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LETTER

Observation of Bright Green Luminescence in Eu^{2+} Complexed Graphene Oxide Composite through Reduction of Eu^{3+}†

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Red light harvesting with Eu^{3+} graphene complex is well known in literature. But embedding Eu^{2+} in graphene oxide matrix is a difficult proposition and could be of paramount interest because of emission tunability. Herein, we report the observation of highly visible green luminescence for Eu^{2+} which occurs due to the transitions between the $4f^7$ ($8S_{7/2}$) ground state and the $4f^6$ 5d excited state with nanosecond time decay through reduction of Eu^{3+} using simple chemical approach. This newly formed luminescence complex may be used as a major potential candidate for applications in optoelectronics and nanobiotechnology.

Recently graphene has drawn much attention due to its fascinating optical and electronic properties for opto-electronics devices.[1-4] Optical properties of graphene can be tuned through several parameters, such as proper functionalization decoration of nanoparticles or introducing a rare earth element onto graphene sheet.[5-11] On the other hand, among the various rare earth elements Europium ion is an excellent candidate for the development of red luminescent graphene. Recently, Gupta *et al.*[12] reported the Eu^{3+} complexed red luminescent graphene nanosheet through solid state reaction. Alternatively, hydrothermally derived luminescent Eu-complexed reduced graphene oxide (RGO) macro-assemblies was successfully prepared by Wang *et al.*[13] Moreover, preparation of Eu(III)-coupled graphene oxide through covalent interaction between the carboxylic group of GO and the amine group of phenanthroline derivatives have also been reported.[14] At the same time, a non-covalent approach was employed to synthesize bright red luminescent rare earth complexes functionalized with GO by CaO *et al.*[15] Successful chemical route attempt was undertaken to develop Eu–acac–phen nanoparticles functionalized GO by Wang *et al.*[16] As it is, till now most of the research has remained restricted towards the development of Eu^{3+}-GO complex as a potential red light emitter. Limited work have been done with Eu^{2+} complexed materials where green to yellow broadband luminescence can be expected due to the transitions between the $4f^6$ 5d excited state and the $4f^7$ ($8S_{7/2}$) ground state. In this regard, many techniques have been employed over the years in which host material with Eu^{3+} is irradiated in presence of X-rays, γ rays,[17] N_2/H_2, H_2,[18] solution combustion[19] for the reduction of Eu^{3+} to Eu^{2+} in various inorganic hosts. Reduction of Eu^{3+} to Eu^{2+} is also possible at normal air atmosphere and carbon reducing atmosphere reported by Peng *et al.*[20-23] Dai *et al.*[24] Xie *et al.* [25] etc. All the previous reduction approaches either need special atmosphere, high temperature or very cumbersome to conduct. Therefore, chemical reduction of Eu^{3+} to Eu^{2+} has been found to draw keen interest in this era. In a recent endeavour Kim *et al.*[26] demonstrated a facile chemical method using oleic acid and hexadecylamine for the reduction of Eu^{3+} to Eu^{2+} embedded within GdS nanoparticles and exhibited the change in the luminescence property as a result of the reduction of europium ion. However to the best of our knowledge there is no report demonstrating bright green luminescence in Eu^{2+} complexed graphene oxide composite through reduction of Eu^{3+}. In this letter, we report a facile synthesis approach to form Eu^{2+} complexed graphene Oxide composite through reduction of Eu^{3+} with azopyridine showing highly visible green photoluminescence which can be easily scaled up for bulk yield important for opto-electronic applications.

From the FTIR results as shown in Fig. 1(a) it is observed that the as-synthesized apGOc (azo-pyridine GO composite) shows a broad peak in the region 3500 to 3000 cm^{-1}, indicating the presence

of both –NH groups and the –OH groups of the keto-hydrazo in the sample.[27] The signature of C=C skeletal vibrations and C=N bonds of the pyridine moiety are observed in the region 1620–1654 cm^{-1}. The azo-group stretching vibration are noticed in the region 1433–1465 cm^{-1} indicating the presence of the N=N bond. Additional vibrational modes such as 1272-1252 cm^{-1} for C–N stretching, 1021 cm^{-1} for C–OH bonding are also noticed as shown in Fig. 1(a).

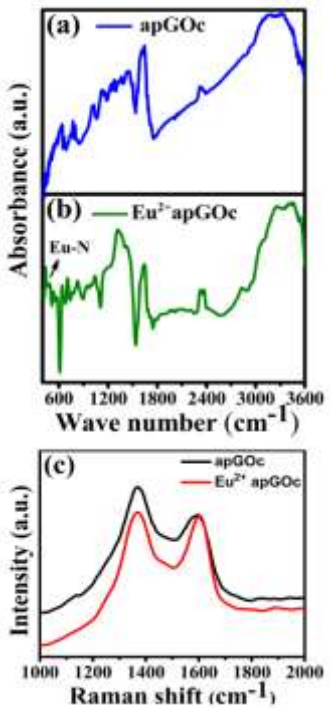
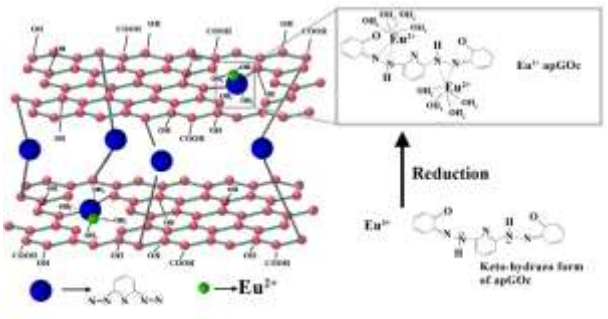


Fig. 1 (a) FTIR spectra of apGOc; (b) FTIR spectra of Eu^{2+}apGOc and clearly showing the Eu-N bonding; (c) Raman spectra of apGOc and Eu^{2+}apGOc.

Presence of peaks in the region 800–650 cm^{-1} points towards the successful formation of apGOc.[27] It is found that the main difference between the FTIR spectra of Eu^{2+}apGOc (Eu^{2+} complexed azo-pyridine GO composite) and the apGOc is the appearance of small peaks around 480 cm^{-1} attributed to the stretching vibration of Eu-N bond[28] as indicated in Fig. 1(b). In Fig. 1(c) the combined Raman spectra for apGOc and Eu^{2+}apGOc is shown. It is well known that Raman spectroscopy is a very important characterization tool to confirm the successful synthesis of carbon nanomaterials and hence it becomes an essential part for our analysis. From the Raman spectra of apGOc and Eu^{2+}apGOc the D and G bands of the apGOc are found at 1365 and 1594 cm^{-1}. However, the I_D/I_G ratio of apGOc is higher than the Eu^{2+}apGOc with a slight shift of G band peak position to higher wavenumber. Minute narrowing of G band FWHM (Full width half maxima) is also observed after reduction of the Eu^{2+} complexes. We propose that the Eu^{3+} ion may be complexed within the sp^2 graphene honeycomb matrix along with some in the azo-pyridine side. As E_{2g} mode is known to be susceptible to stress due to local deformations around sp^2 network hence the minute shift G band can be accounted for.[13]

The synthesis mechanism indicates that reduction of Eu^{3+} to Eu^{2+} occurs when Eu^{3+} was added in the keto-hydrozo group of apGOc system and azo-pyridine act as a reducing agent. It is well established that for the reduction process electron transfers from host lattice to the rare earth element.[24-25,29] In our case the azo-pyridine group donates the electron to Eu^{3+} and Eu^{3+} cation reduces into Eu^{2+} through complexation with azo-pyridine graphene oxide composite(Scheme 1).



Scheme1: A schematic of reduction process from Eu^{3+} to Eu^{2+}.

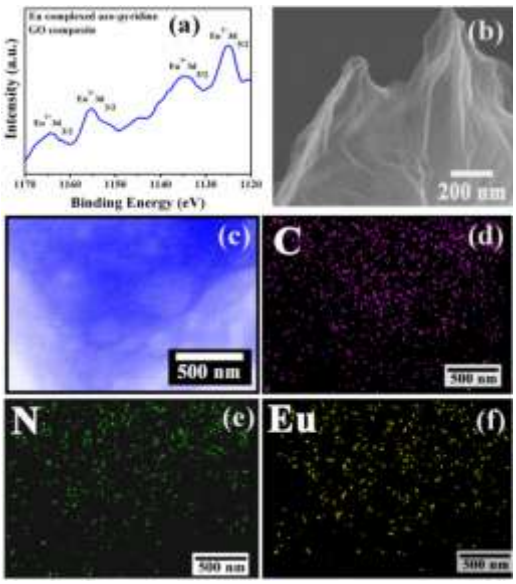


Fig. 2 (a) The high resolution XPS spectrum of Eu in the apGOc indicating the peaks located at 1153 and 1125 eV are ascribed to the Eu^{2+} valance state, corresponding to electronic states Eu^{2+} $3d_{3/2}$ and $3d_{5/2}$ respectively. (b) FESEM image of Eu^{2+}apGOc; (c)-(f) a representative EDX element mapping of the C, N and Eu throughout the Eu^{2+}apGOc.

To further confirm this notion, next we examined the valence state of europium ions of the synthesized Eu^{2+}apGOc by XPS analysis. The high-resolution spectrum in the region of Eu-3d transition is shown in the Fig 2(a). The peaks located at 1153 and 1125 eV are ascribed to the Eu^{2+} valance state, corresponding to electronic states of Eu^{2+} $3d_{3/2}$ and $3d_{5/2}$ respectively and another two peaks located at 1161 and 1132 eV are attributed to Eu^{3+} valance state, corresponding to electronic state of Eu^{3+} $3d_{3/2}$ and $3d_{5/2}$ respectively.[26] It is seen that slight Eu^{3+} is present in the system even after reduction and complete reduction is not attainable. Fig. 2(b) shows the wrinkled morphology of Eu^{2+}apGOc, as observed from FESEM. The EDX mapping images are shown in Fig. 2(c), (d), (e), (f) corresponding to the C, N and Eu respectively. The

mapping clearly indicates to the proper distribution of Eu ions within the GO composite.

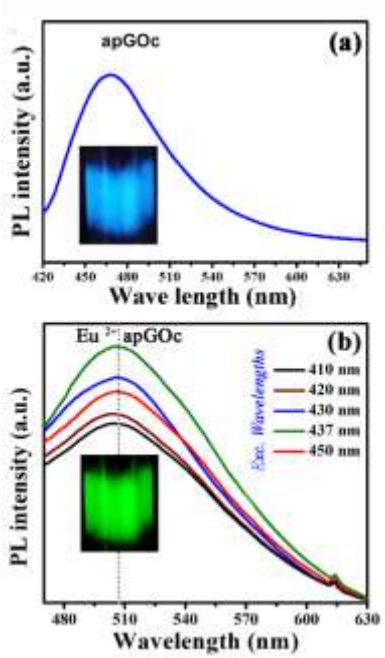


Fig. 3(a) & (b) Photoluminescence spectra of apGOc and Eu^{2+}apGOc when excited the samples at 416 nm and 437 nm respectively.

In Fig. 3(a, b) the photoluminescence (PL) spectra of apGOc and Eu^{2+}apGOc are shown. For the as synthesized apGOc, the maximum PL emission occurs at ~470 nm when excited at 416 nm.[27] This bright blue photoluminescence can be endorsed due to the excited state intra molecular proton transfer (ESIPT) between the –OH group of the phenol moiety and the azo group which results in the transformation of enol-azo (A) form to keto-hydrazo (H) form of the composite which was clearly explained by Gupta et al.[27, 30] But for Eu^{2+}apGOc composite, we obtained green emission spectrum that is easily detected through naked eye. The PL peak shifted to 506 nm with an excitation wavelength 437 nm. This green emission is attributed to transitions from the $4f^6 5d$ excited state to the $4f^7$ ($8S_{7/2}$) ground state of Eu^{2+} which accounts for the broadband emissive feature with the maximum at 506 nm.[26] The excitation (410nm-450nm) dependent photoluminescence property of Eu^{2+}apGOc composite was investigated and no peak shifting was found (shown in Fig. 3b). The position of the peak in the broad emission band remains almost unaltered in the Eu^{2+}apGOc with subject to each excitation wavelength. Therefore it is confirmed that the intense green luminescence in the Eu^{2+}apGOc composite sample arises solely due to excited state to the ground state transition of Eu^{2+}.[31-32, 26] This phenomenon is totally different from the functionalized graphene oxide, graphene quantum dots and carbon dots in which photoluminescence behaviours are excitation dependent i.e. PL peak shifting occurs with the change in the excitation wavelength.[33-36] The digital images of both visible blue and green luminescence are shown in the inset of Fig 3(a) and (b). Additionally, a very weak emission hump is also found around 14 nm due to $^5D_0 \rightarrow {}^7F_2$ transitions,[26] which stems from slight presence of Eu^{3+} even after reduction. It is well reported in the literature that $^5D_0$-$^7F_2$ (at around 614 nm) and $^5D_0$-$7F_1$ transition(at around 584 nm) of Eu^{3+} are electric and magnetic dipole–dipole transitions, respectively. The transitions $5D_0$-$7F_2$ are highly dependent on the local symmetry of the Eu^{3+} ions.[37]The broad and intense Eu^{2+} emission band completely over shadows the other $5D_0$-$7F_1$ transition in the PL spectra. The PL quantum yield was calculated through an analytical approach[38] and the calculated absolute PL quantum yields are found to be 14 % and 20 % for apGoc and Eu^{2+}apGOc, respectively (ESI†). In Fig. 4 the time decay profile for Eu^{2+}apGOc is shown. Time resolved spectroscopy technique was investigated to determine the excited state life time of Eu^{2+} apGOc by keeping the emission at 506 nm. The time decay curve was well fitted to a double-exponential decay equation[39-41] as $I(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$. Where parameters A_1 and A_2 are the fitting constants and τ_1 and τ_2 are the decay components.

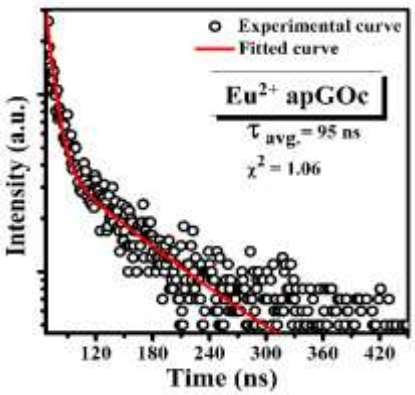


Fig. 4 Photoluminescence decay curve of Eu^{2+}apGOc.

The average life time (τ_{av}) is calculated by the following equation.[42]

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad \text{---------- (2)}$$

The calculated τ_{av} for Eu^{2+}apGOc is found to be 95 ns and it is well matched with the previously reported result.[43-45] The more than one decay components may be arises due to coordination of Europium ion with various ligand environments in the apGOc system.[12] To verify the above result we have also rechecked the time decay analysis of Eu^{2+}apGOc by keeping the emission at 500 nm and 515 nm for better justification of the carrier life time over the emission band. The calculated average life time were found to be 92 ns and 89 ns for 500 nm and 515 nm, respectively.

In summary, highly visible green broadband luminescence has been observed for Eu^{2+} ions in conjugation with apGOc using simplified reduction procedure. XPS analysis revealed reduction of Eu^{3+} to Eu^{2+} within apGOc composite matrix. Moreover a proposed mechanism scheme has been further presented for the same. The results indicate that this material can be utilized for nano-bioimaging and opto-electronic applications.

Experimental

Graphene Oxide (GO) was prepared by modified Hummer's method.[46-47] The diazotization and coupling reaction of graphene

oxide for synthesizing azo-pyridine GO composite was done through following procedure as reported previously.[27] For the preparation of Eu^{2+}complexed azo-pyridine GO composite, 10 mg of azo-pyridine GO and 10 mg $Eu(NO)_3.6H_2O$(Sigma Aldrich) powders were dispersed in 20 ml DI water by ultrasonic treatment of 30 min and thenthe solution was heated at 80 ^oC for 2h. Then the solution was cooled down to room temperature. The resulting solid product was collected after centrifugation and washing 3-5 times with DI water and then dried in vacuum oven for overnight at 40 ^oC.

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Notes and references

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† Electronic supplementary information (ESI) available: Detailed characterization techniques, Photoluminescence Quantum yield (PLQY) calculation, Excitation spectra of apGOc and Eu^{2+}apGOc. Time decay curve of apGOc.

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