



REDUCED GRAPHENE OXIDE SUPPORTED COBALT FERRITE NANOPARTICLES: A STUDY OF SYNTHESIS MECHANISM, STRUCTURAL, MAGNETIC AND THERMAL STABILITY CHARACTERIZATION



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Introduction

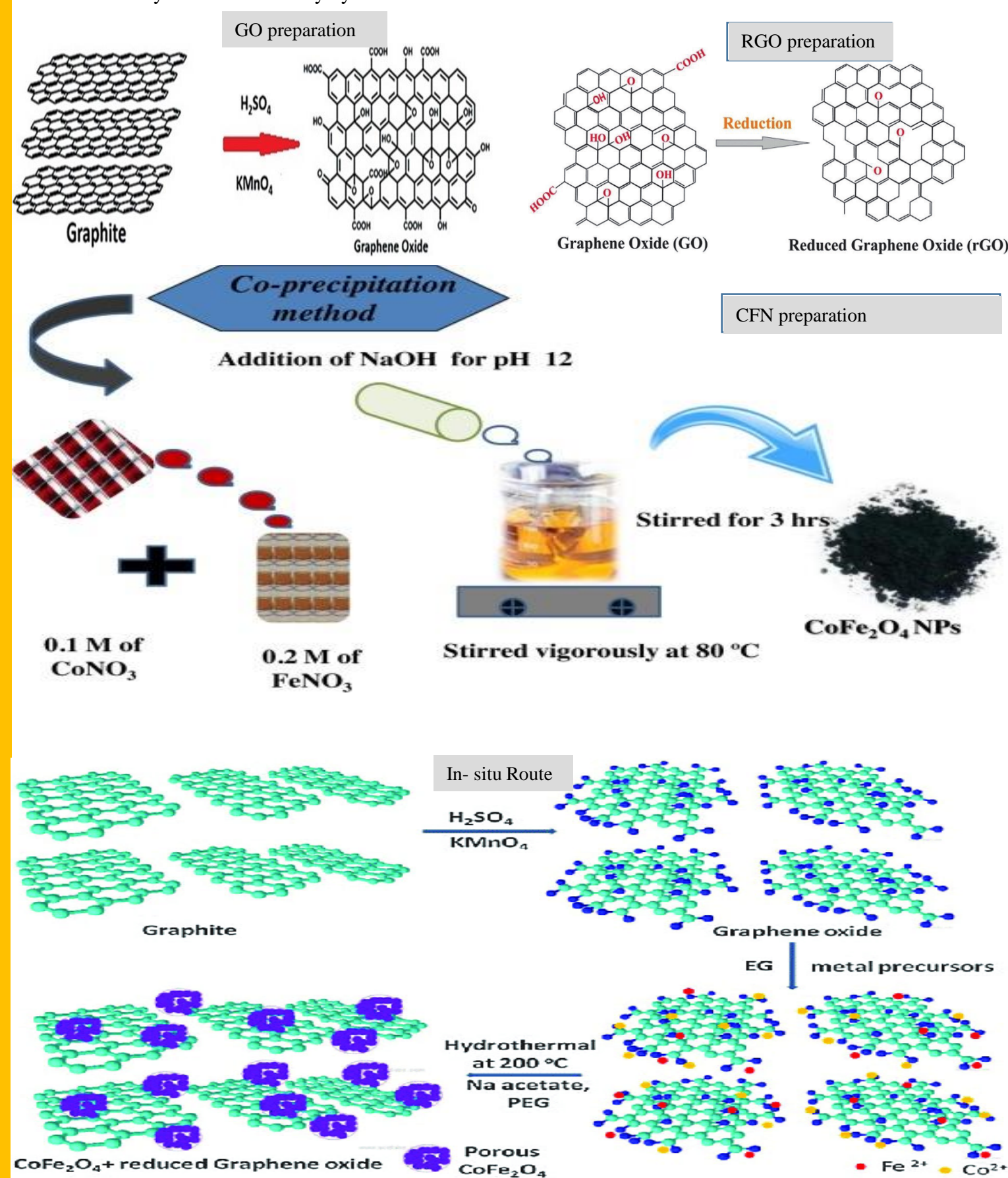
Nowadays because of the rapid increase of the industries the disposal of wastewater is one of the major problems for industrial companies. The toxic elements in the wastewater are needed to be eliminated to save our environment. Recently researchers have focused on the application of nano-structured materials as adsorbents. GO and its composites naturally have significant pore volume, high conductivity, rich surface chemistry, and an exceptionally large aspect ratio which make it favorable for adsorption and catalysis of organic pollutants from wastewater. Moreover ferrites possesses outstanding magnetic properties which can be added in GO nanocomposites for easy removal from solvents after adsorption. Hence the main focus of this research was to synthesize structurally and magnetically a finely tuned RGO-CFN composite that can be used in wastewater treatment.

Abstract

In present study, graphene oxide (GO) synthesized using the modified hummers' method was reduced using hydrazine hydrate to made it perform as a surface for the decoration of cobalt ferrite nanoparticles (CFN) produced via the co-precipitation route. CFN were successfully filled on the surface of reduced graphene oxide (RGO) through the hydrothermal method. The coexistence of RGO and CFN in the nanocomposite was confirmed by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR). The XRD pattern of the nanocomposite exhibits the spinel cubic phase formation with the Fd3m space group with crystallite size 28.55 nm. SEM was used to corroborate the loading of CFN on the RGO nanosheet. FTIR results manifest the functional groups present in all the samples, while Raman study substantiates the reduction of GO. Thermogravimetric analysis (TGA) displays that the nanocomposite showed better thermal stability at high temperature than GO nanosheet. The soft magnetic nature is observed for RGO-CFN nanocomposite with a saturation magnetization of 24.11 emu/g at 300K, by means of a Physical Property Measurement System (PPMS). Such types of structural and magnetic behavior make the nanocomposite a good candidate in various application field such as dye degradation, adsorption, photocatalytic activity, drug delivery etc.

Materials and Method

CFN was prepared through Co-precipitation method by controlling the PH of the solution[1]. The overall reaction of CFN formation is $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} + 2\text{FeCl}_3 + \text{NaOH} = \text{CoFe}_2\text{O}_4 + 8\text{NaCl} + 10\text{H}_2\text{O}$. And GO was prepared through modified hammer's method using H_2SO_4 as oxidizing agent and reduction of GO prepared RGO[2]. RGO-CFN composite was prepared in two ways. Adding RGO and CFN separately and in-situ growth of CFN on graphene oxide. Both ways were followed by hydrothermal method.



XRD Analysis: The XRD peak for graphite occurs at 27.36° corresponds to (002) crystal plane which is due to the sp^2 hybridized carbon atoms in a graphitic hexagonal structure which are stacked in a very high crystalline order of graphite. The interlayer spacing of graphite is 3.25 Å.

For GO, since the intercalation between the graphite layers and the introduction of oxygen containing functional group in the graphene sheet the peak transferred to 11.36° corresponding to (001) crystal plane and the interlayer spacing of GO increased in GO. This is due to the introduction of a number of oxygen containing functional groups on the edge of each layer which increased the distance between the layers. When GO is reduced to form RGO The diffraction peak of GO at 11.36° corresponding to (001) crystal plane disappeared completely, indicating that the GO was reduced by hydrazine hydrate [3].

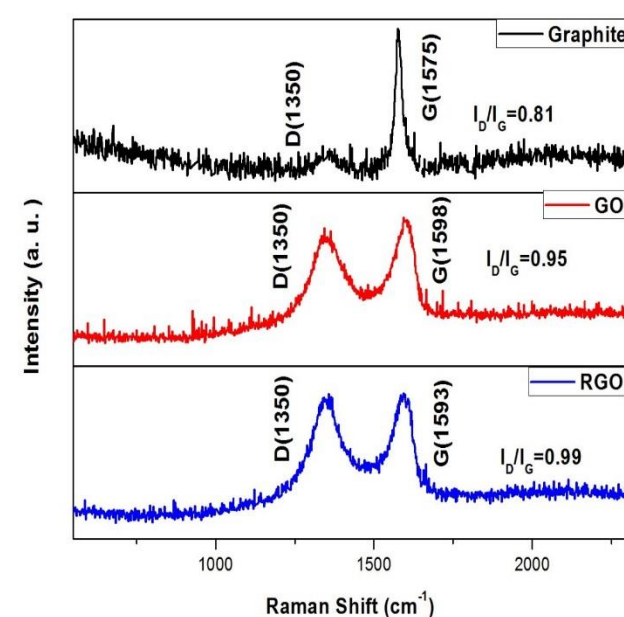


Figure 2. Raman spectra for graphite, graphene oxide and reduced graphene oxide

SEM Study: The individual form of CoFe_2O_4 nanoparticles are not found rather an agglomerated form of the particles was found Figure 5.2 (c). From the SEM image of Figure 5.2 (d) it is clear that CoFe_2O_4 nanoparticles are very well and evenly distributed on GO sheets. The remarkable changes between the surfaces of cobalt ferrite and composite with reduced graphene oxide [Figure 5.2 (c) and (d)] indicates the confirmation of the formation of the composite [5].

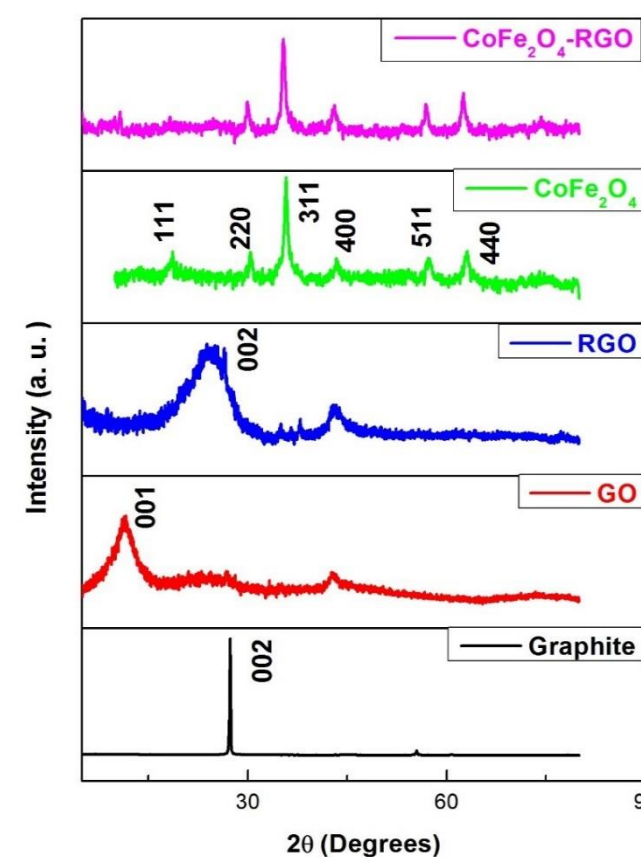


Figure 1. X-ray diffraction patterns for graphite, graphene oxide, reduced graphene oxide, cobalt ferrite and cobalt ferrite-reduced graphene oxide composite

Raman Analysis: The G band in GO is shifted to a higher wave number due to the oxygenation of graphite, which results in the formation of sp^3 carbon atoms. The D (1350) band in GO is broadened due to the reduction in size of the sp^2 domains by the creation of defects, vacancies, and distortions during oxidation. The intensity ratio (I_D/I_G) is increased to 0.95, which indicates a large number of defects in the crystal lattice, and this ratio increase with chemical reduction [4].

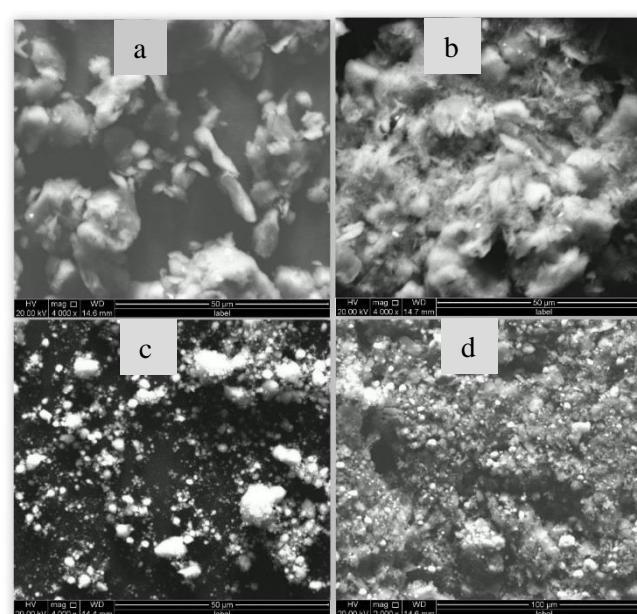


Figure 3. SEM micrographs of (a) graphene oxide, (b) reduced graphene oxide, (c) cobalt ferrite, (d) cobalt ferrite-reduced graphene oxide composite

Results

FT-IR Analysis: The spectra of GO does not contain any peak associated with $\text{C}=\text{C}$ ($1500\sim 1600\text{ cm}^{-1}$) group. The $\text{C}=\text{C}$ bonds missing indicates a strong oxidation to have taken place. The intensity of the peaks at 1725, 1221, and 1050 cm^{-1} related to $\text{C}=\text{O}$, $\text{C}-\text{O}-\text{C}$, and $\text{C}-\text{O}$ stretching vibrations in RGO are decreased comparing with GO, which is due to the reduction of oxygen containing functional groups from GO structure [6].

A considerable decrease in the $-\text{OH}$ peak (3438 cm^{-1}) intensity is observed due to the removal or conversion of oxygen containing functional groups. However, it should be noted that $-\text{OH}$ peak has not completely disappeared indicating that some left over oxygen functionalities still stay behind in the reduced graphene oxide [7].

In the CoFe_2O_4 -RGO spectra the band at 3436 cm^{-1} is ascribed to the $\text{O}-\text{H}$ stretching, the band at 1632 is due to $\text{C}=\text{O}$ stretching and the band at 1212 cm^{-1} is due to $\text{C}-\text{O}-\text{C}$ stretching vibrations. The peak at around 588 cm^{-1} has also been observed, which is due to the $\text{M}-\text{O}$ band in the cobalt ferrite. The intensity of the peaks comparing with the peaks of CoFe_2O_4 is decreased which indicates that the RGO forms a chemical bond with CoFe_2O_4 .

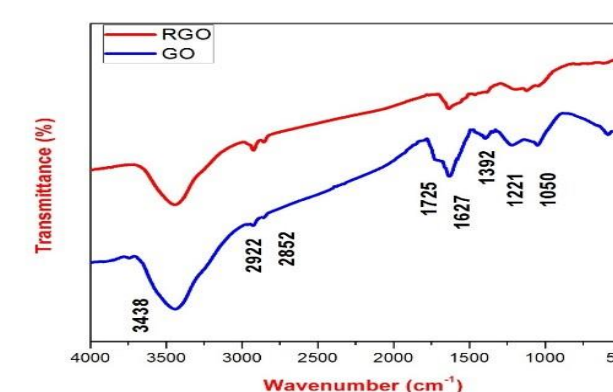


Figure 3.1 FTIR spectra of graphene oxide and reduced graphene oxide

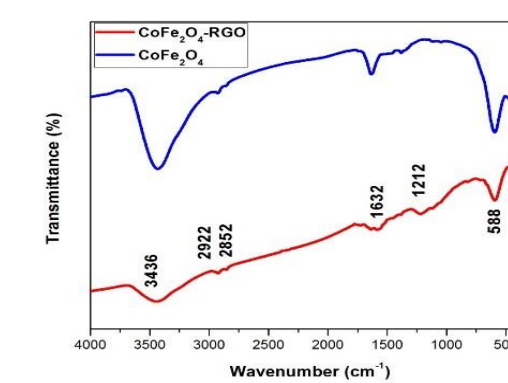


Figure 3.2 FTIR spectra of cobalt ferrite and cobalt ferrite-reduced graphene oxide composite.

TGA Analysis: The initial weight loss of GO at 121°C for GO is due to the removal of adsorbed water. The significant weight loss occurs at approximately 218°C , probably due to the decomposition of the liable oxygen-containing functional groups. A slower and steady mass loss is observed over the whole temperature range between 400°C and 700°C , which can be assigned to the removal of more stable oxygen functionalities of the GO [8].

For CoFe_2O_4 , no significant weight loss is observed, the only weight loss at 180°C is due to moisture. In the composite, of most strong bond that RGO made with CoFe_2O_4 .

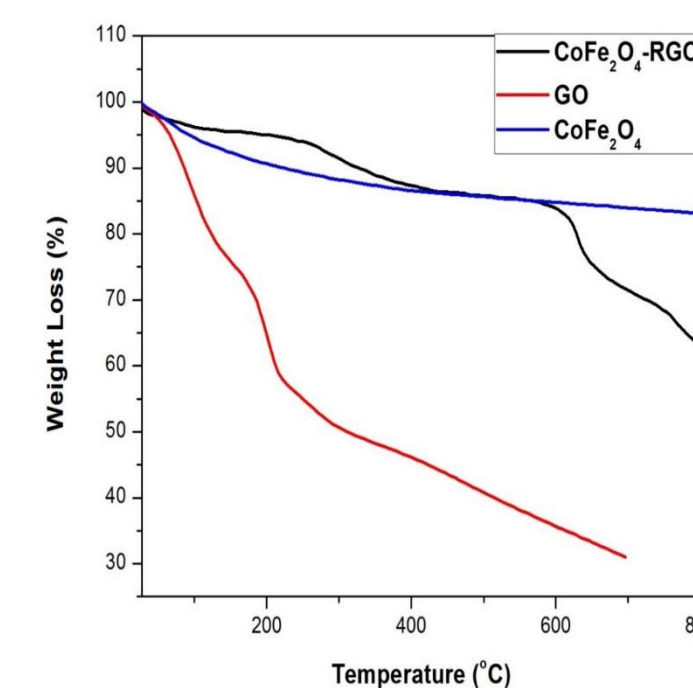


Figure 4. TGA graph of graphene oxide, cobalt ferrite and cobalt ferrite-reduced graphene oxide composite

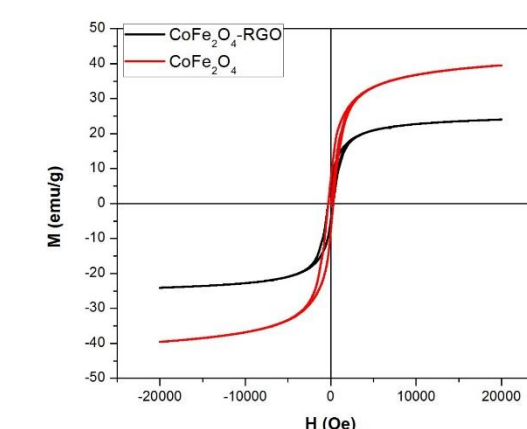


Figure 5. Hysteresis loop of cobalt ferrite and cobalt ferrite-reduced graphene oxide composite

Magnetic Study: At room temperature, the value of saturation magnetization ' M_s ' of the composite is found to be 24.11 emu/g which is lower than the saturation magnetization of CoFe_2O_4 (39.73 emu/g). The observed low saturation magnetization of the composite is due to the introduction of RGO in CoFe_2O_4 which decreases the saturation magnetization, remanence magnetization ' M_r ' as well as coercivity H_c . The CoFe_2O_4 -RGO nanocomposites thus indicating its soft magnetic nature [9].

References

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Conclusion

- The XRD spectrum of CFN confirms the spinel cubic structure of CoFe_2O_4 nanoparticles.
- The SEM image of CFN-RGO nanocomposite showed that the CFN nanoparticles are well distributed on GO sheets.
- The formation of CFN-RGO nanocomposite was confirmed by FTIR and SEM.
- FTIR spectra shows many functional groups present in CFN-RGO nanocomposite for which the composite can be used in the dye removal purpose.
- The magnetic properties of CFN-RGO nanocomposite show that the composite has a soft magnetic nature, which is able to filter the heavy metals from the aqueous solution.
- Since CFN nanoparticles have certain band gap the composite may also be used as photo catalyst.

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