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Sensitivity to Heavy-Metal Ions of Cage-Opening Fullerene Quantum Dots †

Erica Ciotta [1], Paolo Prosposito [1], Pietro Tagliatesta [2], Chiara Lorecchio [2], Iole Venditti [3], Ilaria Fratoddi [3] and Roberto Pizzoferrato [1,*]

[1] Department of Industrial Engineering, University of Rome-Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy; erica.ciotta@uniroma2.it (E.C.); paolo.prosposito@uniroma2.it (P.P.)
[2] Department of Chemical Science and Technology, University of Rome-Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy; pietro.tagliatesta@uniroma2.it (P.T.); chiara.lorecchio@uniroma2.it (C.L.)
[3] Department of Chemistry, University of Rome Sapienza P. Aldo Moro 5, 00185 Rome, Italy; iole.venditti@uniroma1.it (I.V.); ilaria.fratoddi@uniroma1.it (I.F.)
* Correspondence: pizzoferrato@uniroma2.it; Tel.: +39-6-7259-7192; Fax: +39-6-7259-7158

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Abstract: In this study, we have carried out a characterization of the quenching effect produced by some commonly encountered metal ions (Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, As^{5+}) on the photoluminescence of water suspensions of open-cage fullerene quantum dots prepared with a modified Hummers method. The response to heavy-metal ions occurs through a selective quenching of the PL emission and modifications of the absorption spectrum.

Keywords: heavy metal sensing; photoluminescence; absorption

1. Introduction

Heavy metals are potentially toxic elements which can have great impact on the human health. Their presence in the environment has undergone a sharp increase over the last century due to the growth of anthropic activity, at times reaching critical levels of toxicity for flora, fauna and man [1]. Heavy metals are very dangerous because they are not destroyed by normal biological and chemical cycles but, instead, due to bioaccumulation, their concentration can progressively increase trough the food chain.

Due to their photoluminescence (PL) properties, innovative carbon-based nanomaterials, such as graphene quantum dots (GQDs) and graphene oxide quantum dots (GOQDs), have attracted much interest as stable and nontoxic nanomaterials with possible applications in chemical and biological sensors [2,3]. Most importantly, some recent studies [4–7] have demonstrated that the PL intensity is significantly quenched in the presence of certain heavy-metal ions (Hg^{2+}, Fe^{2+}, Cu^{2+}, Pb^{2+}), thus triggering the interest of researchers in view of fast and cheap sensors for these elements.

In the present study, we investigated the sensitivity to heavy metals of a new type of carbon-based nanomaterial obtained from C_{60} fullerene. Due to the peculiar structure of buckminsterfullerene the carbon nanosheets synthesized with this technique have a lattice made of both hexagons and pentagons. This could give rise to a different configuration for the sp^2 domains, the content and location of defects and the functional groups which, in turn, could produce a different response to the surrounding environment.

2. Materials and Method

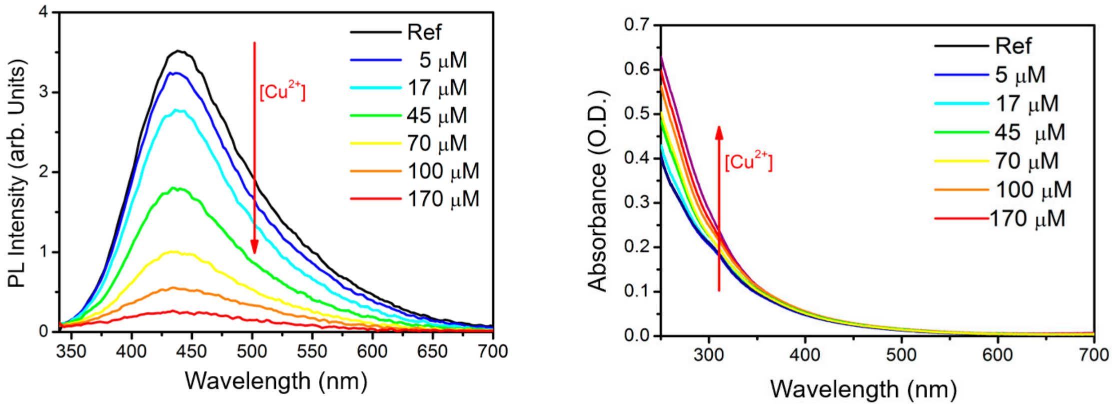
Open-cage fullerene quantum dots (OCFQQs) were prepared from C_{60} fullerene by a chemical oxidation trough modified Hummers method, as reported elsewhere [8]. Briefly, the fullerene was oxidized in water using $NaNO_3$, $KMnO_4$ and H_2SO_4. The reaction was quenched with H_2O_2 and the pH was brought to 8 with NaOH 1 M. To remove all the residual compounds, the OCFQDs dispersion was dialyzed in a dialysis bag (2 KDa) in deionized water for two days.

The final OCFQDs solution and the response to different metal ions were characterized by photoluminescence measurements by using a standard laboratory set-up equipped with a 200-W continuous Hg(Xe) discharge lamp (Oriel Corp. Oxford, UK), an excitation 25-cm monochromator (Photon Technology International, Birmingham, NJ, USA) and an emission 25-cm monochromator (Cornerstone 260, Oriel Corp.) equipped with specific excitation-rejection filters and a R3896 photomultiplier (Hamamatsu Photonics K.K., Shizuoka, Japan) by using conventional 90° geometry on fused-silica cuvettes with an optical length of 10 mm. The typical excitation wavelength of λex = 300 nm was used. Absorptions spectra were recorded on a Cary 50 spectrophotometer. Dynamic light scattering (DLS) measurements were carried out on the OCFQDs aqueous suspensions using a Zetasizer instrument (Malvern, Worcestershire, UK) at a temperature of 25.0 ± 0.2 °C [9].

3. Results

DLS measurements (not reported here) confirmed that the as-prepared OCFQDs had a relatively narrow size distribution with <2RH> 3.5 ± 1.0 nm, in reasonable agreement with the expected dimensions of monodisperse open-cage fullerene. These data, along with the abosrption spectrum of the aqueous solution, are in good agreement with the results of Ref. [8]. Figure 1a shows the quenching of the photoluminescence spectrum of OCFQDs in the presence of different concentrations of Cu^{2+} ion. As it is evident, the PL intensity gradually decreases with the increase of Cu^{2+} concentrations. The Stern-Volmer plot of the quenching experiment (not shown) exhibits a linear behaviour up to 70 μM. Interestingly, along with the fluorescence quenching, OCFQDs also showed a variation of the transmittance spectrum (see Figure 1b) with a decrease of transmittance in the UV region and a relative decrease of the π-π * peak at 300 nm with the increasing Cu^{2+} concentrations.

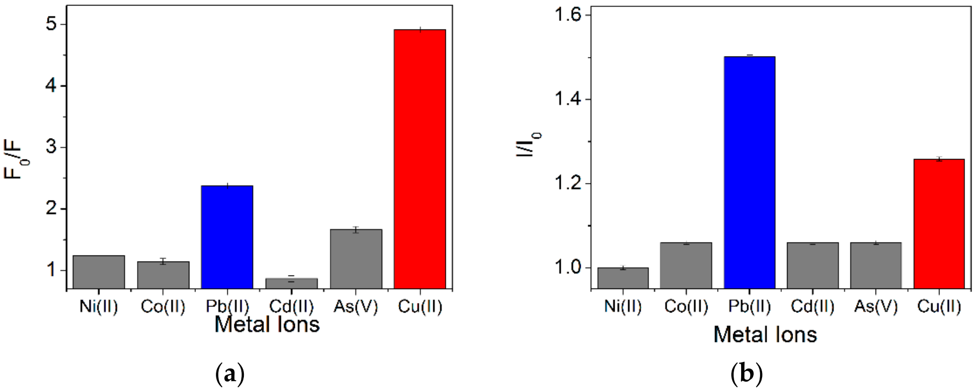
Similar curves, with a lower sensitivity to the ion concentration, were recorded for Pb^{2+} (not shown). Moreover, for this ion, an evident brownish precipitate was observed at the bottom of the titration cuvette after few hours.



(**a**) (**b**)

Figure 1. (**a**) Fluorescence quenching and (**b**) variation of transmittance spectra in the presence of different concentration of Cu^{2+} ions.

Substantially no sensitivity was found to Ni^{2+}, Co^{2+}, Cd^{2+} and As^{5+} as reported in Figure 2 which shows the response of PL (Figure 2a) and absorption (Figure 2b) to a fixed concentration of 100 μM for the different ions. Interestingly, the fluorescence quenching produced by each ion is not proportional with the respective transmittance variation. In other words, copper and lead ions exhibit different ratio of the fluorescence quenching to the trasmittance variation.



(**a**) (**b**)

Figure 2. (**a**) Fluorescence quenching and (**b**) variation of the transmittance spectra in the presence of different metal ions at the concentration of 100 μM.

4. Discussion

The decrease of transmittance with decreasing wavelength, paralleling the fluorescence quenching, can be explained with Rayleigh light scattering due to formation of large OCFQDs aggregates in the presence of metal ions. Aggregation could occur via multiple complexation, i.e., with the divalent ions binding more OCFQDs together, by chelating with the -OH and -COOH groups located at the edges. Once an aggregate is formed, the fluorescent emission can be quenched through a different possible radiationless mechanisms arising inside the aggregate itself. This process had already been suggested, without further analysis, as a possible explanation for the PL quenching in the presence of heavy-metal ions in GOQDs [10,11]. The hypothesis of aggregate formation is verified by DLS measurements (not reported here) which show an increment of hydrodynamic radius from 4 nanometer to 200–300 nanometer both for copper and lead. Moreover aggregate formation is consistent with the appearance of the brownish precipitate observed in the presence of lead. Most interestingly, we note that the combination of fluorescence quenching and transmittance variation makes it possible to discriminate different ions. In fact, the different ratio of the fluorescence quenching to the transmittance variation measured in copper and lead ions, respectively, represents the peculiar signature of each elements which could allow a selective detection of the two specific ions.

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Conflicts of Interest: The authors declare no conflict of interest.

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