Structural and Photocatalytic Properties of Magnesium and Aluminum Co-doped Zinc Ferrite Nanoparticles Synthesized by Co-Precipitation Method

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Abstract. Green synthesis method is a simple and low cost method for the preparation of nanoferrites. In the present study pure and Magnesium and Aluminium co-doped zinc ferrite nanoparticles were prepared by co-precipitation method using lemon peel was used as a reducing agent. The prepared ferrites were studied especially their structural and photocatalytic properties. From XRD studies it was found that the ferrite are cubic in structure and crystallite size was in the range of 9-12 nm. The photocatalytic property was studied using UV-Vis-NIR spectrophotometer and the photocatalytic dye degradation property of co-doped zinc ferrite nanoparticles was observed that degraded the methylene blue dye by 73%.

INTRODUCTION

Ferrites are well known for the past two decades due to their stable structural, thermal, electrical and magnetic properties which find applications in transformers, choke coils, etc. Impressed by their physical properties and wide range of applications, extensive studied were carried and being carried out on various types of ferrites. From the previous studies, it was concluded that the physical properties of these ferrites can be controlled by the process of doping. The doping of materials enhances the properties of ferrites depending on the nature of synthesis and dopants. Generally, transition metals and alkaline earth metals were used as dopants as transition metal ions exhibit good electrical and magnetic properties. Much research has been carried out on zinc ferrites in which the host material was doped by manganese (Mn) and they were used in hyperthermia treatment, biomedical appliances, magnetic recording and in the core of the transformers. Further it is well known that the properties of nanostructured materials for better when compared with their counterparts. As Aluminum is light weight, and highly conducting in nature, the doping of Aluminum in the Manganese zinc ferrite nanoparticles tends to improve the structural and photocatalytic properties of manganese zinc ferrite nanoparticles. Many articles were published on MnZnFe, AlZnFe and GaZnFe to improve their magnetic and photocatalytic properties and mixed results were found. But there are meager reports on magnetic and photocatalytic properties of rare earth doped (RE) nano zinc ferrites. If one could succeed in improving the photocatalytic properties in RE doped zinc ferrites, then they will find many societal applications. For an example, water purifier/filter. The photocatalytic degrading agent helps to reduce the pollution of water by removing harmful dyes from the water bodies. As ferrites are magnetic in nature, if they are used as dye degrading agents, then the traces of ferrites after dye removal can be separated and removed from water bodies by the use of magnets. So, the photocatalytic properties of the Aluminum and Manganese co-doped zinc ferrite synthesized by the co-precipitation method have been studied in detail in this present study.

Experimental Methods

In this present work, Magnesium and Aluminum were co-substituted in zinc ferrite nanoparticles by co-precipitation method using lemon peel extract as the capping agent. The materials like Zinc nitrate [Zn $(NO_3)_2 .6H_2O$], Ferric nitrate [Fe $(NO_3)_3.6H_2O$] and deionized water were used in the synthesis process for the synthesis of pure zinc ferrite nanoparticles. The lemon peels were washed with deionized water and slashed into small pieces. Then 25 g of lemon peel was added to 250 ml of deionized water in a beaker. Then it was kept on a hot plate for about 45 min by at a temperature of 90 ℃ to prepare the extract. The extract was then filtered and poured into a burette and used as a capping agent. Then the prepared extract was added dropwise into the stirring precursor solution. On continuous stirring and adding of lemon peel extract to the solution, zinc ferrite precipitate was formed. Then in order to synthesize Aluminum and Magnesium co-substituted zinc ferrite nanoparticles, the above process was repeated with the following concentrations as dopant and host materials. The nitrates such as zinc nitrate (6 g), of Aluminum nitrate (2 g), magnesium nitrate (2 g) and ferric nitrate (20 g) were taken in 50 ml of deionized water and stirred continuously. A 25 g of extract was added dropwise into the precursor solution and stirred for an hour. The precipitates started to form in the solution. Then the solutions containing the precipitates of pure and co-substituted zinc ferrite nanoparticles were kept for centrifugation at 1000 rpm for 5 min. The precipitates are collected after the centrifugation and then tried in a hot place. Finally, Al and Mg substituted zinc ferrite nanoparticles sample was carefully collected. After drying the precipitate, they were ground once using an agate mortor and pestle and then sintered in a muffle furnace for 4 hrs at 600℃. The nanoparticles were then characterized by X-ray diffractometer for structural studies, UV-Vis-NIR spectrophotometer was used to study photocatalytic dye degradation.

Results and Discussion

Structural Properties

Figure 1 shows XRD profile of undoped and (Mg, Al) co-doped ZnFe. The upper XRD profile indicates the XRD profile of pure zinc ferrites and lower XRD profile indicates the XRD profile of (Mg, Al) co-doped zin ferrites. There is a slight shift in the diffraction peak positions of (Al, Mg) doped zinc ferrite nanoparticles compared to pure zinc ferrite nanoparticles. This shift confirms the doping ions in the lattice of zinc ferrite. The average crystallite size of nanoparticles was calculated using Scherrer's formula. The undoped zinc ferrites shown the crystallite size of 9 nm whereas the (Mg, Al) co-doped zinc ferrites shown a crystallite size of 12 nm. The size clearly indicates the formation of nanoferrites by simple green synthesis method. A decrease in the lattice parameter of (Mg, Al) substituted zinc ferrite was observed when compared with lattice parameter of pure zinc ferrite. The comparison of structural parameters was shown in detail in Table 1. The increase in average crystallite size and decrease in lattice parameter is correlated to the smaller ionic radii of aluminum and magnesium in (Mg, Al) substituted zinc ferrite nanoparticles. When aluminum and magnesium get substituted in the place of zinc, then the length of the lattices decreases to keep the bond intact leading to a decrease in lattice parameter of the nanoparticles. Also, the smaller ionic radii of magnesium lead to increase in number of bonds with its neighbor causing greater average crystallite size.

Photocatalytic Studies

The nanoparticles were mixed with Methylene Blue (MB) dye and stirred for 30 minutes. Then, the mixture was kept in sun light to degrade the dye. The vacant sites will be absorbing the methylene blue leading to a decrease in the intensity of the peak at 664 nm, as this is the maximum absorption point for methylene blue dye. With the increase in time, the MB dye degrades completely and the blue-colored solution turned to transparent solution indicating the degradation of the dye. The decrease in the absorption spectra at 664 nm is shown in figure 3. Then, the percentage of degradation is found using the formula

$$D\% = \frac{(A_0 - A)}{A_0} \times 100 \qquad (1)$$

The increase in the percentage of degradation of dye with the use of (Mg, Al,) incorporated zinc ferrite nanoparticles indicated the use of these nanoparticles as photocatalyst.

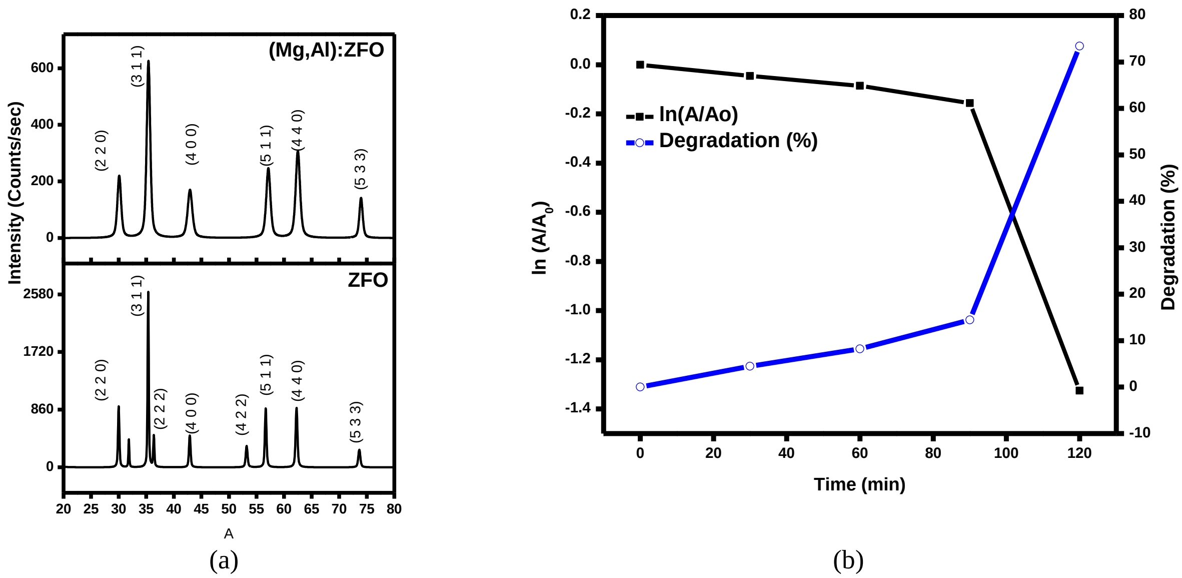

FIGURE 1. (a) X-ray diffraction pattern of pure zinc ferrite (ZFO) nanoparticles and Aluminum, Magnesium co-doped Zinc ferrite nanoparticles (b) Variation of percentage of degradation of dye with respect to time.

TABLE 1. Summary of crystallite size, lattice parameter, strain and dislocation density of Mg doped zinc ferrite and zinc ferrite nanoparticles.

Sample	Crystallite size	Lattice parameter x 10^{-10}m
Zinc ferrite	8.15 nm	8.42
(Mg,Al):Zinc ferrite	11.79 nm	8.40

Conclusion

Aluminium and magnesium co-substituted zinc ferrites nanoparticles were synthesized by co-precipitation method using lemon peel extract as the capping agent. The shifting in the peak position confirms the substitution of Al and Mg in the lattice of zinc ferrite. An optimized concentration of vacant sites was observed in the substituted zinc ferrite nanoparticles. The substitution of metals also inculcated the photocatalytic activity of zinc ferrite nanoparticles. Nearly 73% of Methylene blue dye got degraded after reaction with Al, Mg co-substituted zinc ferrite nanoparticles.

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