Ethylene diamine mediated Cobalt nanoparticle studded graphene oxide quantum dots with tunable photoluminescence properties

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Electronic Supplementary Information

1. UV-Visible Spectroscopy

The UV-Visible titration curves for Co^{2+}, Ni^{2+} and Cu^{2+} with GOQDs-en are shown in Figure S1 (A), (B) and (C) respectively. The titration curve with Co^{2+} shows that the intensity of the peaks at 296 nm and 351 nm gradually increases in intensity as the concentration of Co^{2+} increases and reaches saturation at a concentration of 460 μM Co^{2+}. However, for Ni^{2+} and Cu^{2+} this observation was absent and there was a decrease in the absorbance of the peaks at 296 nm and 351 nm as shown in the figure.

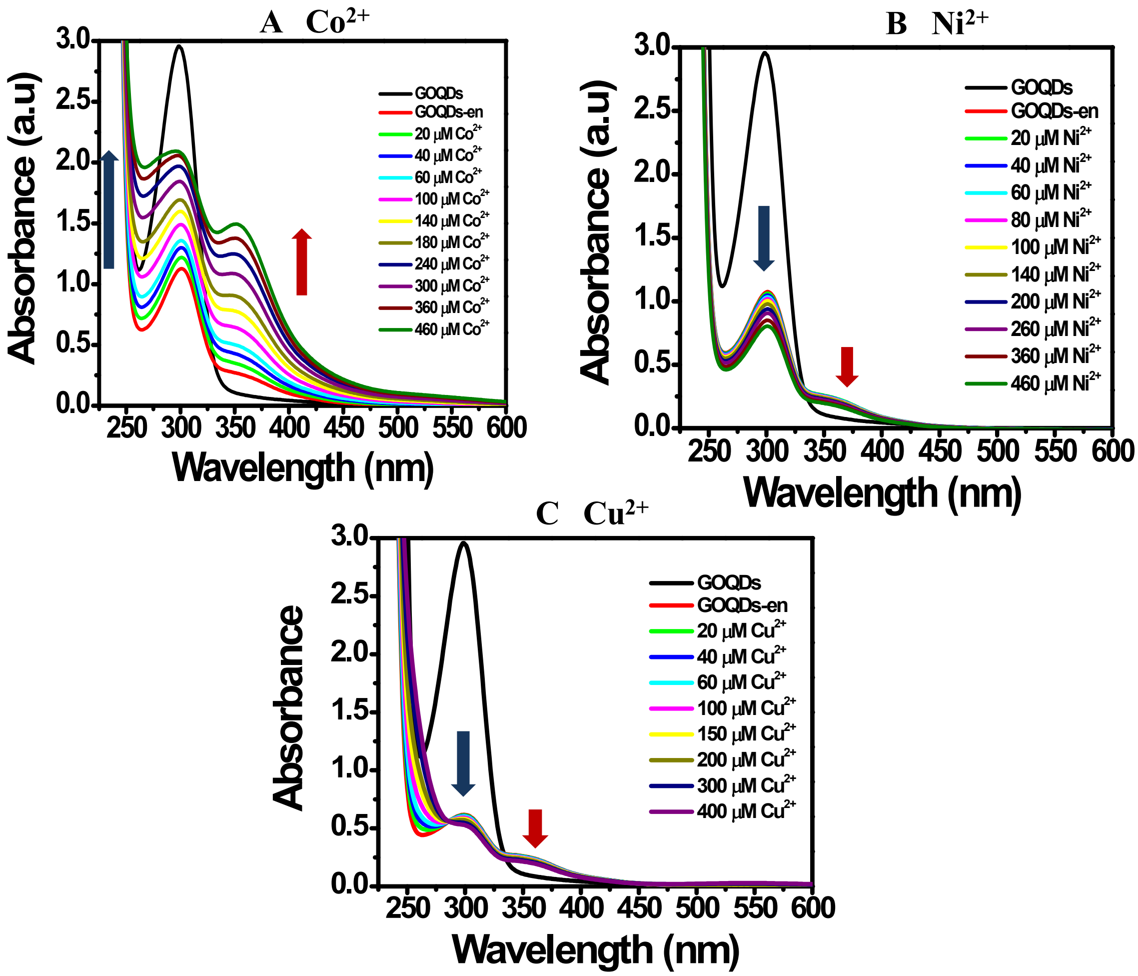

Figure S1. The UV-Visible titration curves for (A) Co^{2+}, (B) Ni^{2+} and (C) Cu^{2+} with GOQDs-en.

2. Fluorescence Spectroscopy

The photoluminescence spectra of GOQDs, en reduced GOQDs (GOQDs-en) and that after titration with Ni^{2+} and Cu^{2+} solution is shown in Figure S2 (A) and (B) respectively. As evident from the figure there is no considerable change in the PL intensity of GOQDs-en upon titration with Ni^{2+} or Cu^{2+} which suggests that there is probably no complexation between en and either of Ni^{2+} or Cu^{2+}.

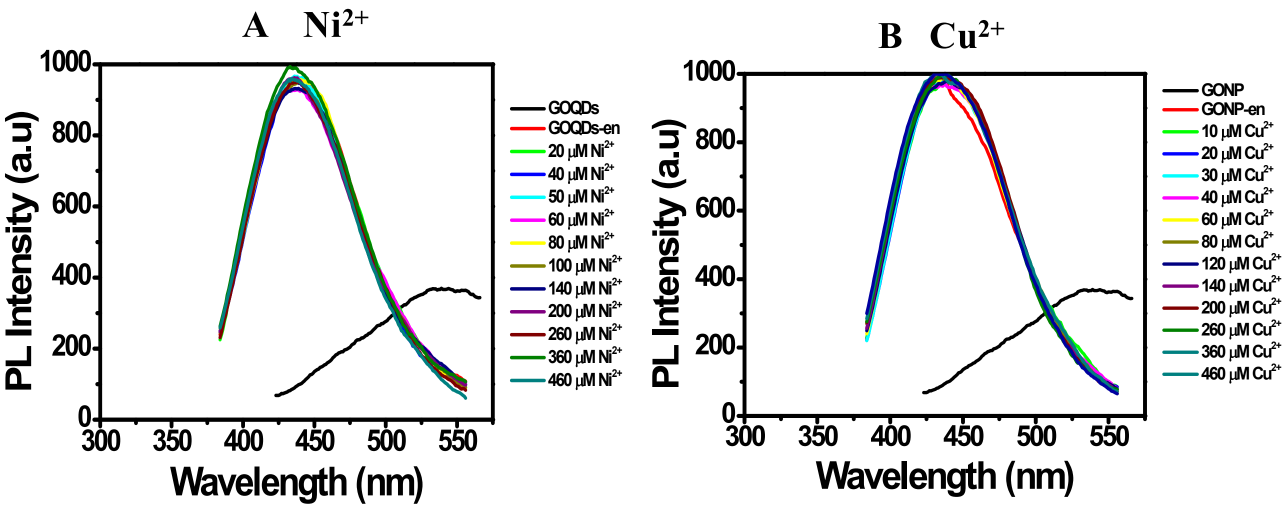

Figure S2. The stacked photoluminescence spectra of GOQDs, en reduced GOQDs (GOQDs-en) and that after titration with (A) Ni^{2+} and (B) Cu^{2+} solution.

In order to investigate the selectivity of the GOQDs-en towards formation of Co_3O_4NPs, similar experiments were carried out with Ni^{2+} and Cu^{2+} ions to check if there is a formation of nanoparticles leading to some change in the fluorescence property of GOQDs-en. The corresponding comparative PL emission spectra after reaction with Ni^{2+} and Cu^{2+} are shown in Figure S3 (A) and (B) respectively. From the spectra it was observed that there was no further enhancement in PL intensity of GOQDs-en system after allowing possible formation of Ni or Cu nanoparticles by the same procedure as adopted for Co_3O_4NPs formation. Rather there was observed quenching of PL intensity at the same value of λexc = 360 nm and also there was no considerable blue shift observed. This suggests that probably Ni and Cu nanoparticles are not formed on GOQDs-en by this process.

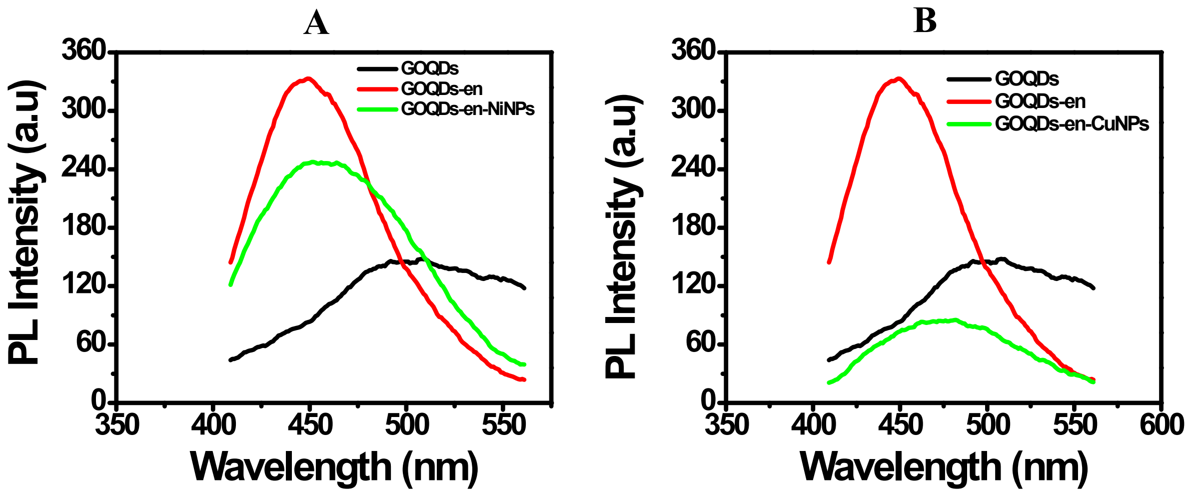

Figure S3. The stacked PL emission spectra of GOQDs, GOQDs-en and that after reaction with (A) Ni^{2+} and (B) Cu^{2+}.

3. Dynamic Light Scattering (DLS) and Scanning Electron Microscopy Experiments

The particle sizes of GOQDs, GOQDs-en and GOQDs-en-Co_3O_4NPs were determined using Dynamic Light Scattering (DLS) technique and Scanning Electron Microscopy (SEM). The corresponding particle size graphs for all the three samples are shown in Figure S4 (A), (B) and (C) obtained from DLS analysis and in (D), (E) and (F) obtained from SEM respectively. The respective zeta potential values are also shown.

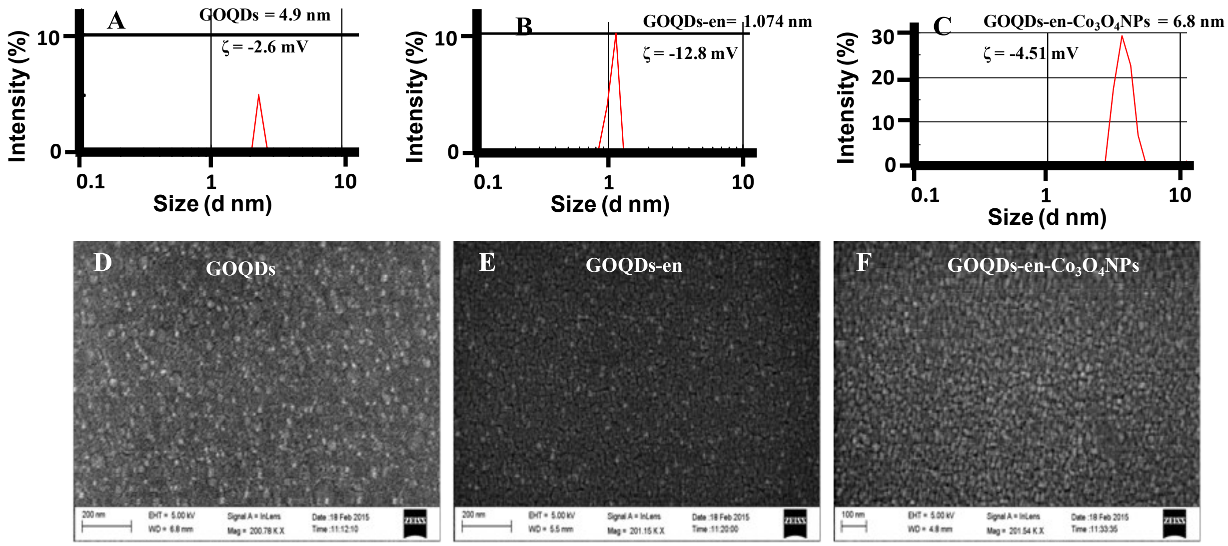

Figure S4. The particle size graphs and zeta potential values of (A) GOQDs, (B) GOQDs-en and (C) GOQDs-en-Co_3O_4NPs obtained from Dynamic Light Scattering (DLS) technique and those obtained from SEM for (D) GOQDs, (E) GOQDs-en and (F) GOQDs-en-Co_3O_4NPs respectively.

From the particle size graphs it is evident that the GOQDs possess particles 5 nm in diameter. On the other hand, GOQDs-en and GOQDs-en-Co_3O_4NPs possess particles 1.074 nm and 6.8 nm in diameter respectively.

4. EDX Analysis

Evidence in support of oxidation of graphene nanoplatelets to form GOQDs and reduction cum functionalization of GOQDs to form GOQDs-en can be drawn from EDX analysis. The respective EDX spectra for GOQDs and GOQDs-en are shown in Figure S5 (A) and (B).

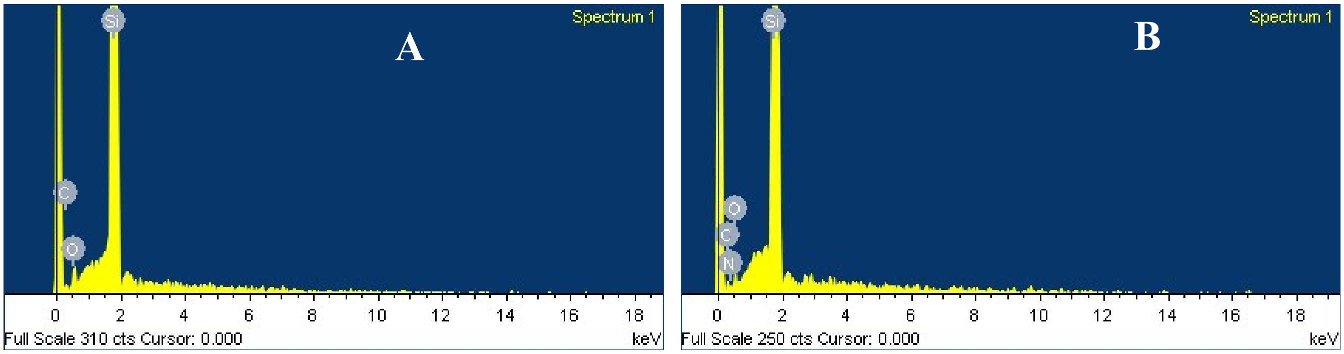

Figure S5. EDX spectra for (A) GOQDs and (B) GOQDs-en.

From the graphs it is seen that the presence of oxygen in the EDX spectra for (A) GOQDs indicate the successful incorporation of oxygen functionalities on the surface of the GO sheets upon acid mixture oxidation of graphene nanoplatelets. On the other hand in the spectrum for (B) for GOQDs-en the presence of Nitrogen is a clear indication of formation of C-NH linkages on the sheets due to formation of amide functionality and en attachment to the sheet structure via ring opening of epoxy groups. Moreover, it is also interesting to note that the weight percentage of oxygen in GOQDs decreases upon reduction and functionalization with en which can be attributed to the conversion of –COOH groups on the GOQDs to $–CONH_2$ upon reaction with ethylene diammine.

5. Powder XRD Analysis

The stacked powder XRD spectra of GOQDs, GOQDs-en and GOQDs-en-Co_3O_4NPs are shown in Figure 4(B). The spectrum of GOQDs-en shows sharp and well-defined peaks at 2θ values of 12.76(110), 15.6(221), 25.5(002) and 38.9(-290) degrees. Apart from the peak at 25.5^{O}(002) characteristic of graphene, the other peaks in the sample were found to match the diffraction patterns of 1,8-Bis(dimethylamino)naphthalene-3-hydroxy benzoic acid (JCPDS Number 00-059-1052), 4'-(aceto-N'-(2-naphthyloxymethylcarbonyl)hydrazone)benzo-15-crown-5 (JCPDS Number 00-056-1881), 3,3'-dimethyl-4,4'-bis(2,4-dinitroanilino)biphenyl (JCPDS Number 00-056-1866). As these compounds are all aromatic amino compounds we can conclude that in GOQDs-en the peaks occur probably due to incorporation of amine functional groups into the planar structure of the GOQDs and therefore GOQDs-en resembles the structure of the above mentioned compounds. Further, as the amine we have used is ethylene diammine, an aliphatic amine thus it points more towards the possibility of the peaks appearing due to amine functionalization of GOQDs to give GOQDs-en. Thus it can be inferred as an indication of successful incorporation of $–NH_2$ groups into the GOQDs.