J Nanostruct 13(3): 845-853, Summer 2023

RESEARCH PAPER

Fabrication of Magnesium Ferrite-Graphene Oxide-Copper Sulfide Nanocomposites to Increase Photocatalytic Properties

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ARTICLE INFO

Article History:
Received 03 March 2023
Accepted 20 May 2023
Published 01 July 2023

Keywords:
Copper sulfide
Graphene oxide
Magnesium ferrite
Nanocomposites
Photocatalyst

ABSTRACT

In this research, a new triplex catalyst of magnesium ferrite-graphene oxide-copper sulfide ($MgFe_2O_4$-GO-CuS) was synthesized for degradation of three various azo dyes Methyl orange, Methyl Red and Eriochrome Black-T under ultra-violet illumination. All three components have synergistic effect in photo-catalytic activities. In this work, magnesium ferrite as a suitable magnetic core, was synthesized by helping hydrothermal method and the graphene oxide sheets were prepared with Hummer's method. On the other hand, these components were mixed with the help of ball milling procedure and ultra sound waves. Finally, CuS nanostructures were coated on the $MgFe_2O_4$-GO applying hydrothermal method. To specify the morphology, structure, particle size, purity, bandgap, and bonds were employed by scanning electron microscopy (SEM), X-ray diffraction (XRD), vibrating sample magnetometer (VSM), and Fourier transform infrared (FT-IR) spectroscopy. The experimental conclusions determined that the $MgFe_2O_4$-GO-CuS nanocomposites were successfully synthesized and had a beneficial effect on the elimination of azo dyes.

How to cite this article
Joulaei M, Hedayati K, Ghanbari D. Fabrication of Magnesium Ferrite-Graphene Oxide-Copper Sulfide Nanocomposites to Increase Photocatalytic Properties. J Nanostruct, 2023; 13(3):845-853. DOI: 10.22052/JNS.2023.03.025

INTRODUCTION

Graphene sheets with large surface area and carbon-carbon bonds (sp^2 hybrid) arranged in a honeycomb lattice have high thermal and electrical conductivities, high chemical stability, and suitable optical transparency. Graphene is an allotrope of carbon constructed of a single layer of carbon atoms that are connected in a repeating pattern of hexagons. Graphene-based nanocomposites due to their suitable physical properties can be used in various industries such as photocatalysis [1-3], sensors [4], electronics [5], solar cells [6], energy conversion, storage [7], and so on. Graphene as an appropriate electron acceptor can provide heterojunction with different semiconductors, and then accept the photo-generated electrons from semiconductors to achieve effective charge separation and enhance the photocatalytic activity of semiconductors. Chemical oxidation of graphite by Hummers' method is the most common method for the preparation of GO. Graphene has been employed as excellent support for metal nanomaterials because of its unique structural and physicochemical properties mentioned above. To utilize the fascinating properties and unique structure of graphene nanomaterials, considerable efforts have been made to develop graphene nanocomposites. Hitherto, graphene sheets have been developed as nanoscale building

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blocks to disperse and stabilize various metal and metal oxide nanoparticles. Graphene sheets as nanoparticle support open up a new pathway for material development [6-11].

Among the most famous magnetic materials, we can mention ferrites, all kinds of normal and inverted spinel ferrites and hexa-ferrites, which have been used daily in industry and society for years. Magnesium ferrite is a very suitable ferrite with suitable magnetism and coercivity. One of the most important advantages of this ferrite is that it is non-toxic and its elements are cheap, and this issue justifies its widespread use in environmental applications [12-15].

Copper sulfide preferentially utilized in nanodevices, as functional materials in sensors, electrodes in batteries, efficient and reusable catalyst. CuS is known for its excellent photocatalytic activity in purifying and decomposing various contaminated components. CuS is one of the metal sulfides with optimal conditions for oxidation reactions, which has been used to produce highly efficient photocatalysts with a suitable bandgap [16-20]. Using photo-catalytic materials is considered to be an optimal solution to decrease organic pollutants such as different azo dyes. In this work a novel nanocomposite was prepared by facile, cost effective and green method and these products can be used for removing toxic aromatic dyes under solar irradiation [21-24]

MATERIALS AND METHODS

Materials

All the chemical materials including graphite powder, $KMnO_4$, H_2SO_4, H_2O_2, $Cu(NO_3)_2$, $Fe(NO_3)_3$, $Mg(NO_3)_2$, thioglycolic acid, NH_3, NaOH, HCl, hydrazine, and all other used materials were purchased from Merck or Aldrich Company and used without further purification.

After coating the samples with gold films, the samples' surface morphology was investigated using a scanning electron microscope (SEM) MIRA3-TESCAN instrument. X-ray diffraction (XRD) measurements was applied by Philips diffractometer (Cu-K_α radiation) in the range of 2θ from 5 to 80º. X'Pert High Score was used to the measure powder diffraction profile. Fourier transform infrared (FT-IR) spectroscopy with the range of 400–4000 cm^{-1} by Bruker Instruments and Ultraviolet-visible (UV-vis) were obtained by Nicolet Instruments.

Synthesis of $MgFe_2O_4$ Nanoparticles

0.01 mol of $Mg(NO_3)_2$ $6H_2O$ and 0.02 mol of $Fe(NO_3)_3$ $9H_2O$ were added to 200 ml of distilled water. 10 mL of ammonia solution (1 M) was dissolved to the solution in a autoclave (Teflon-lined) of 500 ml capacity and was maintained at 200°C for 5 h. The brown product was washed and was dried in the air. The obtained product was calcined at 600°C (2 hours).

Synthesis of Graphene nanosheets

The graphene nanosheets were prepared with Hummer's method by using ultrasound for the synthesis of graphene oxide from graphite powder as the starting material. In this method, 2 g graphite powder was stirred in 35 ml H_2SO_4 for 2 h. 6 g $KMnO_4$ was gradually added to the above solution at a temperature of less than 5 °C. The resulting solution was diluted by adding 90 ml of water under vigorous stirring to obtain a dark brown suspension. The reaction was completed by adding 150 ml of distilled water and 10 ml of 30% H_2O_2 solution. After stirring continuously for 2 hours a temperature of less than 5 °C, the mixture was washed by centrifugation and repeated filtration using 5% aqueous HCl solution to remove residual metal ions. Then, a brown precipitate of graphite oxide was obtained by filtration and allowed to dry in a vacuum. Subsequently, graphite oxide was exfoliated by ultrasonic irradiation and converted to graphene oxide. 0.2 g of the synthesized graphite oxide was redistributed in 200 ml of distilled water and sonicated for 30 minutes, resulting in the graphite oxide into graphene oxide (GO) monolayers. The pH of the solution was adjusted to 10 with NaOH and then 2 ml of hydrazine hydrate was added under ultrasonic irradiation. The nanosheets were thoroughly washed with distilled water and centrifuged at 10000 rpm for 10 minutes.

Synthesis of $MgFe_2O_4$-GO-CuS Nanoparticles

Hydrothermal operations were also used to synthesize $MgFe_2O_4$-GO-CuS. Firstly, for the preparation of $MgFe_2O_4$-GO, 1g of $MgFe_2O_4$ and 1g of GO were mixed under ball milling method at 400 rpm. Finally 1g of synthesized $MgFe_2O_4$-GO was dispersed in 200 ml of distilled water, then 1 g of $Cu(NO_3)_2.5H_2O$ was dissolved in the solution. After that, 100 ml of thioglycolic acid (0.1 M) was added to the solution and stirred for 30 minutes under pH of 11 and it was stirred for 1h. The solution was

transferred to a Teflon-lined autoclave (500 mL) and the reaction remained at 200°C for 12h. The product was washed repeatedly with alcohol and distilled water and centrifuged 3 times and dried in the oven at 45°C for 12 h.

Photo-degradation of azo-dyes

30 mL of Methyl orange, Methyl Red and Eriochrome Black-T (100 ppm) were used as a model pollutant to determine the photocatalytic activity. 0.2 g of catalyst was applied for degradation of 30 mL solution. The solution was mixed by a magnetic stirrer for 1h in darkness to determine the adsorption of the dye by the catalyst. The solution was placed under ultra-violet light irradiation in the middle of the reactor.

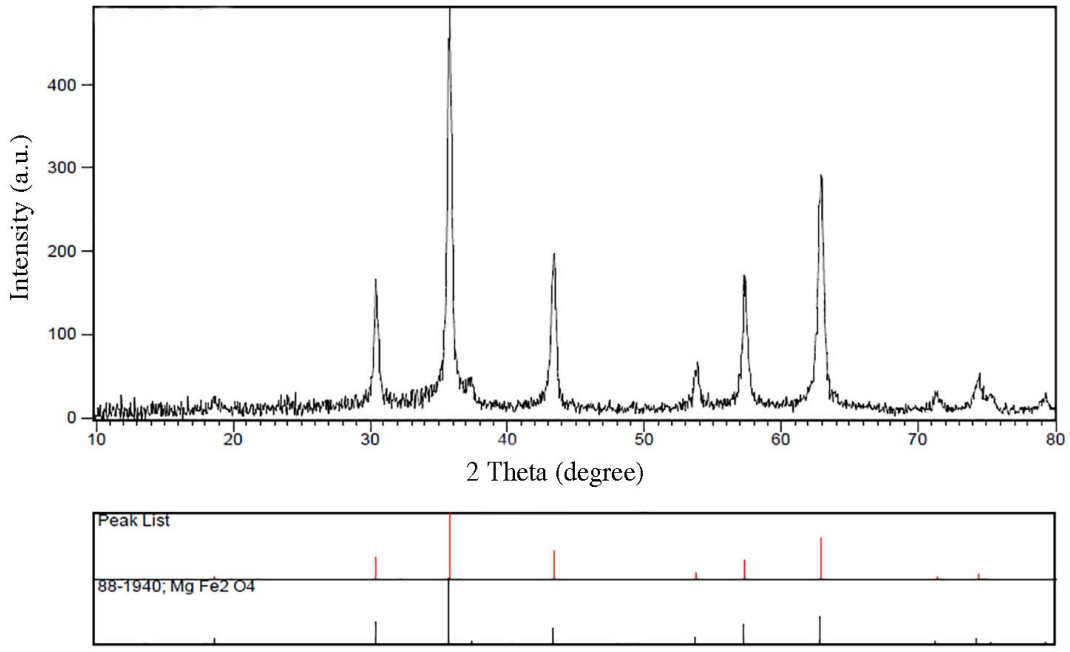

Fig. 1. XRD pattern of $MgFe_2O_4$ product

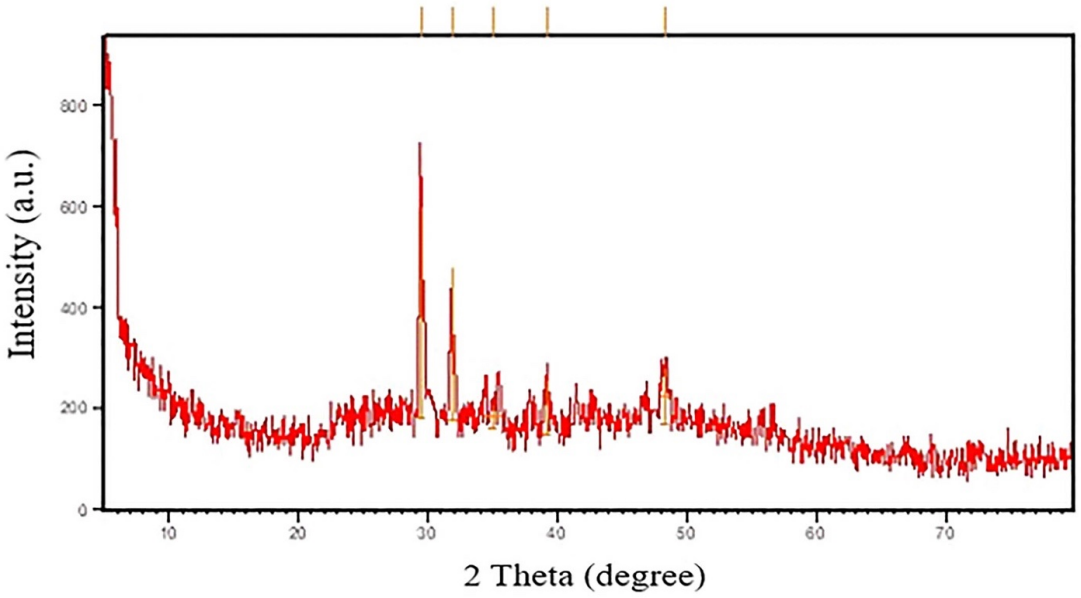

Fig. 2. XRD pattern of the copper sulfide.

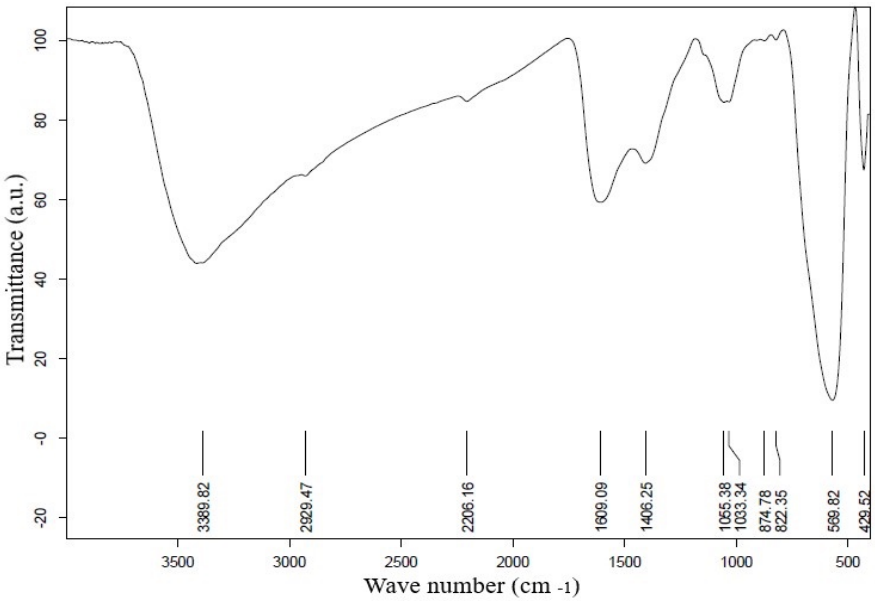

Fig. 3. FT-IR spectrum of $MgFe_2O_4$ nanoparticles.

The samples were filtered and centrifuged and their concentration was determined by UV-vis spectrometry.

RESULTS AND DISCUSSION

The XRD pattern of $MgFe_2O_4$ nanosheets is shown in Fig. 1. The pattern matched the standard peaks of JCPDS card no. 88-1940 and approved the production of ferrite. Narrow sharp peaks indicate that nano-structures are well synthesized. The XRD pattern of copper sulfide nanoparticles are illustrated in Fig. 2. The resulting copper sulfide has

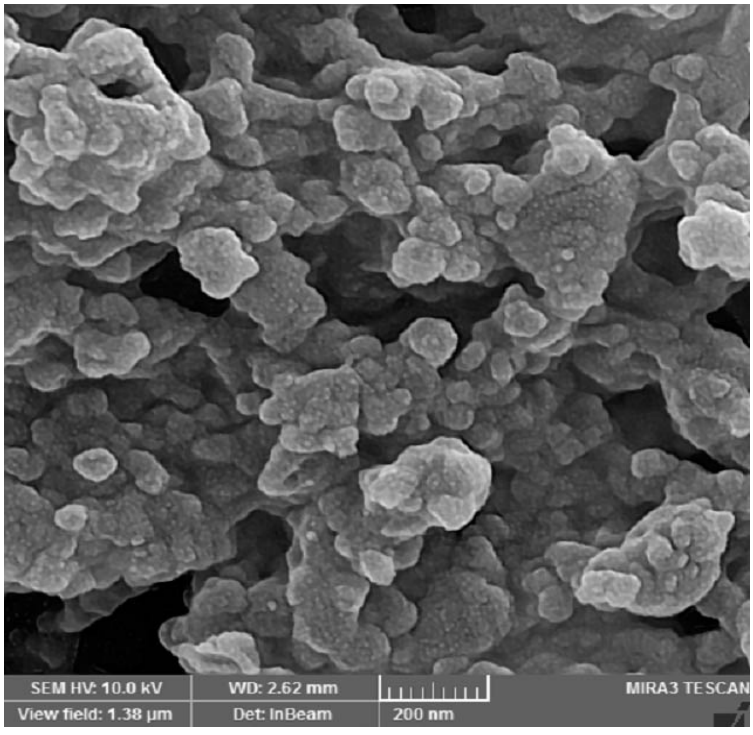

Fig. 4. SEM image of $MgFe_2O_4$ nanoparticles.

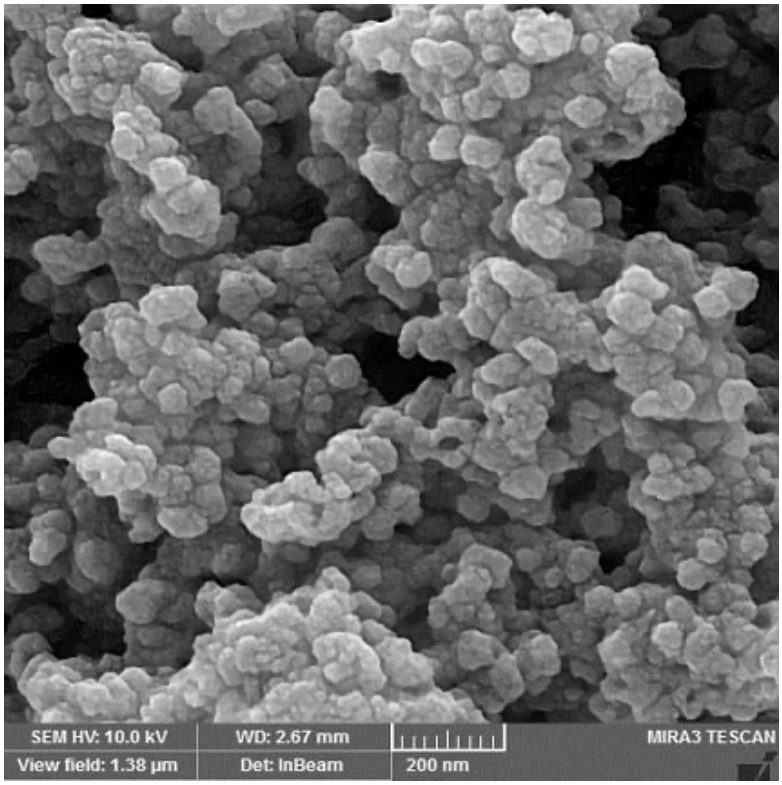

Fig. 5. SEM image of copper sulfide nanoparticles.

a structure between crystalline and amorphous structures. Diameter of crystal sizes is found about 40 nm calculated by Scherer equation, D=0.9λ/βCosθ, (β is the width of the observed diffraction peak at its half maximum intensity) and λ is (Cu-Ka radiation of X-ray, wavelength: 0.154 nm) [24].

Fig. 3 shows the FT-IR spectrum of the prepared $MgFe_2O_4$ nanoparticles, peaks at 492 and 569 cm^{-1} are related to the Mg–O and Fe–O bonds in $MgFe_2O_4$. The absorption peak at 3389 cm^{-1} is because of O–H groups that are adsorbed on the surface of nanoparticles.

Scanning electron microscopy was used to evaluate the morphology and particle size of the products. Fig. 4 illustrates SEM images of the $MgFe_2O_4$ nanoparticles. Results show

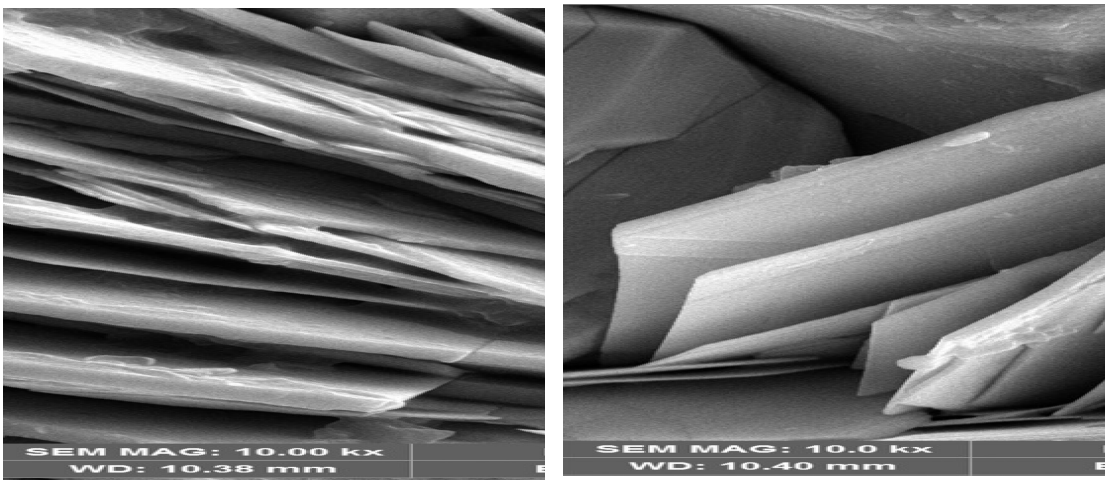

Fig. 6. SEM images of graphene oxide nanosheets.

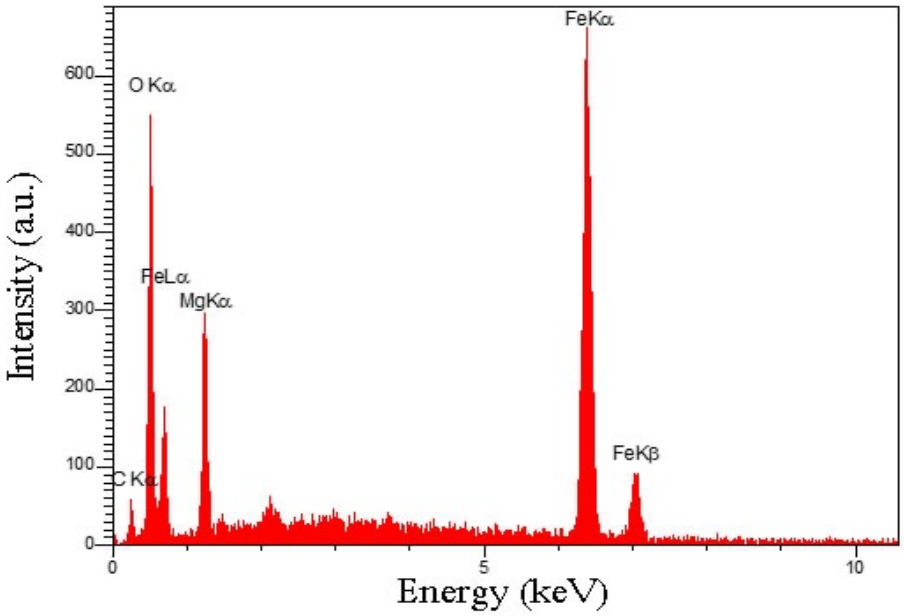

Fig. 7. EDX spectrum of magnesium ferrite nanoparticles.

agglomerated nanostructure was obtained. The sizes of nanoparticle are less than 50 nm. Shape and particle size can be controlled by the super-saturation during the nucleation and crystal growth processes, which can strongly be affected by precipitation conditions. Fig. 5 illustrates SEM images of the uniform copper sulfide nanoparticles. The shape of nanoparticles strongly influences their properties. Hydrothermal is the best chemical methods for preferential growth under high pressure. At the hotter place of reactor, the component solute dissolves, while at the cooler place it is deposited on a crystal.

The SEM images of graphene nanosheets

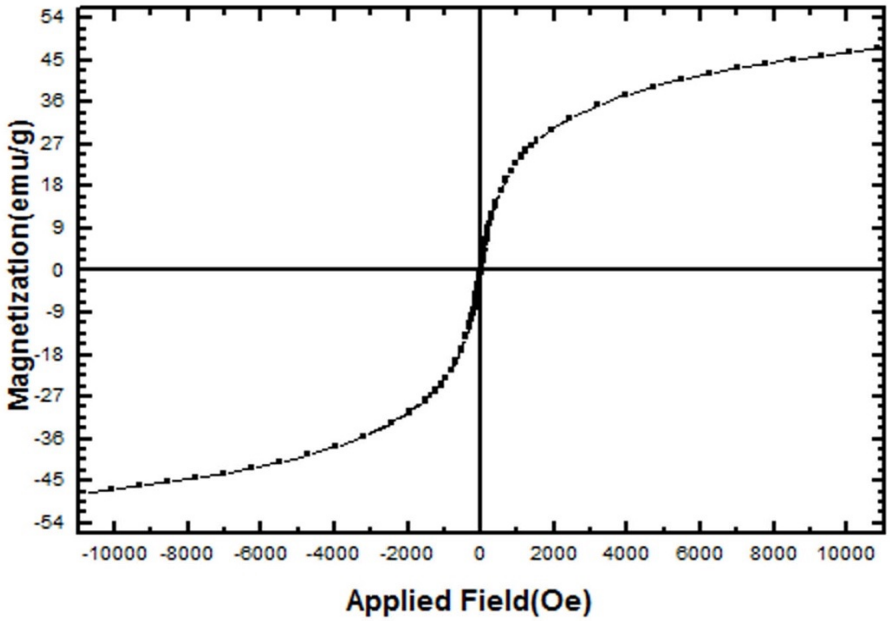

Fig. 8. VSM curve of magnesium ferrite nanoparticles.

prepared by Hummer's method are shown in Fig. 6. These images confirm the production of sheet nanostructures with an average thickness of less than 80 nm. Energy-dispersive X-ray spectroscopy of magnesium ferrite is shown in Fig. 7, K_a, K_b, L_a of iron and K_a of magnesium and oxygen obviously was confirmed. There is no main novelty in the patterns and confirm purity of the product.

The magnetic properties were investigated using the vibrating sample magnetometer technique. The hysteresis loops of pure $MgFe_2O_4$, $MgFe_2O_4$-GO and $MgFe_2O_4$-GO-CuS are shown in Figs. 8, 9

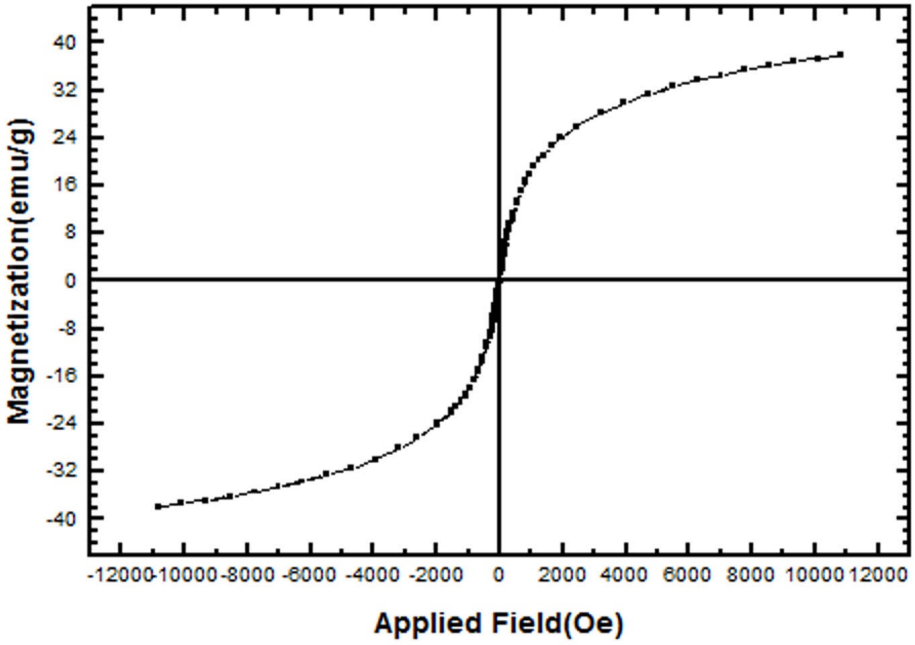

Fig. 9. VSM curve of magnesium ferrite- graphene oxide nanocomposite.

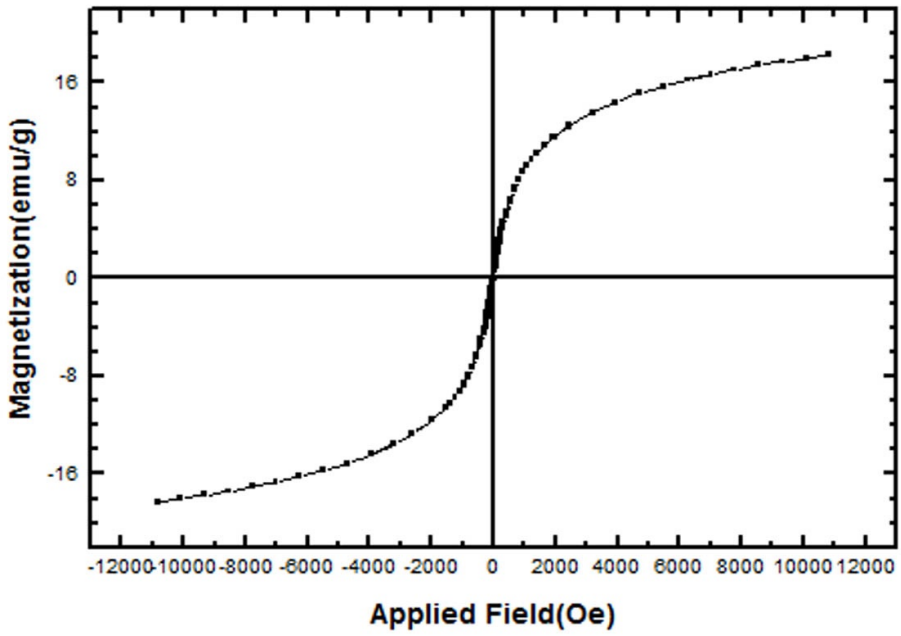

Fig. 10. VSM curve of magnesium ferrite- graphene oxide-copper sulfide nanocomposite.

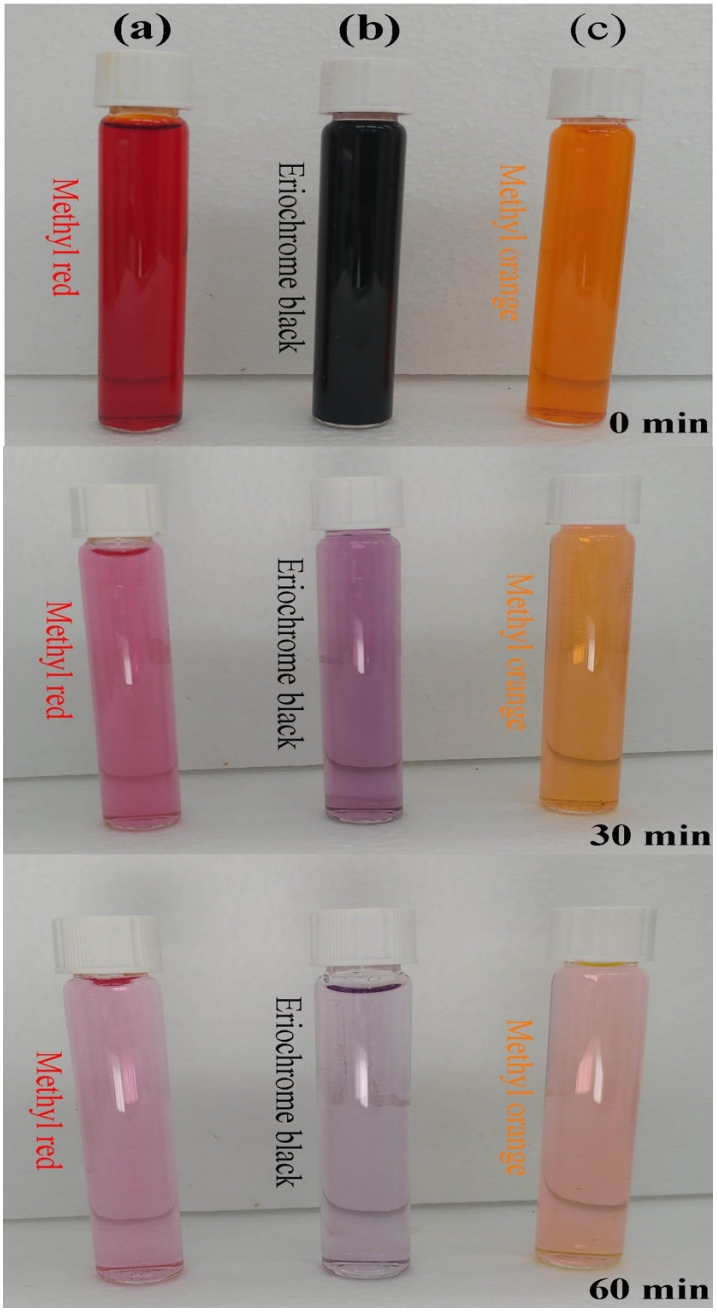

Fig. 11. Photo-degradation of (a) Methyl Red (b) Eriochrome Black-T and (c) Methyl orange under UV irradiation 0 min, 30 min and 60 min.

and 10, respectively. Magnetic cores have good magnetization, which makes them suitable for recyclable photocatalyst core. Ferrite nanoparticles show saturation magnetization of 48 emu/g and a coercivity of about zero Oe. The $MgFe_2O_4$-GO has a saturation magnetization of about 37 emu/g and a coercivity of about 10 Oe. The $MgFe_2O_4$-GO-CuS has a saturation magnetization of about 18 emu/g and a coercivity of about 30 Oe. Magnetization is a quantitative quantity in nanocomposite, there is a non-magnetic grapheme oxide and copper sulfide coating, so the magnetization of nanocomposite is reduced. Also, the interaction between ferrite and grapheme oxide also copper sulfide, this

interaction leads to an increasing (from 0 Oe to 30 Oe) of nanocomposite coercivity.

The photocatalytic activity of $MgFe_2O_4$-GO-CuS nanocomposite was evaluated by monitoring the decomposition of Methyl Red, Eriochrome Black-T and Methyl orange in aqueous solution under sunlight. Changes in color concentration in 60 min are shown in Fig. 11. Over time, more dyes are absorbed into the nanocomposite catalyst, and organic dyes decompose into carbon dioxide, water, and other less toxic or non-toxic residues. By the time the UV- Vis adsorption peak of Methyl orange, Methyl Red and Eriochrome Black-T, disappeared in about 60 min.

CONCLUSION

Magnesium ferrite nanoparticles were synthesized via a hydrothermal method in presence of cost-effective materials and procedure, then $MgFe_2O_4$-GO-CuS nanocomposites were prepared by hydrothermal method. The photocatalytic behavior of the $MgFe_2O_4$-GO-CuS nanocomposite was tested by applying the degradation of three azo dyes under ultra violet irradiation. Results introduce a new class of magnetic and photo catalyst materials for solving Environmental pollutions.

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