Quantum dots in aqueous medium. Size, quantum efficiency and stability.

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Semiconductor nanocrystal quantum dots (QDs) have been explored as fluorescent biological labels due to their photostable, size-tunable, narrow bandwidth photoluminescence and chemically functionalizable surfaces. The unique optical properties of QDs make them appealing as fluorophores in a variety of biological investigations, in which traditional fluorescent labels based on organic molecules fall short of providing long-term stability and simultaneous detection of multiple signals. Currently, there are lots of essays trying to improve the methods of synthesis of QDs and it can be considered a powerful area that involves several fields of science.

Organic solvent approach for these QDs synthesis is complex and harmful to the environment and the "as-prepared" QDs cannot be directly used in biological applications due to their hydrophobic character.

Our studies report an easy strategy to synthesize highly luminescent, water soluble and biocompatible CdS NCs by the reaction of Cd²⁺ and S²⁻ in the presence of mercaptoacetic acid (MAA) as capping agent (stabilizant), under normal pressure and atmospheric temperature (Fig. 1 y 2). We also systematically investigate the influence of various experimental variables, including the pH (Fig. 3 y 4) value, Cd-to-S ratio (Fig. 5) as well as Cd-to-MAA ratio, on the optical properties and the growth rate of CdS NCs. Through the temporal evolution of the UV-VIS absorption and PL emission spectra (Fig. 6) we have studied mean particle size and size distribution of CdS NCs (foto). This highly luminescent water-soluble QD can be expected to be very promising biological label.

There is quite a wide range of available methods of CdSe nanoparticles preparation but these techniques have many inherent limitations, such as the utilization of high toxic precursors, in particular organometallic cadmium and selenium compounds, high temperatures, high-energy irradiation, and others.

Our studies have been focused on the development of a synthesis of water-soluble CdSe quantum dots. Due to the difficulties of the reaction in organic medium, our method for the preparation of CdSe QDs consists in using CdCl₂ and Na₂SeSO₃ as precursors (pH=4-5, Fig. 9) and mercapthoacetic acid (Fig. 10) as a stabilizing agent in aqueous medium (Fig. 6 y 8).

The Na_2SeSO_3 has a very slow kinetic hydrolysis at $4^{\circ}C$. In these conditions the nanocrystals have a high quantum efficiency (IF~1000u with slits of 3 nm). The stability of the QDs is longer than 100 days (Fig. 11).

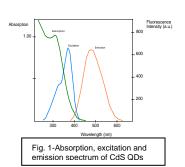
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¹ J. O. Winter, N. Gomez, S. Gatzert. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 254 (2005) 147-157

² Igor L. Medintz, H. Tetsuo Uyeda, Ellen R. Goldman, Hedi Mattoussi. *Nature Materials* **4**, 435 - 446 (2005)

³ A. M. Smith, S. Nie. *The Analyst* 129 (2004) 672

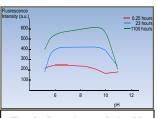
CdS QDs



Total Total

Fig. 3- Colour of the **CdS QDs** with different pH

Fig. 2- X-Ray difractogram of



Fluorescence intensity (a.e.)

400

300

200

400

600

800

1000

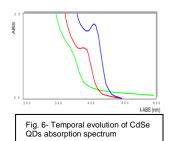
Time (bours)

Fig. 5- Temporal evolution of CdS QDs

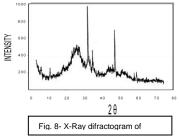
Fig. 3- Dependence of the PL emission intensity on the pH, at different times. Choice of the optimal pH for the synthesis

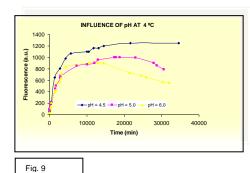
Fig. 4- The optimum conditions of quantum yield and stability are achieved for Cd-to-S ratios higher

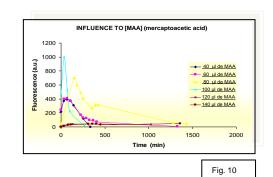
CdSe QDs











FLUORESCENCE VS TIME EVOLUTION

1400
1200
1000
8 800
200
0 10 20 30 40
Time (days)