CHAPTER 9

Multifunctional Co-graphene nanocomposite

This Chapter elucidates the synthesis of cobalt-graphene nanocomposite by solution based reduction technique. Characterization of the samples using i) XRD, ii) TEM, iii) UV-Vis spectroscopy, and iv) FTIR spectroscopy are discussed in details. The magnetic and photoluminescence properties of the nanocomposite are studied in details. The properties of reduced graphite oxide and cobalt-graphene composite are compared.

9.1 Introduction

Graphene is an interesting two-dimensional sheet which consists of single layer of sp² hybridized carbon atoms. Graphene has been attracting extensive scientific interest due to its extraordinary electronic, mechanical and thermal properties. The extraordinary properties include high carrier mobility exceeding $10^4$ cm²/Vs [1], high thermal conductivity of $10^3$ W/mK [2], extremely high surface area of 2630 m²/g [3] and large value of Young’s modulus ~1 TPa [4]. A great deal of scientific attention has been generated towards the optical properties of graphene because of the insight they provide into the excited states of this remarkable material, and because of the potential that they offer for novel applications [5, 6]. Apart from the weak inelastic scattering associated with vibrations through the Raman process, no report of emission from graphene is available in the literature. Perfectly exfoliated single layer graphene sheet is a zero band gap semiconductor, and is therefore not likely to show any photoluminescence. In such a material, carriers can fully relax through
rapid electron-electron and electron-phonon interactions which are much faster processes compared to light emission. However, if ultrafast pump-probe processes are applied, some light emission can be observed in graphene [7]. Therefore creating photoluminescent graphene based nanocomposite is a major challenge of optoelectronics. Recently, glucose-derived water-soluble crystalline graphene quantum dots (GQDs) with an average diameter as small as 1.65 nm (~5 layers) were prepared by a facile microwave-assisted hydrothermal method, which exhibited deep ultraviolet (DUV) emission of 4.1 eV, the shortest emission wavelength among all the solution-based quantum dots. The emission wavelength is independent of the size of the GQDs. The unique optical properties of the GQDs are attributed to the self-passivated layer on the surface of the GQDs [8]. Green luminescent, graphene quantum dots (GQDs) with a uniform size of 3, 5, and 8.2(±0.3) nm in diameter were prepared electrochemically from MWCNTs in propylene carbonate by using LiClO₄ at 90°C, whereas similar particles of 23(±2) nm were obtained at 30°C under identical conditions [9]. A Co-CoO-Graphene nanocomposite is recently shown to have very high catalytic activity for electrochemical reduction of oxygen [10]. The synthesis of this composite is quite different from our procedure and the shape and size as well as the Co-CoO nanoparticle decoration of graphene (G) sheets is different. However, this readily shows the importance of these classes of materials. In fact, the combination of such an extraordinary material with functional nanomaterials may lead to interesting nanocomposites for a variety of applications. For this reason, graphene decorated with metal [11, 12], metal oxides [13-15] and sulphides [16, 17] nanoparticles has also attracted a great deal of attention recently. Graphene-based hybrid nanostructures with inorganic nanomaterials provide a link between solid-state nanostructures and two-dimensional molecular science. Reduced graphene oxide serves as a support material to stabilize metal nanoparticles and its high surface area makes it an attractive choice as the matrix for nanocomposites.

In this chapter, we report the synthesis of Co-graphene nanocomposite (Co-G) by co-reduction of graphite oxide (GO) and salt of Co²⁺ in solution, at room temperature and in ordinary atmosphere. We have observed strong violet-blue emission in the composite, which is not observed till now in metal-G nanocomposites. Yang et al [18] synthesized Co-Graphene nanocomposites by pyrolysis of organometallic-graphene composite precursor at 800°C in Ar atmosphere. Ji et al [19] synthesized Co-G through in situ reduction in ethylene glycol medium at 110°C in N₂ atmosphere. Chen et al [20] synthesized porous Co-G nanocomposite by annealing graphene/Co₃O₄ nanocomposite at 623K under Ar/H₂ gas flow.
9.2 Experimental Details

9.2.1 Materials

Natural flake graphite was purchased from Loba Chemie. All the other reagents used in the experimental process were analytical grade, purchased from Merck and used without further purification.

9.2.2 Methods

GO was prepared from natural graphite using modified Hummers method [21]. In the typical synthesis of Co-G, 0.04 g GO was dispersed in 30 ml water using ultrasonication to form stable dispersion. 30 ml aqueous solution of hydrated cobalt nitrate (Co(NO$_3$)$_2$. 6H$_2$O) (5mM) was formed separately. Two solutions were mixed under constant stirring condition to form homogeneous solution. Subsequently, sodium hydroxide (NaOH) solution and 0.14 g sodium borohydride (NaBH$_4$) was added and kept in an ultrasonicator. After 30 min, a black precipitate was formed which was collected by centrifugation and washed several times with water and ethanol. The precipitate was left to dry in vacuum and the dried powder was used for further characterization. The schematic presentation of synthesis procedure is presented in fig. 9.1. For comparison, graphene was also synthesized by reducing GO with NaBH$_4$ under similar conditions.

![Fig. 9.1. Flowchart of synthesis procedure.](image)
9.2.3 Characterization

The synthesized samples were characterized using different techniques. Fourier transform infra-red (FTIR) and UV-Vis spectra of the samples were recorded using Shimadzu FTIR 8400S and Varian Cary 5000 UV-Vis-NIR spectrophotometers respectively. The morphology was visualized using JEOL 2010 Transmission Electron Microscope (TEM) operated at 200 kV and equipped with a detector for energy dispersive X-ray spectroscopy study. Magnetic properties were investigated using a superconducting quantum interference device (SQUID) magnetometer (supplied by Quantum Design, USA) over the temperature range 2–300 K. Photoluminescence spectrum of Co-G nanocomposite at room temperature was recorded on F-2500 FL spectrometer, Hitachi.

9.3 Results and Discussion

9.3.1 Morphological study

The morphology of Co-G nanocomposite was examined using transmission electron micrographs (TEM). A typical micrograph is presented in fig. 9.2(a). The figure shows a thin graphene sheet embedded with Co nanoparticles (higher electron density portions on the G sheet). It is clearly visible that the G sheet is very thin with folded edges and Co nanoparticles are in form of clusters. The weak contrast between the background and G sheet confirms the thinness of the sheet. Interestingly, the shape of the Co nanoparticles are not spherical but are in form of one-dimensional rod-like structure of average diameter ~3 nm and average length ~30 nm (fig. 9.2(b)). The high resolution transmission electron micrograph (HR-TEM) of Co-G sheet confirms the rod-like structure of Co nanoparticles (fig. 9.2(c)) and shows the lattice fringe with d-spacing 0.21 nm corresponding to (111) plane of Co. The elemental composition of Co-G nanocomposite was determined from energy dispersive spectrum and is presented in fig. 9.2(d). The spectrum confirms the presence of elements C, Cu and Co. The element Cu is attributed to the carbon coated copper grid on which the sample for TEM was cast. The weight fraction of Co compared to C was found to be within 10%.
Fig. 9.2. (a) Transmission electron micrograph of Co-G nanocomposite, (b) Transmission electron micrograph showing Co nanorods embedded on G sheets (c) high resolution transmission electron micrograph showing (111) plane of Co, (d) energy dispersive spectrum of Co-G nanocomposite.

9.3.2 FTIR spectroscopy

The FTIR spectra of GO, G and Co-G are presented in fig. 9.3. The FTIR spectrum of GO shows the presence of C-O (alkoxy) stretching bond (~1065 cm\(^{-1}\)), the C-O (epoxy) stretching peak at (~1227 cm\(^{-1}\)), C=C stretching bond (~1634 cm\(^{-1}\)) and stretching mode of C=O (~1725 cm\(^{-1}\)) [22]. The peak at 1390 cm\(^{-1}\) corresponds to deformation of O-H group of adsorbed water molecules respectively. It can be clearly seen that the characteristic absorption bands of oxide groups in GO are almost absent in G and Co-G, except the peak at 1200 cm\(^{-1}\), confirming the complete reduction of GO. The peaks corresponding to C=C and C-C aromatic bonds (~1629 cm\(^{-1}\) and ~1500 cm\(^{-1}\)) remain the most prominent signatures in G and Co-G.
9.3.3 UV-Visible absorbance spectroscopy

Fig. 9.4 shows the UV-Visible optical absorption spectra of GO, G and Co-G nanocomposite dispersed in ethanol.
The peak within the range 255-270 nm is present in all the three samples and corresponds to $\pi \rightarrow \pi^*$ transitions of aromatic C=C rings [23]. The peak at 256.4 nm in GO red shifts on reduction, as is found in G and Co-G nanocomposite. The presence of this particular peak in Co-G confirms that carbon network is not interrupted in presence of Co nanoparticles. The Co-G nanocomposite shows an additional broad peak at 398.2 nm which is attributed to surface plasmon resonance (SPR) of Co nanoparticles [24], where this absorption peak arises from oscillation of conduction band electrons in presence of interacting electromagnetic field. The combined effect of graphenic structure and Co nanoparticles is reflected in the optical spectrum of Co-G nanocomposite.

### 9.3.5 Magnetic properties

As the modification is different in our case compared to the previously reported Co-G or Co-CoO-G nanocomposites [10, 18-20], a different magnetic property is expected compared to these reports. Magnetic properties of the Co-G and G were studied by using zero-field-cooling (ZFC) and field-cooling (FC) procedures and field-dependent magnetization measurements. Measurements of the ZFC, FC magnetization as a function of temperature were performed between 2 K and 300 K under an applied field of 500 Oe and 1000 Oe for Co-G and G respectively and the results are shown in fig. 9.5.

![Fig. 9.5. ZFC-FC curve of Co-G nanocomposite and G sheets in presence of 500 Oe field.](image-url)
Bifurcation of ZFC and FC curve is observed in the temperature range 2-9 K suggesting the presence of unblocked ferromagnetic state in this temperature range. It reflects the superparamagnetic nature of the nanocomposite. The blocking temperature ($T_B$) is determined from the intersection of the ZFC and FC curve and the value of $T_B$ as obtained from ZFC-FC curve is 8.8 K. Whereas, the G synthesized by chemical reduction of GO is diamagnetic in the whole temperature range. Thus by embedding Co nanoparticles on graphene sheets superparamagnetic property can be induced and the composite can be used as contrast agent for MRI.

The M versus H plot (fig. 9.6) below $T_B$ proves the ferromagnetic behavior of the composite at lower temperatures. The M-H loops at 2 K have finite coercivity of 590 Oe where as the M-H loops above 10 K have zero coercivity and remanant magnetization further confirming the superparamagnetic nature of the samples.

![Fig. 9.6. M versus H loops of Co-G nanocomposite.](image)

In this context, we would like to add a comment that Ji et al [19] have observed the graphene nanosheets are well decorated with ~3 nm Co nanoparticles. Almost no free Co nanoparticles were detected outside the graphene sheets, indicating the perfect combination between Co nanoparticles and G nanosheet are very densely populated. Although the particle size is small enough to show superparamagnetism, the nanocomposite was found to show room temperature ferromagnetism. This might have resulted from clustering of Co nanoparticles. This is the reason we kept the concentration of Co-nanoparticles rather low
deliberately. Our intention is to create a stable fluid suspension of the composite, which may lead to a very interesting ferrofluid based on water. We are currently working on the optimization of parameters for such a purpose. Although, a much better control is shown in the work by Guo et. al [10] and Co-CoO nanoparticles show superparamagnetism at room temperature, unfortunately, the magnetic property of the nanocomposite is not reported. Thus we can see that a small variation in preparation techniques for these kind of nanocomposites can lead to large variations in microstructure, optical and magnetic properties as well. In fact, large simulation effort is needed to address that how metal nanoclusters will decorate the G sheets in these composites.

9.3.4 Photoluminescence properties

Fig. 9.7 shows the room temperature photoluminescence spectrum of Co-G nanocomposite after exciting the system with wavelength 250 nm. Various emissions in UV and visible region are observed in the sample. The PL peaks at 326, 350 and 381 nm originates from radiative recombination of electron–hole pair which generated at the defect sites of grapheme [23.] Additionally, strong violet emission (~402 nm) and blue emission (~426 nm) are observed.

![Photoluminescence spectrum of Co-G nanocomposite at room temperature.](image)

Fig. 9.7. Photoluminescence spectrum of Co-G nanocomposite at room temperature.
Pasricha et al [25] have shown that Ag nanoparticles may get trapped inside two monolayers of GO, while forming the Ag-GO nanocomposite, resulting into a more stable structure emitting stable PL in the visible range, at similar position to that of graphite powder. Simple graphite powder is known to show discrete sharp peaks in the visible region.

GO can show similar kind of photoluminescence when a nanocomposite is prepared with silver, attributed to destabilized system, while changing from bulk to nano form. Although, by this method, there is large increase of surface area of the resultant composite, it could still retain characteristic photoluminescence of graphite structure. Metallic nanoparticles interact with the GO sheets through physisorption, electrostatic binding, or through charge-transfer interactions [26] which then modify the local electronic structure. Under favourable condition, this leads to photoluminescence in GO. A broad photoluminescence (PL) are usually observed from pure GO in solid as well as liquid phase [27], the origin of which is not yet clearly understood. However, by fine tuning of the relative sp²/sp³ hybridization it was shown to be possible to produce blue luminescence from GO [23] even without metal nanoparticle decoration. It is understood, that in order to generate photoluminescence, one needs localization of sp² structure, either by sp³ network, or by defects, with local modification of the defect levels with metal nanoparticle. Distortion of sp² network may also produce confinement of well crystalline sp² island, while G is created by reduction. The better crystalline the sp² network, less is the chance to generate photoluminescence.

Optoelectronic properties of carbon related materials mostly depend on π states of sp² hybridization [28]. In GO, π and π⁺ states of SP² clusters are localized within the band gap of σ and σ⁺ states created by sp³ network. The structure of GO is more like a nanocomposite of these two network, with sp² island with crystalline nature, sitting inside sp³ network. The localized electron-hole recombination based on the relative size of these hybridizations generates tunable photoluminescence. The graphene based QDs [8, 9] showing photoluminescence also indicate, confinement of well crystallized sp² crystal structure. As these QDs are water soluble/dispersed, so by some passivation they are rendered from collapsing on each other.

In our case, when chemically reduced GO is produced from such system by borohydride treatment, sp³ hybridization along with epoxide and hydroxyl group may get removed to a large extent. But this restoration process by itself may leave behind distortion and defects, resulting into localization.
The advantage with GO is its solution processibility. When chemically reduced GO is produced from GO in water, two disadvantages appear in the resulting materials. The graphene sheets tend to collapse on each other as the surface of graphene sheet is highly hydrophobic [29]. As a result, quick precipitation due to agglomeration happens for the chemically reduced GO in water due to strong van der Waal interaction and multilayer reduced GO is produced. Usually, collapse of many graphene sheets onto one another, provides faster path for charge carrier to relax.

The decoration of G sheet by Cobalt nanorods actually reduces the collapsing tendency, keeping the composite materials suspended in water for longer time. In the resulting nanocomposite, Co nanoparticles are therefore creating a situation, where this relaxation could not take place. As a result, the localization of the network could promote the photoluminescence. Additionally, these embedded Co nanoparticles modify the electronic states of graphene inducing photoluminescence in the nanocomposite, although they themselves are not photoluminescent. The modification of electronic states by Co nanoparticles is confirmed from photoluminescence and UV-Vis absorbance spectra.

9.4 Conclusion

In summary, we have prepared luminescent Co-Graphene nanocomposite by coreduction of GO and Co$^{2+}$ salt solution at room temperature. The FTIR and UV-Vis spectra of the composite are evidence of the presence of graphenic structure in the nanocomposite. The composite is superparamagnetic in nature with blocking temperature ~8.8 K. Functional nanomaterials with both magnetic and luminescence properties are important for application in biological systems. The Co-graphene nanocomposite has strong possibility to find applications in optoelectronics, catalysis, biological labelling and MRI contrast enhancer.
References