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RESEARCH PAPER

Hydrothermal Synthesis of Magnetic and Photoluminescence $CuFe_2O_4$-Carbon dots Nanocomposite as a Sensor for Detecting of Hg(II) Ions

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ABSTRACT

Carbon quantum dots were prepared by using ethylene-diamine and citric acid materials. Micro-wave was applied for synthesis of copper ferrite, hydrothermal method was used as an effective method for preparation of product with preferential growth. Finally, $CuFe_2O_4$ and magnetic copper ferrite-carbon nanocomposite were synthesized. The effects of power and cycles on the morphology and particle size were investigated. Nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microsco-py (TEM), Fourier transform infrared (FT-IR) spectroscopy, ultra violet-visible (UV-Vis) absorption and photo-luminescence (PL) spectroscopy. The prepared product show suitable photo-luminescence under ultraviolet irradiation. Vibrating sample magnetometer (VSM) shows ferromagnetic property of the both $CuFe_2O_4$ and copper ferrite-carbon nanocomposite. The results show that this method for preparation of magnetic and luminescence nanocomposite as a candidate for sensor applications.

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INTRODUCTION

Carbon dots (CDs) or carbon quantum dots with diameters less than 10 nm introduce a new type of carbon nano-materials. Compare to conventional aromatic dyes and semiconductor quantum dots, CDs have specific properties such as low toxicity, flexible functionalization, bio-compatibility and reliable photoluminescence [1]. These carbon nanoparticles progressively turn into applicable nanomaterials because of their low-priced nature and their usages in optoelectronic devices, biological labeling, specific sensing, medicine delivery and biomedicines. Luminescent carbon dots are superior because of aqueous solubility, high quantum yields, size-tunable emission, chemically and physically stability, narrow spectral bands, easily surface modification, resistance to photobleaching. For choosing low price precursors low energy reactions, various methods are being chosen [1-3]. Carbon due to the different electron orbital types (e.g. sp, sp^2 or sp^3 hybrid) and size dependent electric and surface properties have shown giant potential including nanoelectronics, catalyst supports, sensors, drug delivery and electrochemical energy storage. [1-5]. Q-Dots are colloidal semiconductors comprising elements from the periodic groups II–VI, III–V or IV–VI, which are harmful to health. This has limited the scope of usage especially for those related to biomedical and health diagnostic applications. Leaching of the heavy metal ions will be dangerous towards

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the biological system and the environment. CDs are not only less toxic, but also reported to have less fluorescent blinking effect and different possible precursors while basically synthesis steps are similar. C-Dots obtained often show variation in optical properties related to different precursors, carbonization conversion methods, and/or the pre-treatment performed [6-9]. A large amount of biocompatible fluorescence nanomaterials, such as quantum dots, metal nanoclusters, and fluorescent polymers, has been developed. photo bleaching, no optical blinking, circumscribed by their photo bleaching or intrinsic potential hazards of heavy metal elements [10-13] Several methods were reported to prepare nanomaterials using natural biomass, which exhibited potential applications in various fields, such as energy nanomaterials, analytical sensing, and other functionalized materials. Many procedures were developed for the preparation of CQDs with desired properties including arc discharge, ion beam radiation and laser ablation, electrochemical, chemical oxidation, using various precursors including graphite, fullerene, solvothermal, sonochemical, and microwave methods. Between them, solvo or hydro-thermal preparation was considered to be a simple and efficient way to prepare CQDs. Herein, fluorescent carbon quantum dot were prepared by one-pot hydrothermal treatment in which turmeric juice was used as natural material [14-19].

MATERIALS AND METHODS

$Fe(NO_3)_3\ 9H_2O$, $Cu(CH_3COO)_2\ 4H_2O$, NaOH, , distilled water and methanol were purchased from Merck Company. XRD analysis was obtained by Philips, X-ray diffractometer (Ni-filtered CuK_α radiation). SEM images were obtained using KYKY instrument model 1455VP. All the chemicals were used as received without further purifications. Room temperature magnetic properties were investigated using vibrating sample magnetometer (VSM) device, (Meghnatis Kavir Kashan Co., Iran) in an applied magnetic field sweeping between ± 10000 Oe. the The samples were coated by a very thin layer of Pt (using a BAL-TEC SCD 005 sputter coater) to make the surface conductor and avoid charge accumulation, and obtaining a better contrast. A multiwave ultrasonic generator (Bandeline MS 73), equipped with a converter/transducer and titanium oscillator, operating at 20 kHz with a maximum power output of 100 W was used for the ultrasonic irradiation.

Synthesis of carbon quantum dots

In typical synthesis, 0.1 mol of ethylene-diamine and 0.2 mol of citric acid were dissolved in 40 ml of deionized water, and it was stirred for 30 min. Then the solution was transferred into Teflon lined stainless autoclave at 180-200 °C for 10-48 h. Different parameters such as time, temperature, frequency and power were studied. The optimum condition was 24 h and 200 °C. The final product was soluble in water.

Synthesis of $CuFe_2O_4$ nanoparticles

0.01 mol of copper acetate tetra hydrate and 0.1 mol of ethylene-diamine and 0.2 mol of citric acid were dissolved in in 200 ml of water. 20 ml of NaOH (1M) was added to the solution until reaching pH to the 11. Then the dispersion was transferred into autoclave under microwave irradiation 600W, 10 min, the brown-black precipitate was centrifuged and washed by distilled water for 2 times.

Preparation of $CuFe_2O_4$-carbon quantum dot nanocomposite

0.1 g of copper ferrite was dispersed in 10 ml of turmeric solution and the dispersion was transferred into Teflon lined stainless autoclave at 200 °C for 24 h. The precipitate was washed by distilled water and ethanol.

RESULTS AND DISCUSSION

Schematic diagram for preparation of carbon quantum dot from ethylene diamin and citric acid using hydrothermal procedure is depicted in Fig. 1. Fig. 2 illustrates synthesized GQDs at 200 ° C respectively under day light and UV light (366 nm). CQDs was used for writing on black tissue. Typing word is not visible under ambient light; however, it can be seen under UV light. Basically, synthesis of C-Dots contains three main steps; carbonization, passivation, and surface functionalization [4]. Carbonization is the process that starting organic precursors convert into its basic carbon element or carbon containing residues via pyrolysis, strong dehydration, or destructive distillation. Pure carbon nanoparticles are usually non-fluorescent and the chemical treatment of the surface also known as passivation step is usually needed. In this step an insulating shell on the surface minimizes the impact of surface-defect, trap, and quenching from the surrounding, which lead to increase in fluorescence emission. Finally, the functionaliza-

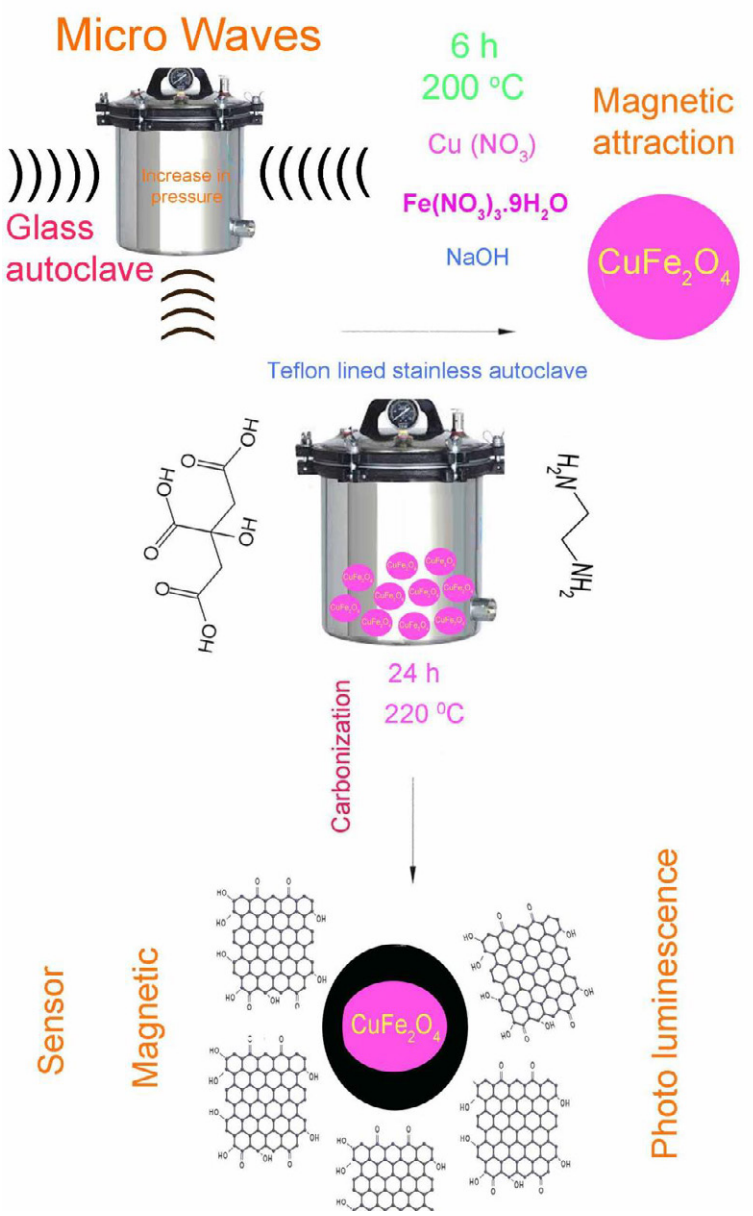

Fig. 1. Schematic of preparation of copper ferrite-carbon dot nanocomposite

tion step is performed to add a specific chemical or biological reactivity on the surface of the C-Dots [4-7].

Fig. 3 illustrates XRD pattern of $CuFe_2O_4$ product. Pure cubic phase of ferrite (JCPDS No.77-0010) can be observed in this pattern. The understanding of the origin of fluorescence in carbon nanoparticle is far from sufficient. For example, information on the microstructure and surface ligands remains unclear and details of the organic passivation is not sufficient to aid understanding of the surface states beneficial for light emission.

Fig. 4 depicts FT-IR spectrum of CDs at 200 °C for 48h. product obtained after hydrothermal reaction at 180 °C for 24 h. Peaks at 1630 and 3410 cm^{-1} are related to C=O and O-H group respectively. Peak at 1050 cm^{-1} are attributed to presence of C-O group. Absorption at 2930 cm^{-1} is related to C-H bonds. Peaks at 1620 and 3350 cm^{-1} attribute to carboxyl and hydroxyl group respectively.

Fig. 5 shows scanning electron microscopy image of $CuFe_2O_4$ nanoparticles that approve forma-

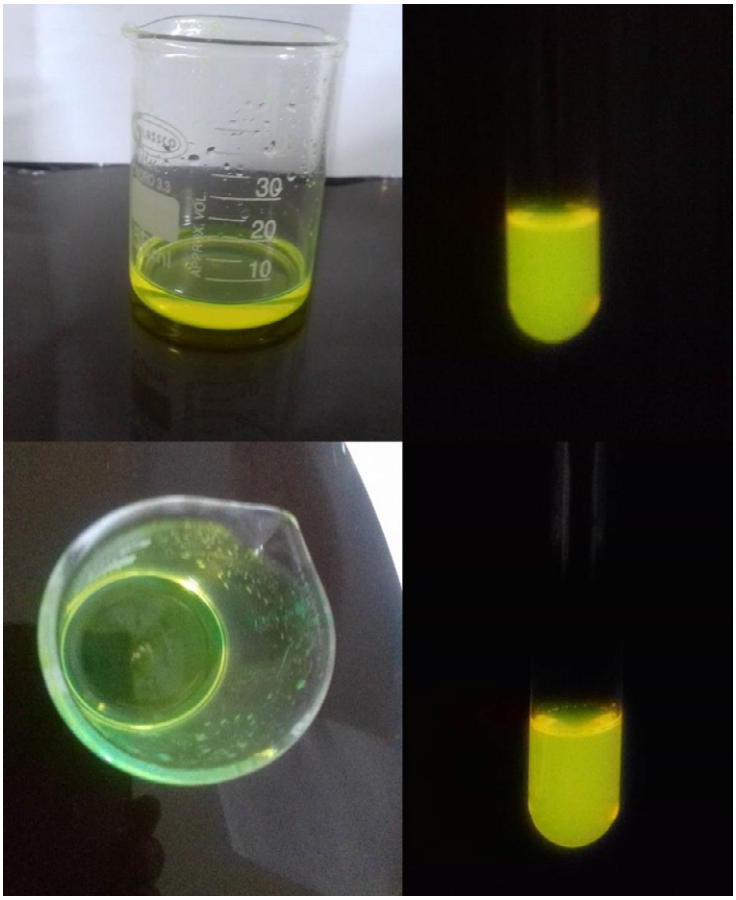

Fig. 2. Carbon quantum dot under UV irradiation

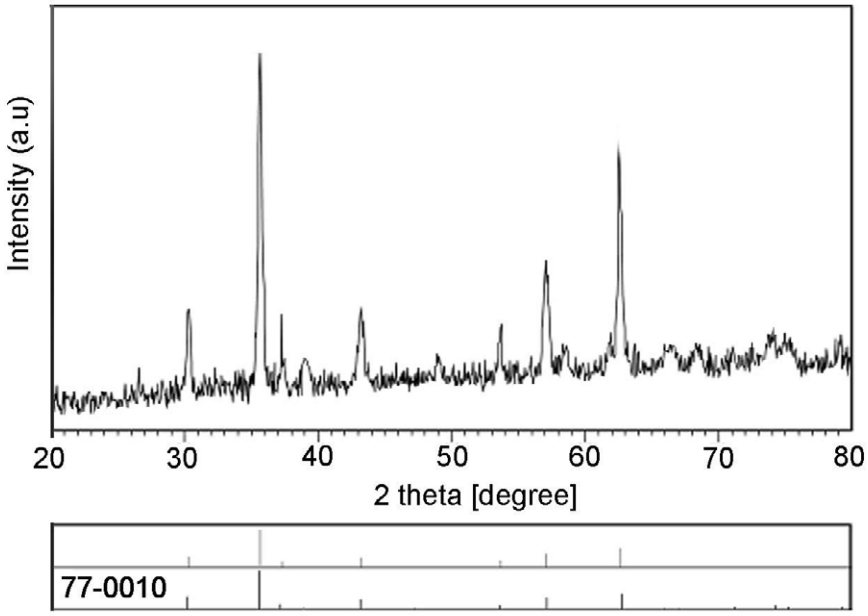

Fig. 3. XRD patterns of $CuFe_2O_4$-carbon dot nano composite

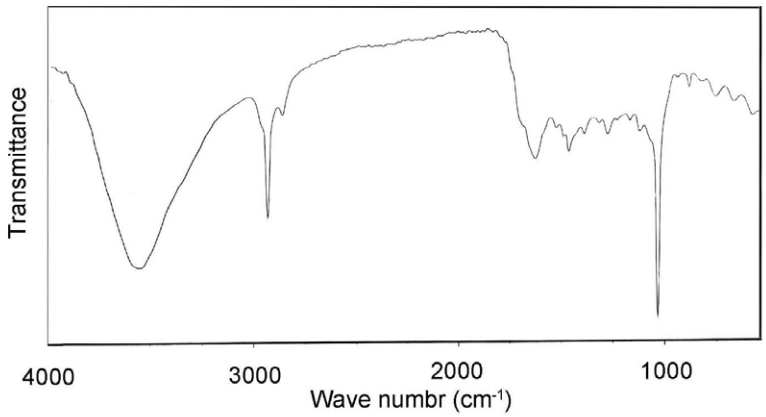

Fig. 4. FT-IR spectrum of $CuFe_2O_4$-carbon dot

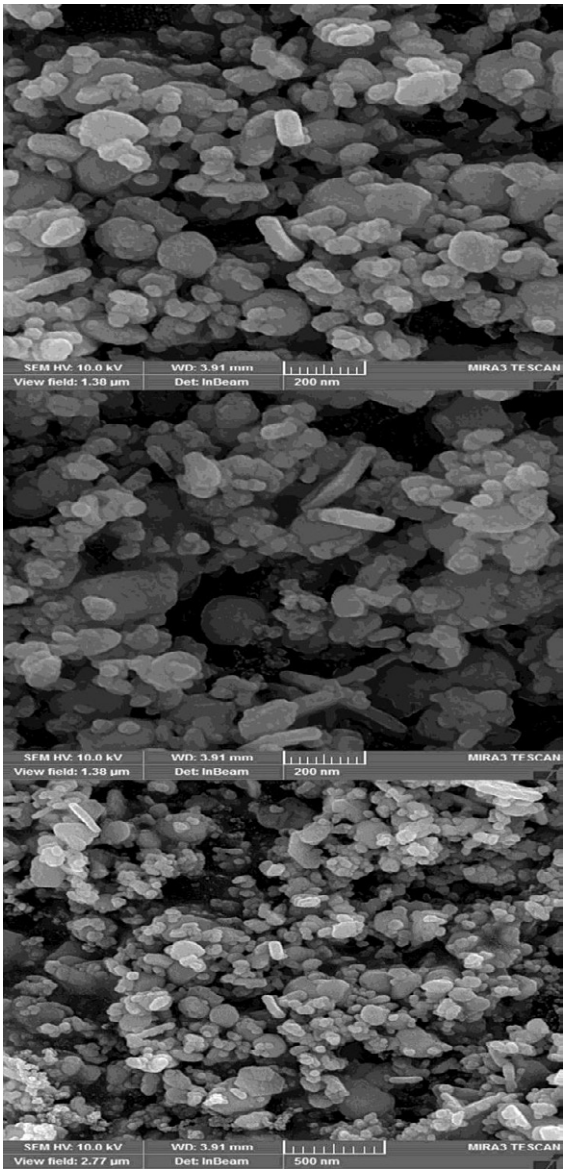

Fig. 5. SEM image of $CuFe_2O_4$ nanoparticles 10 min 600W

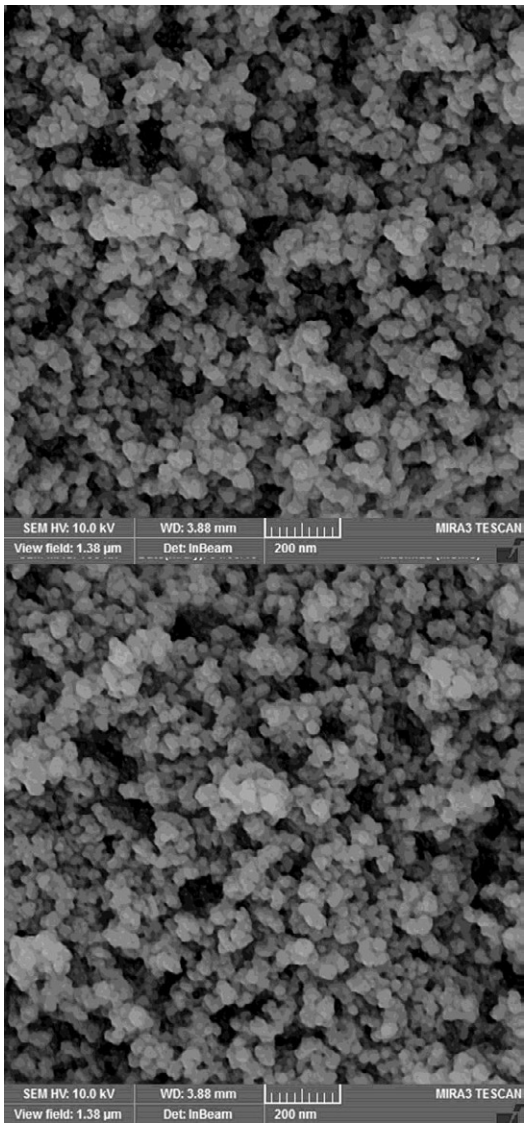

Fig. 6. SEM images of carbon dot at 200 °C for 24h

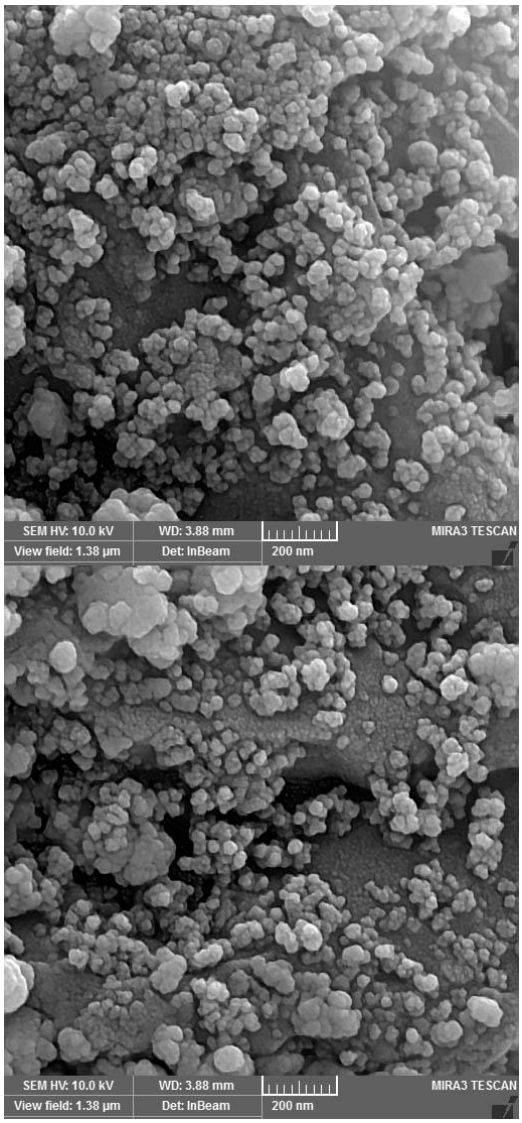

Fig. 7. SEM images of $CuFe_2O_4$-carbon dot at 200 °C for 24h

tion of mono-disperse nanoparticles, average particle size is less than 70 nm.

Fig. 6 illustrate SEM of carbon dots prepared at 200 °C for 24h. SEM images of the obtained product show that these GQDs are uniform in size ranging from 40 to 100 nm in diameter. CQDs stacking to form large particles. Qin Li and et el report that this happens because at higher temperature most of tiny particles stack and form larger particles with inhomogeneous sizes [12].

Fig. 7 show SEM images of the prepared $CuFe_2O_4$-carbon dot that show these CQDs are uniform in size around 50 nm in diameter. According to the image, CQDs stacking to form large particles. This also happens because at higher temperature most of tiny particles stack and form larger particles with inhomogeneous sizes [11-17].

UV-Vis spectrum of graphene quantum dots at various temperature and time at 200 °C at 48 h is shown in Fig 8. The Graphene Quantum Dots shows absorption bands around 400 nm which is attributed to π-π* transition of graphene quantum dots that confirm preparation of graphene from natural turmeric.

Properties of graphene quantum dots and carbon dots such as optical properties strongly depend on preparation method and precursors. Here graphene quantum dots are prepared by

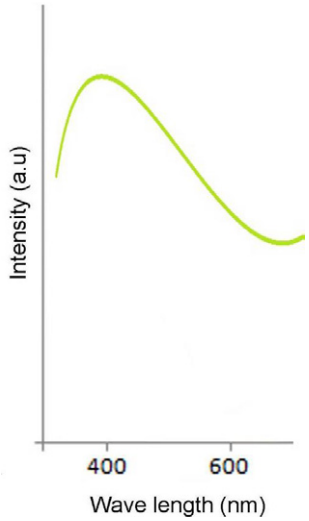

Fig. 8. UV-vis absorption analysis of carbon dot nanoparticles

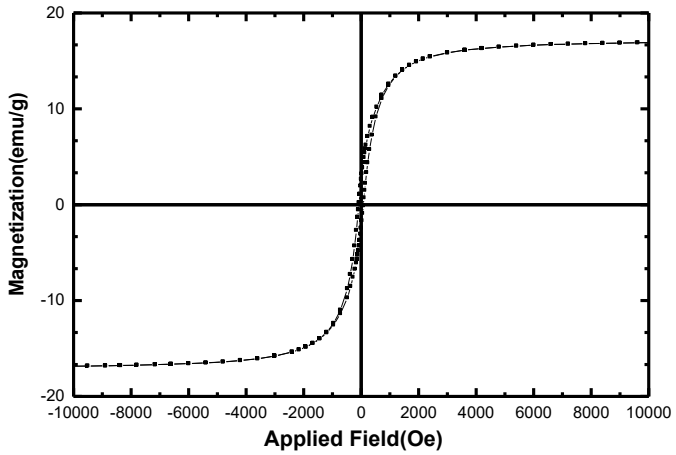

Fig. 9. VSM curve of $CuFe_2O_4$ nanoparticles

using turmeric and hydrothermal as starting materials and synthesis method, respectively. This is the first time that graphene quantum dots are prepared by this method and these starting materials. As-synthesized graphene quantum dots show high quantum yield, which make them a suitable candidate for fluorescent probes in fluorescence detection. Quantum yield for prepared Graphene quantum dots is 20%. and has stability fluorescence after six months. Quantum Yield can be expressed by this equation $\phi = \phi_r \times A_r/I_r \times I / A \times n^2/n_r^2$, ($\phi$ is the quantum yield; ϕ_r is the reference quantum yield that is for Rhodamine B, equal to 0.31. A_r and I_r respectively are reference absorption and integral area under the curve). The A and I illustrate respectively sample absorption and integral area under the curve [20-25].

Room temperature magnetic properties of samples were studied using VSM instrument. Hysteresis loops of magnetic $CuFe_2O_4$ nanoparticles and $CuFe_2O_4$-carbon nanocomposite are shown in Figs.9 and Fig.10 respectively. The nanoparticle samples exhibit sufficient magnetizations which can simply be attracted by a magnet, making them appropriate for core of recyclable photocatalyst. The hysteresis loop also indicates that the as-synthesized nanoparticles show ferromagnetic behaviour with saturation magnetization of 16 emu/g and nearly 400 coercivity. The hysteresis of $CuFe_2O_4$-carbon nanocomposite also show ferromagnetic behaviour with saturation magnetization of 8 emu/g and nearly 500 coercivity.

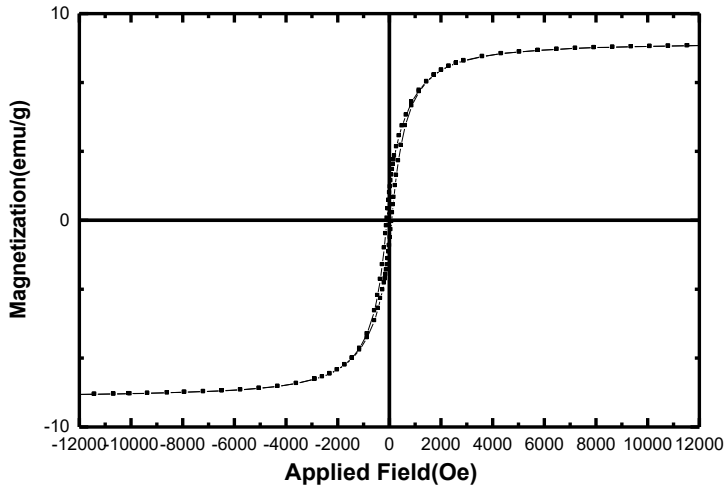

Fig. 10. VSM curve of $CuFe_2O_4$-carbon dot nanocomposite

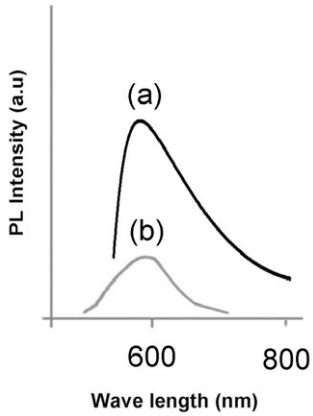

Fig. 11. PL spectra of products at 200 °C (a) pure (b) after addition of Hg(II) ions

We studied the magnetic interaction between the nanoparticles surrounded by carbon dots. This interaction leads to an increase (from 400 Oe to 500 Oe) of nanocomposite coersivity in comparison to pure cobalt ferrite nanoparticles. Apparently, magnetic domains are pined by carbon dots and as a result higher magnetic field is needed for changing in magnetic domains of ferrite.

Photo luminescence of pure sample at 200 °C at 48h is shown in Fig 11a, PL intensity around 500-565 nm were obtained with the excitation wavelength of 330 nm. About PL mechanism of GQDs, two main reasons are proposed. First, surface/ edge state in GQDs that explains when grapheme is cutting along different directions, armchair and zigzag edges can be obtained. Edge types is more important key in electronic properties of GQDs. In addition, oxygen and amine based groups on surface of GQDs affect optical band gap. For this reason, synthesis method and starting materials play important role on electronic properties of GQDs. Second is attributed to quantum confinement in GQDs. After addition of Hg(II) ions luminescence intensity was reduced intensively Fig 11b.

CONCLUSION

Copper ferrite, carbon quantum dots and copper ferrite-carbon with high quantum yield were prepared by using turmeric, these prepared quantum dots show long term fluorescence stability. The graphene quantum dots synthesized by turmeric extract were prepared in a very simple way and its quantum yield was as high as ca. 20%. The effect of time and temperature on the morphology and particle size was investigated. Nanostructures were characterized by XRD, SEM, TEM, FT-IR, VSM, UV-Vis and PL spectroscopy. The prepared product show suitable photo-luminescence under ultraviolet irradiation. The results show that turmeric assisted and green synthesis is a suitable method for preparation of magnetic and luminescence nanocomposite as a candidate for sensor applications.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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