transport material in the photocatalysis process. The photogenerated electrons can be transferred instantly between the conduction band of semiconductor and graphene via the percolation mechanism, resulting in a minimized charge recombination and offering an enhanced photocatalytic activity. The photogenerated electrons and holes can react with the adsorbed oxygen (O_2) and water molecules to give $\text{O}_2^{\bullet-}$ and $\text{OH}^{\bullet}$. These radicals are the main responsible for the degradation of MB. The process of photodegradation of MB in the presence of $\text{rGO/Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, under visible light irradiation is schematically illustrated in fig.9. As previously mentioned, electron transport between rGO and ferrite particles improved by incorporation of Zn in the spinel structure of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$. Although, this is a good reason to justify the enhancement of photocatalytic activity by increasing the Zn content, but it is not enough. Because, the specific surface area is the other predominant factor that significantly affecting the activity of the catalysts.

Fan et al [21] reported that the specific surface area of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ is strongly related to its composition and increased from 52 m^2/g to 124 m^2/g by only 0.2 enhancement in Zn content (X). Fig.10 shows the influence of Zn content on the specific surface area of the samples which was evaluated by the BET(Belsorp mini II, BelJapan) method. It is possible that the reduction of the particle size and grain size with respect to Zn content, caused to increasing the porosity and consequently improvement of the specific surface area. Therefore, the promotion of the photocatalytic activity can be attributed to improvement of the specific surface area and electron transport between ferrite particles and rGO support. It must be noted that, as expected, the photocatalytic activity of $\text{rGO/Co}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ was considerably higher than $\text{Co}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$. Improvement in the photocatalytic activity of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, like the other semiconductors (TiO_2 , ZnO , MnFe_2O_4 , ZnFe_2O_4 and etc) is believed to be due to several reasons [47] such as; 1) the extraordinary electron mobility of graphene provides a way to enhance the separation between the electrons and the holes that are produced in a photoexcitation process. 2) Graphene is able to directly capture the visible light and improves the absorption range. 3) Graphene increases the

interaction area and adsorption of dyes with the semiconductor particles by creating a π - π interaction with its delocalized electrons.

IV. CONCLUSION

In summary, Co_{1-x}Zn_xFe₂O₄ nanoparticles have been grown on the rGO support via a simple solvothermal method. As-prepared rGO/Co_{1-x}Zn_xFe₂O₄ samples showed high photocatalytic activity for the degradation of methylene blue under visible light irradiation. It was revealed that the photocatalytic activities increased by increasing Zn content. FE-SEM images and XRD patterns showed that graphene sheets were exfoliated by the formation of Co-Zn ferrite nanoparticles. The effect of solvothermal reaction time on the growing of ZnCo_{1-x}Fe₂O₄ nanoparticles on the graphene support was also investigated. It was shown that, the size of Co_{1-x}Zn_xFe₂O₄ nanospheres are highly influenced by the solvothermal reaction time. Magnetic and electrical properties of the samples were also evaluated. at the first, when the Zn²⁺ content in the initial solution was lower than 0.6, the saturation magnetization of the samples increased by increment the Zn content and then decreased by further increase in the Zn content. This is while, the electrical conductivity continuously improved by increasing Zn content. These nanocomposites have potential applications in dye removal, super capacitors, sensors, drug delivery and MR imaging.

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VI. Acknowledgments

In performing our paper, we got the help of some respected persons that we appreciate all of them. The completion of this paper gives us much pleasure.

Table 1. Lattice parameters derived from X-ray diffraction pattern of rGO/Co_{1-x}Zn_xFe₂O₄ with various Zn contents.

Zn content	Space distance (Å)	Lattice parameter (Å)	Crystallite size (Å)
0.4	2.52610	8.378	100
0.5	2.52810	8.384	96
0.6	2.54006	8.424	94
0.7	2.55758	8.483	91

Figure 1 Schematic illustration of a) the basal plane of GO sheets which are heavily decorated by the epoxide and hydroxyl groups b) formation of Co_{1-x}Zn_xFe₂O₄ ferrite nanosphere between the rGO sheets c) grown Co-Zn sphere that leads to the exfoliation of rGO sheets d) tetrahedral (blue parts) and octahedral (yellow parts) sublattices in the crystal structure of Co_{1-x}Zn_xFe₂O₄ ferrite.

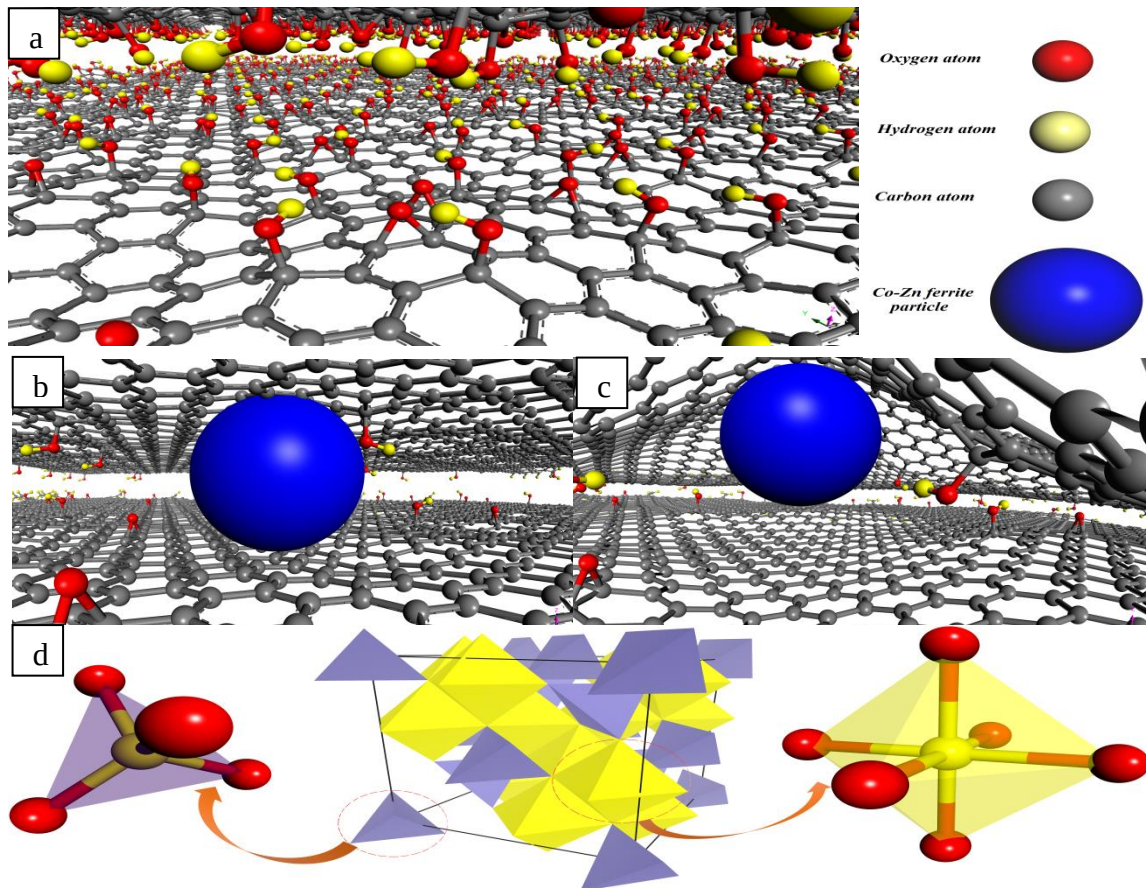


Figure 2 Separation of precipitate in to two parts, the floated part of precipitate showed high tendency to rise up in the solution and contains less amount of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite particles compared with the sediment part.



Figure 3 FE-SEM images of a) GO b) $\text{rGO}/\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ sample, prepared through a solvothermal reaction for 12 hr at 200 C c) $\text{rGO}/\text{Co}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ sample, prepared through a solvothermal reaction for 18 hr at 200 C d) $\text{rGO}/\text{Co}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ sample, prepared through a solvothermal reaction for 12 hr at 200 C.

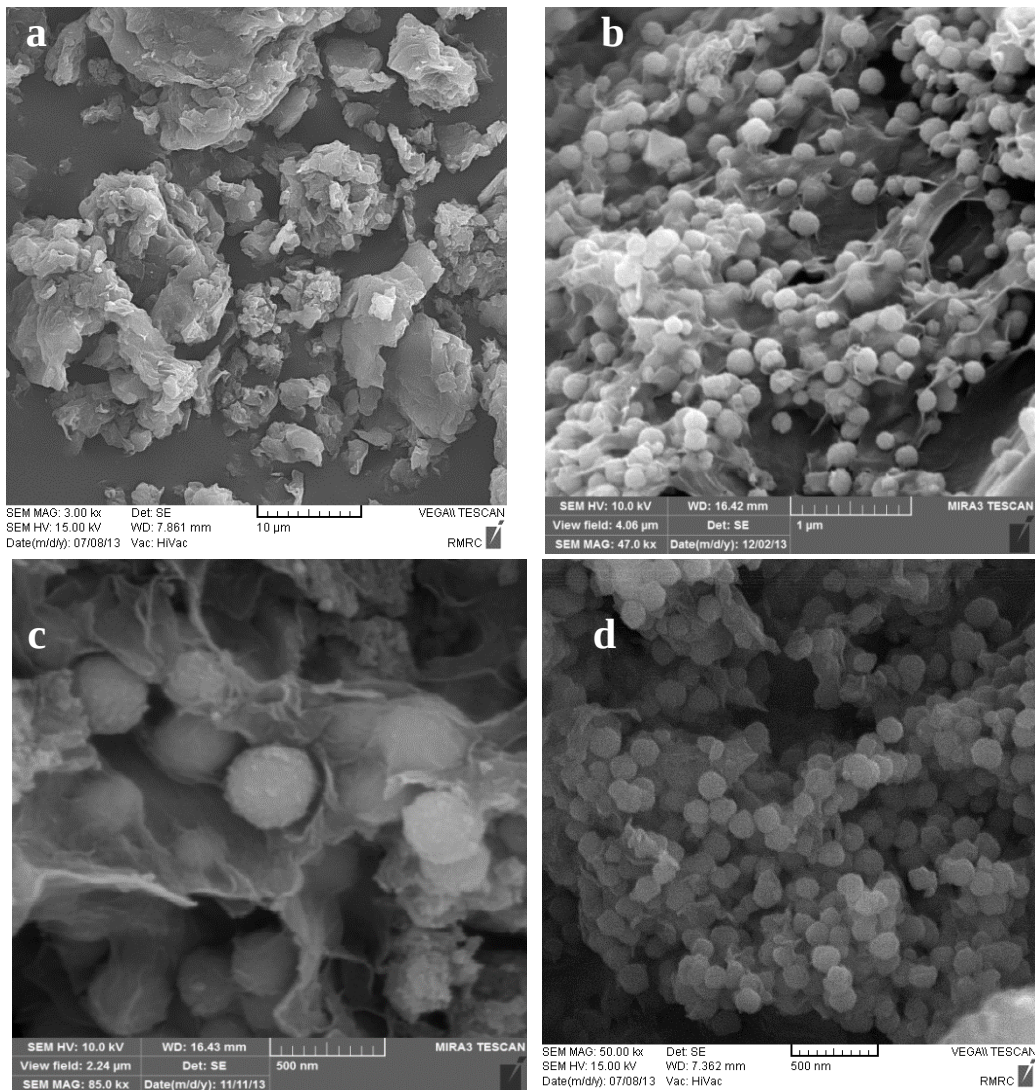


Figure 4 FE-SEM images of a) rGO sample, prepared through a solvothermal reaction for 12 hr at 200 C and at low magnification b) rGO sample, prepared through a solvothermal reaction for 12 hr at 200 C and at relative high magnification c) floated part of rGO/Co_{0.4}Zn_{0.6}Fe₂O₄ sample, prepared through a solvothermal reaction for 18 hr at 200 C and at low magnification d) floated part of rGO/Co_{0.4}Zn_{0.6}Fe₂O₄ sample, prepared through a solvothermal reaction for 18 hr at 200 C and at relative high magnification.

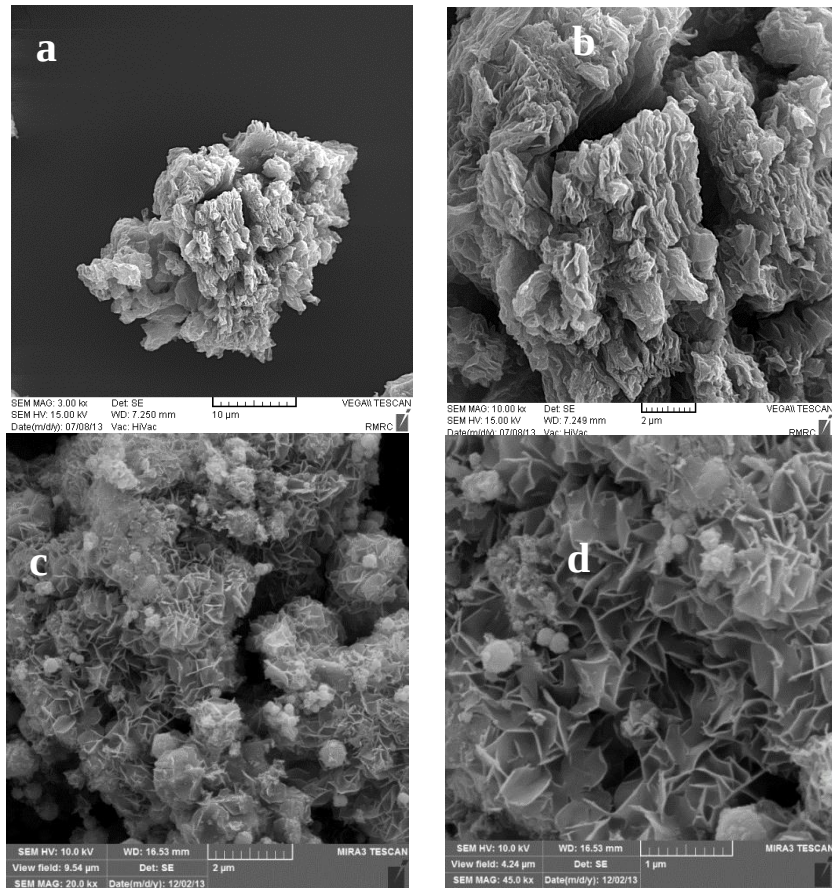


Figure 5 XRD patterns of GO, rGO and rGO/ Co_{1-x}Zn_xFe₂O₄ samples

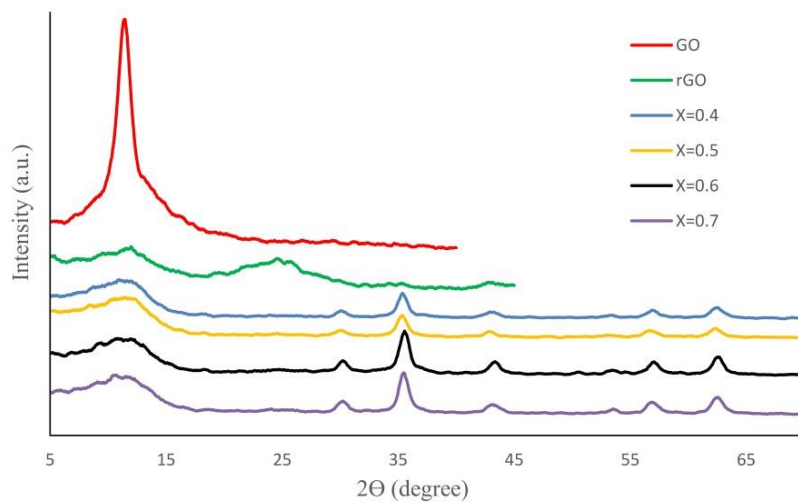


Figure 6 Variation of electrical conductivity of the rGO/Co_{1-x}Zn_xFe₂O₄ samples with composition

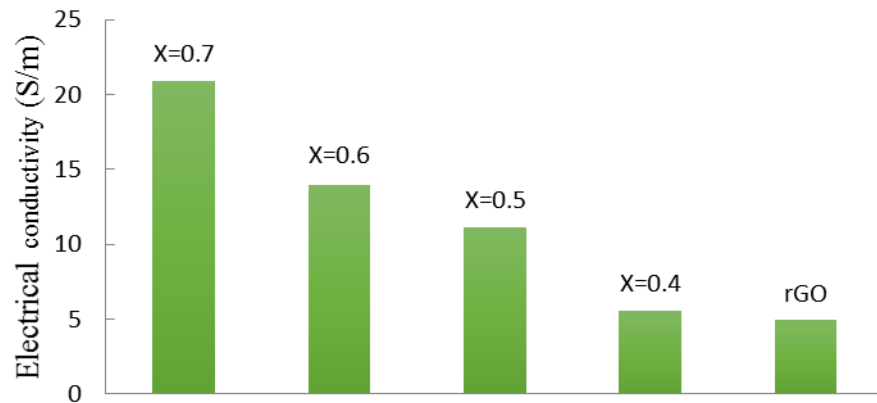
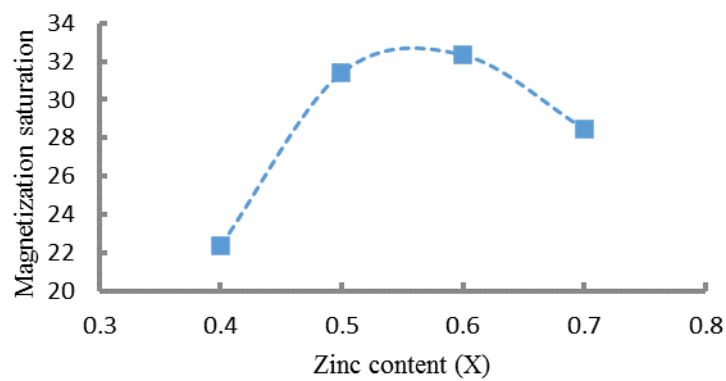
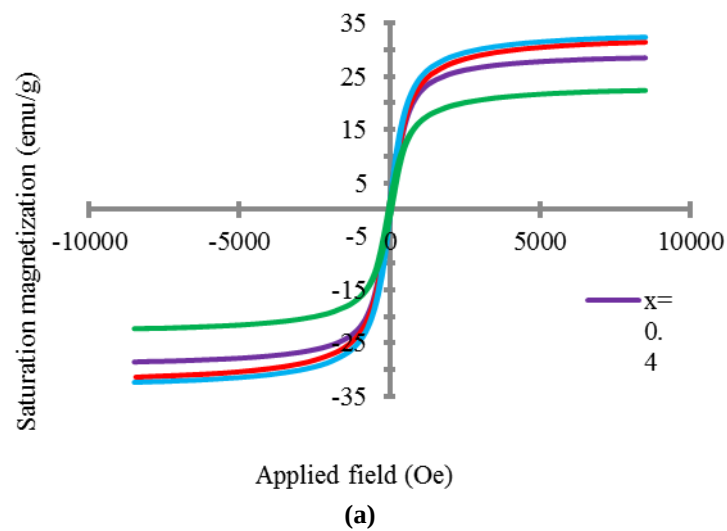
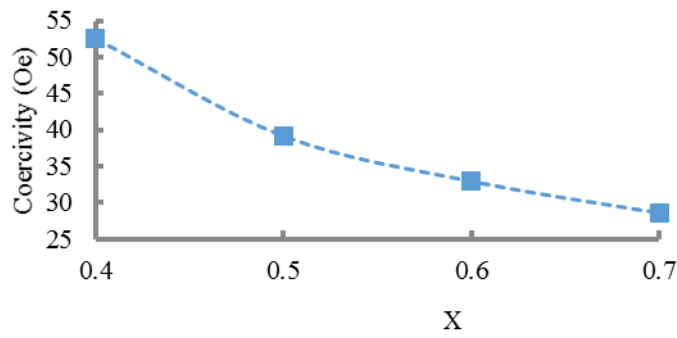


Figure 7 a) Magnetic hysteresis loops b) Magnetic coercivity c) Saturation magnetization curves of rGO/Co_{1-x}Zn_xFe₂O₄ samples.





(c)

Figure 8 Photodegradation of MB in the presence of $\text{rGO}/\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples monitored as the normalized Concentration change vs. irradiation time under visible light irradiation.

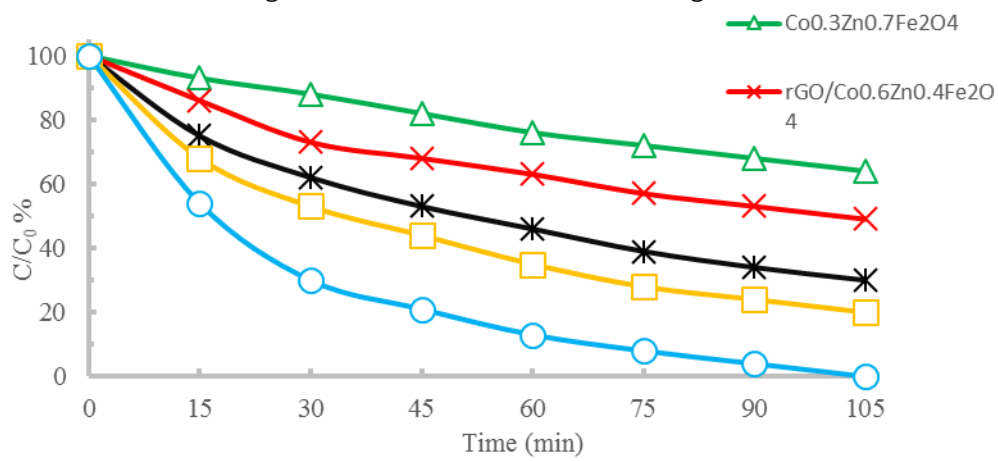


Figure 9 Schematic illustration of the photodegradation of MB in the presence of $\text{rGO}/\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ photocatalyst under visible light irradiation

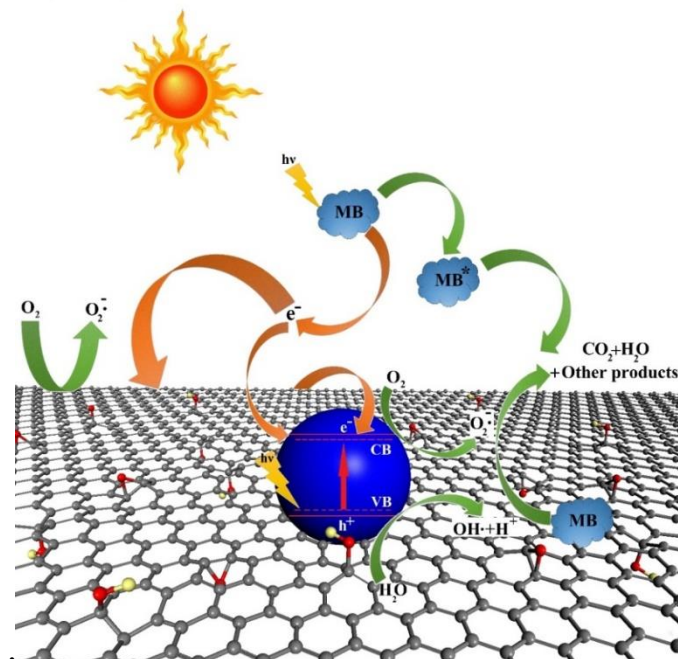


Figure 10 Relation between the specific surface area of the $\text{rGO}/\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples and Zn content calculated by BET method

