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 Co1-xZnxFe2O4 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 microscope (FE-SEM) and powder X-ray diffraction (XRD). The influences of the Zn2+ content on photocatalytic activity, electrical conductivity and magnetic property of the samples are also investigated. The results showed that ZnxCo1-xFe2O4 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 sp2 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 it’s coercivity [15]. Incorporation of a certain amount of zn2+ ions in the spinel structure of cobalt ferrites make a new structure that is called Co-Zn spinel ferrites(Co1-xZnxFe2O4) (fig.1d). Co1-xZnxFe2O4 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, photons crystal and high density information storage systems[16-21].

Recently, the photocatalytic activity of ZnxCo1-xFe2O4 nano particles under visible light irradiation was investigated [21]. It was revealed that, compared to conventional photocatalysts such as TiO2 and ZnO, ZnxCo1-xFe2O4 samples exhibited appreciable photocatalytic activity in the degradation of methylene blue under visible light irradiation. The little band gap of ZnxCo1-xFe2O4 (1.73-1.9 eV) allows it to be photocatalitically active in the visible light region, while photocatalytic activity of TiO2 and ZnO is limited to wavelengths below the visible light region due to their relatively large band gap (3.2 eV). In addition, ZnxCo1-xFe2O4 nanoparticles have a magnetic property, which makes themself 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/ZnxCo1-xFe2O4 magnetic nanocomposites with tunable magnetic, electrical and photocatalytic properties are prepared via a solvothermal method. Therefore, four samples of thermally reduced graphene oxide (TrGO)/ZnXCo1-xFe2O4 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 at 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 CoxZnxFe2O4 on graphene support

Four rGO/CoxZnx1-xFe2O4 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: Co1-xZnxFe2O4 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/Co0.4Zn0.6Fe2O4 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 ZnxCo1-xFe2O4 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/Co1-xZnxFe2O4 samples

The size and morphology of rGO/Co1-xZnxFe2O4 samples was observed by FE-SEM(VEGA II TESCAN). The representative FE-SEM images of as-obtained GO, TrGO and rGO/Co1-xZnxFe2O4 samples are displayed in Fig. 3 and 4. It is obvious that transparent graphene flakes are exfoliated and decorated with Co1-xZnxFe2O4 nano-spheres. The crystal growth of Co1-xZnxFe2O4 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 Co1-xZnxFe2O4 ferrite nanoparticles (fig.4a,b,fig.3a). In addition, the Co1-xZnxFe2O4 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 Co1-xZnxFe2O4 ferrite particles compared with the sedimanted part (fig.4c,d,fig.3d). Indeed, the magnetic property and higher density of Co1-xZnxFe2O4 ferrite compared to rGO sheets is the main reason for the separation of ferrite reach part from the graphene reach part of the precipitate. The XRD patterns of of the as-prepared GO, rGO and rGO/Co1-xZnxFe2O4 samples samples was characterized by X-ray Diffraction (Siemens D500 ) are shown in Fig. 5. Almost all the diffraction peaks of rGO/Co1-xZnxFe2O4 can be assigned to spinel-type Co1-xZnxFe2O4 [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 Co1-xZnxFe2O4 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/Co1-xZnxFe2O4. This may be due to the fact that GO flakes were exfoliated by the intercalated Co1-xZnxFe2O4 nanoparticles, 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/Co1-xZnxFe2O4 samples. The values of lattice constant and crystallite size are given in Table 1. The lattice constant (a) was calculated using inter-planar spacing (dhkl) 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 inverse spinel structure of CoFe2O4, force Fe3+ ions to migrate from the A sites to the B sites that can be described as follows:

\[ \text{Zn}_2(\text{Fe}^{3+}+\text{Fe}^{3+})(1-x)\{\text{Co}^{2+}(1-x)\text{Fe}^{3+}+(1-x)\}\text{BO}_4 \]

As a result, the lattice will be expanded. In order to calculate the crystallite size, the Debye- Scherer’s method was applied [27]. According to this method, the average crystallite size (Dhkl) 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 Co1-xZnxFe2O4 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 Co1-xZnxFe2O4

In order to investigate the effect of Zn content on crystal growth of Co1-xZnxFe2O4 ferrite, four samples of rGO/Co-Zn ferrite was 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 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 Co1-xZnxFe2O4 ferrite, three samples of rGO/Co1-xZnxFe2O4 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 analyzes reveals that the particle size distribution obviously improved with rising the reaction time.

### C. Electrical conductivity of compacted rGO/Co1-xZnxFe2O4 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/Co1-xZnxFe2O4 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 sp3 carbon atoms and non-oxidized regions that consist of trigonally bonded sp2 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 Co1-xZnxFe2O4 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/Co1-xZnxFe2O4 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 Co1-xZnxFe2O4 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 Fe2+ and Fe3+ located on the octahedral sites, is the primary mechanism which allows electrical transport. This mechanism can be explained by the following process:

\[
\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + e^{-}
\]

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 Fe2+ is replaced by another divalent Me2+, the interchange of electrons is no longer possible between the trivalent Fe3+ and the divalent Me2+ ions at the B-sites without having the final state differ from the initial one [37]. Therefore, substitution of Fe2+ by a divalent ion like Co2+, significantly reduces the electrical conductivity of CoFe2O4 compared to Fe3O4. In the case of Co ferrite, Co2+ and Co3+ ions are available for hopping. Hence the main contribution of conductivity may be due to the hole hopping.

On the other hand, introducing the Zn2+ ions in the reverse spinel structure of cobalt ferrite can easily alter the distribution of Fe3+ ions. Because Zn2+ have a strong preference for the A sites which is occupied by Fe3+ ions. Increase in the zinc concentration diminishes the hole hopping by increasing Fe3+ and decreasing the Co2+ and Co3+ 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 Co1-xZnxFe2O4 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 through the graphene sheets can be also affected by the distance between the layers [45], which depends on the compression and the size of Co1-xZnxFe2O4 particles. The presence of Co1-xZnxFe2O4 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 weaken by the larger particles. With considering this fact that the Co1-xZnxFe2O4 ferrite is a very weak conductive ceramic, electron transport trough 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 Zn2+ ion increases their saturation magnetization. Fig. 7a, b shows the dependence of saturation magnetization (Ms) and coercivity (Hc) of the rGO/Co1-xZnxFe2O4 samples on Zn content. The saturation magnetization value of the rGO/Co1-xZnxFe2O4 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 Fe3+ ions from A sites to B sites. Therefore, the magnetic moment of a sites (MA) decreases and the net magnetization (MB-MA) 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 Co2+ by Zn2+ ions weakens the A–B superexchange interactions which cause the B-B interaction to getting 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:

\[ Hc \geq 2 \times 1 \mu 0 \text{Ms} (1) \]

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

E. Photocatalytic properties

The photocatalytic activities of the rGO/Co1-xZnxFe2O4 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 photoradiation 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 rGO/Co1-xZnxFe2O4 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 (O2) and water molecules to give O2- • and OH- •. These radicals are the main responsible for the degredation of MB. The process of photodegradation of MB in the presence of rGO/Co1-xZnxFe2O4 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 Co1-xZnxFe2O4. 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 Co1-xZnxFe2O4 is strongly related to its composition and increased from 52 m2/g to 124 m2/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 rGO/Co1.3Zn0.7Fe2O4 was considerably higher than Co1.3Zn0.7Fe2O4. Improvement in the photocatalytic activity of Co1-xZnxFe2O4, like the other semiconductors (TiO2, ZnO, MnFe2O4, ZnFe2O4 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, Co1–xZnxFe2O4 nanoparticles have been grown on the rGO support via a simple solvothermal method. As-prepared rGO/Co1–xZnxFe2O4 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 ZnxCo1-xFe2O4 nanoparticles on the graphene support was also investigated. It was shown that, the size of Co1–xZnxFe2O4 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, supper capacitors, sensors, drag delivery and MR imaging.

V. References


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/Co1-xZnxFe2O4 with various Zn contents.

<table>
<thead>
<tr>
<th>Zn content</th>
<th>Space distance (Å)</th>
<th>Lattice parameter (Å)</th>
<th>Crystalite size (Å)</th>
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<tr>
<td>0.4</td>
<td>2.52610</td>
<td>8.378</td>
<td>100</td>
</tr>
<tr>
<td>0.5</td>
<td>2.52810</td>
<td>8.384</td>
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<tr>
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<tr>
<td>0.7</td>
<td>2.55758</td>
<td>8.483</td>
<td>91</td>
</tr>
</tbody>
</table>

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 Co1-xZnxFe2O4 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 Co1-xZnxFe2O4 ferrite.
Figure 2  Separation of precipitate into two parts, the floated part of precipitate showed high tendency to rise up in the solution and contains less amount of $\text{Co}_x\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrite particles compared with the sediment part.

Figure 3  FE-SEM images of a) GO b) 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) 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) 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/Co0.4Zn0.6Fe2O4 sample, prepared through a solvothermal reaction for 18 hr at 200 °C and at low magnification d) floated part of rGO/Co0.4Zn0.6Fe2O4 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/Co1-xZnxFe2O4 samples
Figure 6  Variation of electrical conductivity of the rGO/Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples with composition

Figure 7  a) Magnetic hysteresis loops  b) Magnetic coercivity  c) Saturation magnetization curves of rGO/Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples.
Figure 8  Photodegradation of MB in the presence of rGO/Co$_{1-x}$ZnxFe$_2$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 rGO/Co$_{1-x}$ZnxFe$_2$O$_4$ photocatalyst under visible light irradiation.
Figure 10  Relation between the specific surface area of the rGO/Co$_{1-x}$ZnxFe$_2$O$_4$ samples and Zn content calculated by BET method