Synthesis and characterization of graphene quantum dots/cobalt ferrite nanocomposite

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Abstract. A facile method has been developed for the synthesis of a graphene quantum dots/cobalt ferrite nanocomposite. Graphene quantum dots (GQDs) were synthesized by a simple bottom-up method using citric acid, followed by the co-precipitation of cobalt ferrite nanoparticles on the graphene quantum dots. The morphology, structural analysis, optical properties, magnetic properties were investigated using transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-vis absorption spectroscopy, fluorescence spectroscopy, vibrating sample magnetometry (VSM) measurements. The synthesized nanocomposite showed good fluorescence and superparamagnetic properties, which are important for biomedical applications.

1. Introduction

Graphene quantum dots (GQDs), the zero-dimensional graphene nanoparticles with unique properties such as photoluminescence and biocompatibility [1–3] have attracted remarkable interest in the field of nanoscience. These properties along with quantum confinement and edge effects make graphene quantum dots a promising candidate for drug delivery providing real-time fluorescence imaging of cellular structures [4–6].

Both top-down and bottom-up methods for the synthesis of GQDs have been reported over the years. Top-down methods which involve the breaking down of carbon-based materials, are often unsatisfactory due to the requirement of expensive equipment, long synthesis times, treatment with strong acids and the need for difficult purification steps to remove byproducts [1,3,4,6–8]. In 2012, Dong and co-workers synthesized GQDs by refluxing carbon black with concentrated nitric acid. Although this method resulted in the high yield production of GQDs, the purification step involved long hours of dialysis [3]. Zhang et al demonstrated that the electrolysis of graphite rod will result in the formation of GQDs [9]. In 2014, Yin Zhang and co-workers synthesized GQDs by chemical exfoliation of graphene oxide by treating it with a strong acid mixture [10]. In the bottom-up approach,
GQDs are synthesized from organic precursors to synthesize graphene quantum dots [2,11]. Gu et al used glucose, a low-cost carbon source to synthesize high yield GQDs by a hydrothermal method [11]. Wu et al developed a low-cost method to synthesize highly fluorescent GQDs by the pyrolysis of L-glutamic acid [12]. Recently Liu and co-workers fabricated GQDs with uniform size using hexa-peri-hexabenzocoronene [13].

Magnetic resonance imaging (MRI) is a versatile non-invasive diagnostic biomedical imaging tool. Different types of magnetic nanoparticles (MNPs) have been used in the recent years to act as MRI contrast agents. These contrast agents work by shortening the relaxation times of the tissues they have accumulated in. Positive contrast agents produce T₁ weighted images by causing a reduction in the T₁ (longitudinal) relaxation time of the water protons. The images appear brighter and are useful in the differentiation of anatomical structures. Negative contrast agents reduce the T₂ (transverse) relaxation time. The T₂ weighted images are preferred as they provide pathological information since abnormal tissues filled with water appear brighter than the surrounding normal tissues [14]. The relaxivity of a contrast agent is an important parameter in deciding its efficacy. Higher the relaxivity, higher will be the image contrast [15].

Super-paramagnetic iron oxide (SPIO) nanoparticles are being used as T₂ (negative) contrast agents for many years [16]. Magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and hematite (α-Fe₂O₃) are the three main iron oxides [17]. Many works have been reported that also shows the significance of ferrites of transition metals like Cu, Co, Mn, and Ni as superparamagnetic contrast agents [14,18,19]. Of the ferrites, Co₃O₄ has been gaining more attention, due to its high coercivity, moderate magnetization and great physical and chemical stability [20]. Many recent studies confirm the prospects of using cobalt ferrite as an efficient contrast agent [19–22]. The immobilization of CoFe₂O₄ nanoparticles on GQDs will result in a multifunctional nanoplatform for effective drug delivery and monitoring by fluorescence imaging and magnetic resonance imaging. In this article, we discuss the synthesis of GQD/CoFe₂O₄ nanocomposite by a simple co-precipitation of cobalt ferrite nanoparticles on graphene quantum dots and its characterization using various techniques.

2. Experimental

2.1. Materials and characterizations
Citric acid (C₆H₈O₇) (Benzer Multitech), Sodium hydroxide (NaOH) (Rankem), Ferric chloride (FeCl₃·6H₂O) (Merck), Cobalt nitrate (Co(NO₃)₂·6H₂O) (Merck) were used as purchased.

UV-vis absorption studies were performed using Shimadzu UV-vis 1800 spectrophotometer. Photoluminescence studies were carried out on Shimadzu RF 6000. IR spectra were recorded using Thermo Scientific Nicolet IS10 instrument. X-ray diffraction studies were carried out on a BrukerD8 Advanced instrument. Raman analysis was performed on a Bruker RFS 27 instrument TEM was performed on an [FEI TECNAI] F 20 instrument. VSM studies were performed on a Lakeshore (model: 7410) instrument.

2.2. Synthesis of graphene quantum dots (GQDs)
GQDs were synthesized by the carbonization of citric acid (CA) as previously described in the literature [2]. Typically, 2g of citric acid was taken in a beaker and heated to 200°C in a heating mantle. After a few minutes, the liquid CA which was colourless turned to pale yellow and then to orange, confirming the formation of GQDs. The obtained liquid was neutralized to pH 7 by adding it drop by drop into 100 mL of 10 mg mL⁻¹ NaOH solution to obtain an aqueous solution of GQDs.
2.3. Synthesis of GQD/CoFe$_2$O$_4$ nanocomposite
10mL of the initially synthesized GQD solution was taken in a beaker. To this solution, 4mM FeCl$_3$.6H$_2$O and 2mM Co(NO$_3$)$_2$.6H$_2$O was added with vigorous stirring. 10 mL of NaOH solution was then added to maintain the pH at 11. This mixture was maintained at 80°C for 1 hour to precipitate the nanoparticles. Once the temperature of the mixture was bought down to room temperature, the product was isolated by centrifugation and dried at 70°C to obtain the nanocomposite.

3. Results and discussion

3.1. Optical Studies
The optical properties of the synthesized GQDs were studied using UV-vis and PL spectroscopy. The absorption spectrum of GQDs does not show any peak as seen in figure 1(a). The fluorescence spectra of GQDs can be seen in figure 1(b). The GQDs were excited at wavelengths 360 nm, 380 nm and 400 nm and the PL emission peaks were observed at 476 nm, 477 nm, 482 nm respectively. The emission peaks show a gradual red shift with an increase in the excitation wavelengths. It can be seen that the color of the aqueous GQD solution is pale yellow under visible light, in contrast to the greenish-blue fluorescence when excited at 365 nm UV light (inset of figure 1(b)).

![Figure 1](image1.png)

**Figure 1.** (a) UV-Vis absorbance spectra of GQDs. (b) Fluorescence spectra of GQDs. Inset shows photographs of GQD solution taken under visible light (pale yellow) and 365 nm excitation (green)

![Figure 2](image2.png)

**Figure 2.** Fluorescence spectra of GQD/CoFe$_2$O$_4$
The change in fluorescence after the co-precipitation of cobalt ferrite nanoparticles on GQDs was also studied. The PL spectra of GQD/CoFe$_2$O$_4$, excited at wavelengths of 360 nm, 380 nm and 400 nm is shown in figure 2. The PL emission peaks were observed at 475 nm, 467 nm and 455 nm respectively. It can be seen that with the increase in excitation wavelengths, the emission peak undergoes a blue shift. This difference in the PL characteristics when compared to the GQDs is due to the change in the surface chemistry of the nanocomposite suggesting a possible growth of cobalt ferrite nanoparticles on the GQDs, causing a change in the surface properties of GQDs.

3.2. FT-IR

Figure 3. FTIR spectra of GQD/CoFe$_2$O$_4$

Figure 3. shows the FTIR spectrum of the GQD/CoFe$_2$O$_4$ nanocomposite. The broad peak at 3416 cm$^{-1}$ is attributed to the O-H bond stretching, indicating the absorbance of water by the nanocomposite. The peaks at 2981 cm$^{-1}$ and 1451 cm$^{-1}$ are due to the C-H stretching vibration from residual citric acid, suggesting the incomplete carbonization of citric acid [2]. The peak obtained at 863 cm$^{-1}$ is due to the bending vibration of the C-H bond. The peak seen at 681 cm$^{-1}$ is attributed to the vibration of Co-O bond. The formation of the magnetic nanoparticles can be confirmed by the the peak obtained at 582 cm$^{-1}$, which is due to the stretching vibration of Fe-O bond [23].

3.3. XRD

The X-ray diffraction peaks of the nanocomposite was in good agreement with the pure cobalt ferrite (JCPDS 22-1086) showing prominent peaks at 20 = 17.15, 30.59, 32.73, 38.38, 41.88, 45.78, 57.46 and 62.92, which can be assigned the (111), (220), (311), (222), (400), (331), (511) and (440) planes of CoFe$_2$O$_4$ respectively (Figure 4). The diffraction peak of GQDs (004) (JCPDS 26-1080) is not observable as the cobalt ferrite crystals have grown between the GQDs.
3.4. Raman Analysis

The Raman spectra for the synthesized GQDs as seen in figure 5(a) shows the characteristic G band at 1677 cm\(^{-1}\) and D band at 1446 cm\(^{-1}\) with an intensity ratio \(I_D/I_G\) of 0.81. The G band corresponds to the vibration of the \(sp^2\) bonded C atoms in the two-dimensional hexagonal lattice structure. The D band signifies the crystal defects due to the destruction of the \(sp^2\) bonded C atoms by the \(sp^3\) bonded C atoms. It can be seen in Figure 5(b) that compared to the Raman spectrum of GQDs, the characteristic G and D bands have shifted to higher frequencies. The G band is observed at 2094 cm\(^{-1}\) and D band is observed at 1814 cm\(^{-1}\) with an intensity ratio \(I_D/I_G\) of 0.83. This increase in the intensity ratio compared to that of GQDs shows the degree of disorder caused due to the introduction of cobalt ferrite nanoparticles [21,24].
3.5 TEM analysis

The morphology, composition and structural properties of a sample can be studied using TEM. Figure 6(a) shows the TEM image of GQD/CoFe$_2$O$_4$ in which the darker region corresponds to the agglomerated cobalt ferrite nanoparticles on graphene quantum dots. The HRTEM image (figure 6(b)) depicts the lattice fringes with a d spacing of 0.25 nm which corresponds to the (311) plane of cobalt ferrite. Figure 6(c) shows the SAED pattern with diffraction rings corresponding to the (400), (222), (220), (440) planes of cobalt ferrite crystal. The TEM data is thus in good agreement with XRD.

![TEM images](image_url)

**Figure 6.** (a) Low magnification TEM image of GQD/CoFe$_2$O$_4$ (b) HRTEM image of GQD/CoFe$_2$O$_4$ (c) SAED pattern GQD/CoFe$_2$O$_4$
3.6. Magnetic study
The magnetic properties of GQD/CoFe$_2$O$_4$ were studied by VSM at room temperature from -20,000 Oe to 20,000 Oe, as shown in figure 7. The field-dependent magnetic curve shows negligible remanent magnetization ($M_r$) and coercivity ($H_c$), showing superparamagnetic behaviour at room temperature. The saturation magnetization ($M_S$) of the obtained GQD/CoFe$_2$O$_4$ nanocomposite is 24 emu/g. The saturation magnetization is lower with respect to that of the pure CoFe$_2$O$_4$ (94 emu/g) [21]. This can be attributed to the presence of GQDs and the surface defects of CoFe$_2$O$_4$ crystallites [21]. These results prove that the obtained GQD/CoFe$_2$O$_4$ nanocomposite is superparamagnetic and is useful for magnetic resonance imaging.

![Magnetization curve of GQD/CoFe$_2$O$_4$ nanocomposite](image)

Figure 7. Magnetization curve of GQD/CoFe$_2$O$_4$ nanocomposite

4. Conclusions
Graphene quantum dots/cobalt ferrite nanocomposite was synthesized by a simple co-precipitation method. The GQD/CoFe$_2$O$_4$ nanocomposite was characterized by XRD and TEM to understand the morphology and formation of cobalt ferrite nanoparticles on GQDs. The as-synthesized nanocomposite showed good fluorescence. The VSM result confirmed the superparamagnetic behavior of the nanocomposite with a saturation magnetization of 24 emu/g. The fluorescence and magnetic properties of this nanocomposite could be exploited in biomedical applications like fluorescence imaging and magnetic resonance imaging. Further work will include the application of this nanocomposite for drug delivery and diagnostics.

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