

## Sensitivity to heavy-metal ions of cage-opening fullerene quantum dots

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Heavy metals are potentially toxic elements and are highly related to the environment and humans health. The heavy metal streams that are traced in nature have undergone a sharp increase due to the anthropic activity of the last century, at times reaching critical levels of toxicity for flora, fauna and people [1].

Heavy metals tend to accumulate in the environment because they are not destroyed by normal biological and chemical cycles. The progressive increase of the pollutants in the environment is the major problem originating from bioaccumulation.

These metals can be absorbed by living organisms through the respiratory tract, by ingestion of food or water. Pb, Cd, Cu, Zn, Ni, Co, As, Bi, Sb, and Hg have a high tendency to form stable organometallic complexes with the phosphoryl groups of phospholipids rich in nerve cells and cause mutations in the DNA that can cause the onset of tumors.

To monitor these metals, it is necessary to develop efficient sensors which can be pursued also by using nanomaterials and nanostructures.

Recent studies [2] have demonstrated that the photoluminescence (PL) of aqueous solution of GOQDs, prepared by a variety of different methods, can be selectively quenched in presence of some heavy-metal ions ( $\text{Hg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ). This characteristic has attracted the interest of researchers in view of implementing fast and cheap sensors for those heavy metals that are long known to be harmful to environment and toxic for human health. However, few experimental studies have been carried so far and they reported quite scattered and partially contradictory results which seem to depend on the synthesis method and the experimental conditions. Very recently, an innovative approach to preparation of photoluminescent carbon nanosheets was developed by Pumera *et al.* by using the low-temperature cage-opening of  $\text{C}_{60}$  buckminsterfullerene [3]. Due to the buckminsterfullerene structure, this material is like graphene oxide quantum dots (GOQDs) but with a different lattice structure, in fact, the carbon Cage-Opening Quantum Dots (COQDs) have a lattice made of both hexagons and pentagons. This could give rise to a different configuration of  $\text{sp}^2$  domains, defects and functional groups which, in turn, could produce a new scenario for the response to chemical environment.

In this study, we have carried out a systematic evaluation and characterization of the quenching effect produced by some commonly encountered metal ions ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{As}^{3+}$ ) on the PL of COQDs prepared with a modified Hummers method. Typical absorption and fluorescence spectra assured the successful synthesis of COQDs, while the average size of nanoparticles was found to be 4 nm as measured by Dynamic Light Scattering (DLS). Figure 1 shows the quenching of the photoluminescence spectra with different concentrations of  $\text{Cu}^{2+}$ . As evident, the PL intensity gradually decreases with the increase of  $\text{Cu}^{2+}$  concentrations. The up-ward Stern-Volmer plot (not shown) indicates a combination of static quenching (complexation) and dynamic quenching. Similar curves, with a lower dependence on the ion concentration, were recorded for  $\text{Pb}^{2+}$  and  $\text{As}^{3+}$ , while substantially no response was found to  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$ , as reported in Figure 2 which illustrates the inverse of the PL quenching in the presence of different ions at a concentration of 100  $\mu\text{M}$ . Interestingly, the absorption spectrum is significantly modified only in presence of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , with the disappearance of the  $\pi\text{-}\pi^*$  peak, while in the case of  $\text{As}^{3+}$  the curve shows much smaller variations. Moreover, only in the case of  $\text{Pb}^{2+}$  an evident brownish precipitate was observed at the bottom of the titration cuvette, which suggests a greater level of complexation leading to aggregation of COQDs. We believe these differences are quite important since they allow a selective detection of each of the three specific ions.

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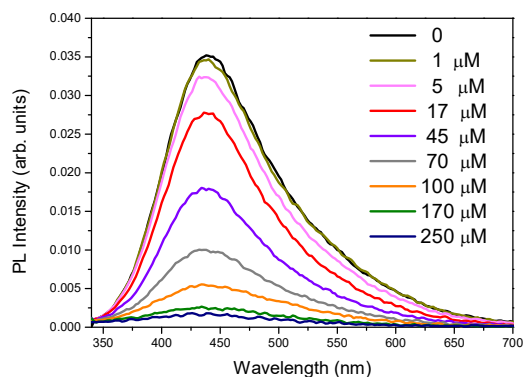


Figure 1. Fluorescence emission spectra of COQDs with different concentrations of  $\text{Cu}^{2+}$ . The PL intensity decreases with the increase of ions concentration.

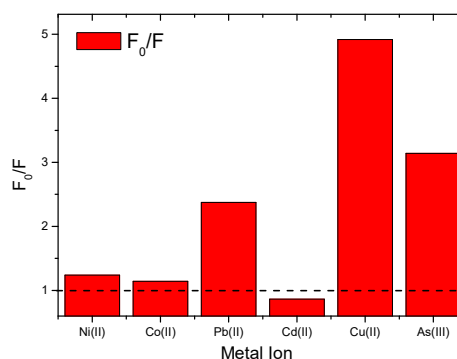


Figure 2. Sensitivity of COQDs to the different ions at a concentration of 100  $\mu\text{M}$