SURFACE-MODIFIED WATER-SOLUBLE CdSe QUANTUM DOTS AS LUMINESCENT ION PROBES.

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Quantum Dots (QDs) are a special class of colloidal nanocrystalline semiconductors roughly spherical and with sizes typically ranging from 1 to 12 nm in diameter. At such reduced sizes these nanoparticles behave differently from bulk solids due to quantum confinement effects [1]. In fact, quantum confinement is the main responsible of the remarkable attractive optoelectronic properties exhibited by the QDs, including high emission quantum yields, size tuneable emission profiles and narrow spectral bands [2]. Moreover, their strong size-dependent properties result in an unprecedented tuneability, enabling special applications in science and technology. However, although QDs optical properties are very promising in the development of new methods for chemical analysis, most of the applications have been focused so far on their use in microelectronics and opto-electrochemistry areas.

Recent developments stressed the importance of adequate surface chemistry in the development of highly luminescent, water-soluble and biocompatible quantum dots for bioanalysis and diagnostics purposes. Moreover, analytical chemists have also recently started to explore these nanomaterials for the development of a new generation of luminescent optical probes.

Luminescence of quantum dots is very sensitive to their surface states; therefore, it is reasonable to expect that chemical or physical interactions between a given chemical species with the surface of the nanoparticles would result in changes on their surface charges affecting the efficiency of the core electron-hole recombination [3]. Following this approach, in this communication QDs are reported for optical sensing of small ions in water media, using as transduction signal the measurement of the fluorescence changes that occur after the interaction between the target analyte and the nanoparticle surface.

Surface modified water-soluble CdSe QDs (Figure 1) are here proposed for the very sensitive and highly selective determination of free cyanide and copper (II) ions in aqueous solutions based on fluorescence quenching measurements.

Luminescent surface-modified CdSe semiconductor QDs, with nanoparticle size distribution in the order of 2 - 7 nm, have been synthesized for optical determination of free cyanide ions via analyte-induced changes in their photoluminescence. The nanoparticles have been functionalised with 2-mercaptoethane sulphonic acid for cyanide detection in aqueous media exhibiting a strong fluorescent emission at about 580 nm. A detection limit as low as 1.1×10^{-7} M (2.9 ng ml^{-1}) of cyanide ions was obtained, while the interfering effect of other inorganic anions (including NO^{3-}, Cl^- or SCN^-) was negligible even at two-hundred-fold level concentrations in excess of cyanide.

On the other hand, the use of water-soluble luminescent CdSe QDs whose surface was modified either with 2-mercaptoethane sulphonic acid or with 2-mercaptoacetic acid, was investigated for the sensitive and selective determination of copper (II) ions in aqueous solutions based in fluorescence quenching (see figure 2). Detection limits for Cu(II) of 3.2 nM, a dynamic range up to 500 nM, and a RSD of $\pm$ 2.8 % for ten replicates of a 40 nM Cu(II) solution were obtained. Besides, the influence on the fluorescence signal of foreign

cations (including Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{3+}, Ag^{+}, Hg^{2+}, Cd^{2+} and Fe^{3+}) was studied, achieving a high selectivity of the sulphonic modified QDs towards Cu(II) ions.

In both cases, after QDs synthesis, a photoestimulation was necessary in order to obtain a stabilized emission profile and to provide reliable responses to the presence of the analytes. The photoactivated QDs turned out to exhibit excellent long-term stability when stored in the dark (no significant changes in QDs luminescence emission intensity was observed even after two months from synthesis). Moreover, the addition of surfactant agents to the measurement aqueous solution was found to further greatly stabilize the QDs and thus the fluorescent signals resulting in a very high sensitivity for the target analytes detection.

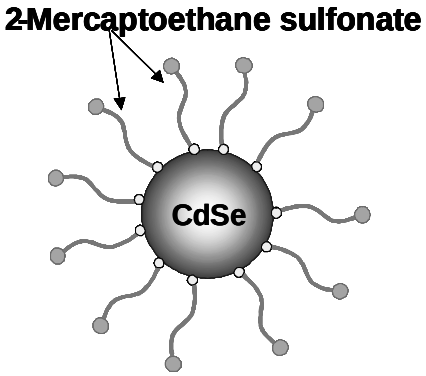

Figure 1. Scheme of surface-modified water-soluble CdSe QDs synthetized for monitoring the highly toxic cyanide anion.

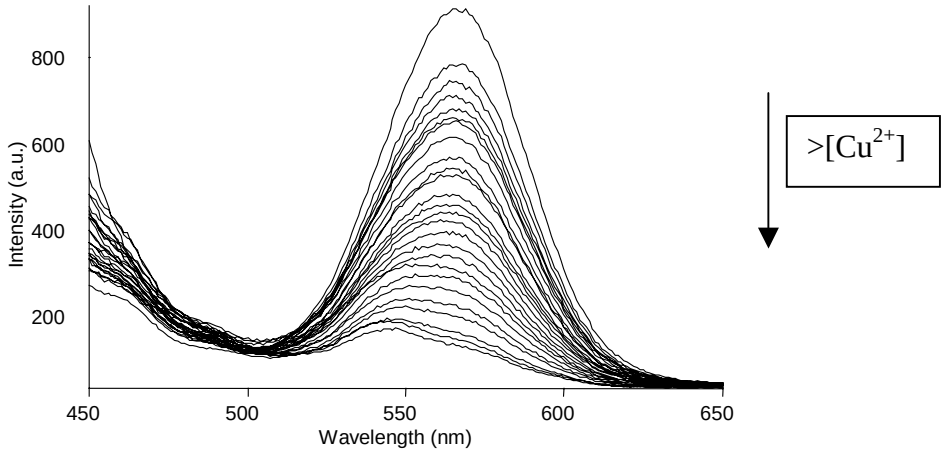

Figure 2. *Effect of the addition of trace amounts of copper on sulphonic capped CdSe-QDs.*

References

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