Water-soluble colloidal quantum dots for the detection of ionizing radiation

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cQDs synthesis

In a typical synthesis of the CdSe cores, 0.75 ml of $Cd(Ol)_2$ 0.5 M, 2g of TOPO 90% and 8 ml of octadecene were first place in a three neck round bottom flask under vacuum and then stirred for 1 hour at 100°C. After three purges, the solution was place under N_2 flow and heat up at 280 °C. Then, a solution of 3 ml of oleylamine, 1ml of octadecene and 4 ml of TBP-Se 1M were injected in the Cd precursor solution. The temperature was decrease to 250°C and the cQDs were allowed to grow for 8 minutes follow by a cooling down to room temperature. The cQDs were washed three times with a solution of 1:1 methanol/ethanol by centrifugation and then redispersed in 6 ml of hexane for subsequent coating.

A successive ionic layer adsorption and reaction (SILAR) synthesis has been used for $Cd_xZn_{x-1}S$ shell for which the concentration and size of the cQDs were calculated by Peng and Bawendi method and the monolayer calculation by Peng method [1-3]. In a three neck round bottom flask, 1ml of CdSe, 2 ml of oleylamnine and 3 ml of octadecene were stirred under vacuum at 100°C for 1 hour. After 3 purges, the temperature solution was raise to 240°C and then 3 monolayers of CdS, 2 monolayers of $Cd_{0.5}Zn_{0.5}S$, 1 monolayer of ZnS and 1 monolayer of Zn were added within 10 minutes intervals with a solution of $Cd(Ol)_2$ 0.1M as a Cd precursor, $Zn(Ol)_2$ 0.1M as a Zn precursor and S 0.1M in octadecene as a sulphur precursor. For the last injection the temperature was raise to 260°C and the solution was stirred for 30 minutes before cooling down to room temperature. The core shells were washed 3 times with a solution of 1:1 methanol/ethanol by centrifugation and then redispersed in 6 ml of hexane.

Transfer of cQDs in aqueous media

For the transfer of the core shell into aqueous media, a ligand exchange with dihydrolipoic acid (DHLA) was made based on previous method [4]. Typicaly, 2 ml of core shell were mixed with 6 ml of DHLA and keep in a drying oven at 70°C overnight. A mixture of 10 ml of DMF and 500 mg of t-BuOK were added to the solution and centrifuge at 14 000 rpm for 5 minutes. The supernatant was removed and the cQDs were redispersed in 4 ml of water basified with t-BuOk (pH 13). The cQDs were then neutralized with 3 washing of borate buffer 25 mM by ultracentrifugation (10 000Da marque GE) and then redispersed in 5 ml of borate buffer 25 mM pH 8. The concentration of the solution was estimated by comparison with the cQDs in hexane.

Liquid scintillation counting parameters

LSC Data were acquired using the following parameters: multiples (5 or 12) cycles of 1 hour counting for an acquisition energy range from 0 to 2000 keV, except if mentioned.

1   **Effect of the cQDs concentration on the ^{226}Ra signal by LSC.**
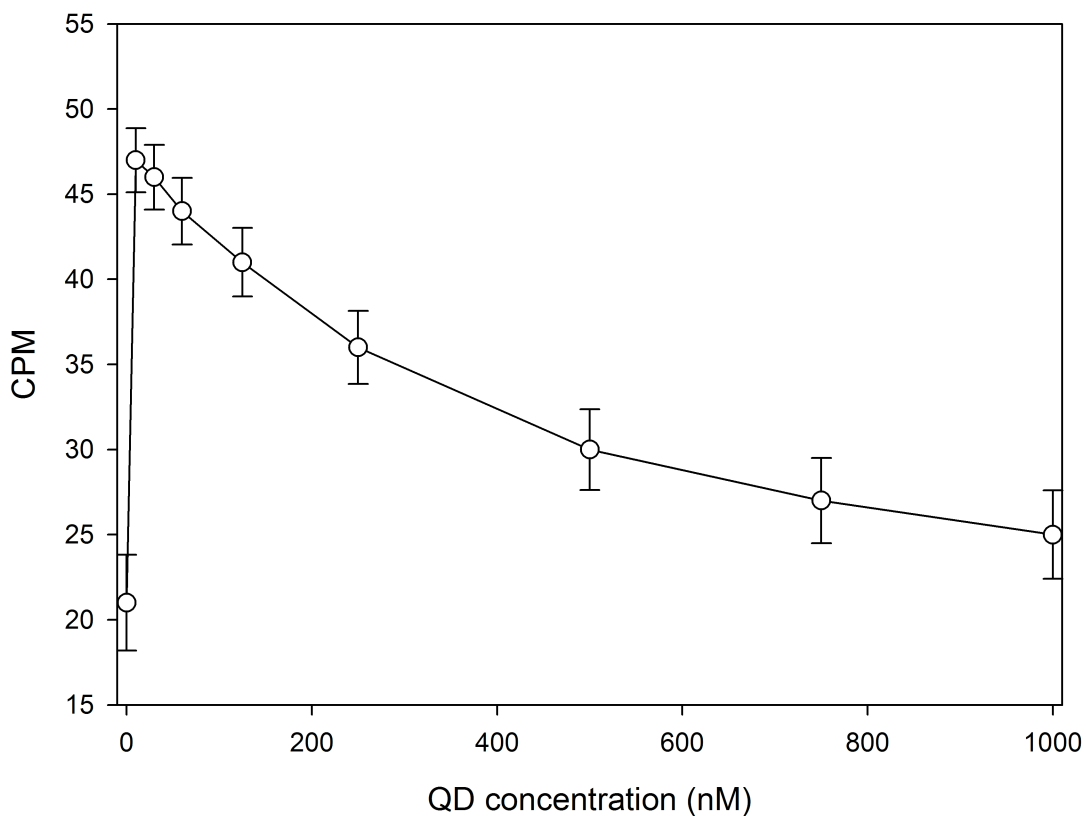
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3
4   **Figure S1. Effect of the cQDs concentration on LSC signal**

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6   **Table S1. Counting statistics and detection efficiencies for cQDs and various commercial scintillation cocktails.**
7   **(^{226}Ra activity = 750 mBq, counting time = 4 hours)**

Scintillation cocktail	Number of counts (CPM)		Detection efficiency (%)
	Blank standard	^{226}Ra standard	
Cytoscint ES (Fisher Scientific)	35	342	682
Ultima-Gold XR (Perkin-Elmer)	36	343	682
Permafluor (Perkin-Elmer)	33	230	438
cQDs	21	47	58

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1   **Detection of ^{90}Sr and ^{238}U using cQDs**
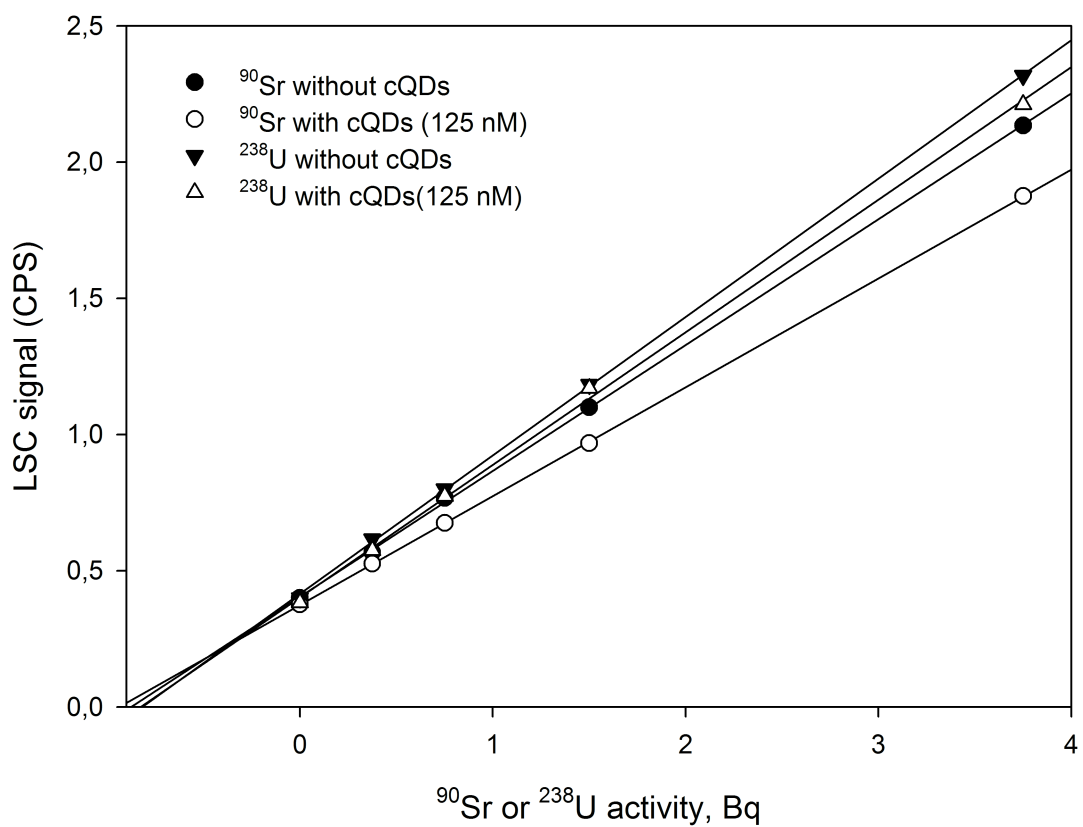
2

3   **Figure S2. LSC calibration curves for ^{90}Sr (at secular equilibrium with its progenies) and ^{238}U standards with**
4   **and without cQDs (125 nM). Counting time = 1 hour.**
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Calculation of the quantum yield (QY)

The optically dilute measurements method was used for the quantum yields determination [5,6]. Two standards were used: rhodamine B in absolute ethanol with a QY of 0.66[7] and fluoresceine in 0.1 M NaOH aqueous solution with a QY of 0.92[8]. Absorption spectra were acquired with a Cary 50 with 1 cm optical path quartz cuvettes for rhodamine B and PMMA cuvettes for fluoresceine and cQDs dispersion. The absorbance was taken at 480 nm. Emission spectra were acquire with a Fluorolog (Horiba Jobin Yvon) with a xenon lamp, an excitation double monochromator with 1200 grooves gratings blazed at 330 nm, an emission double monochromator with 1200 grooves gratings blazed at 500 nm, each with a 0.3 nm resolution, and a cooled Hamamatsu R928P photomultiplicator tube. The excitation wavelength used was 480nm and the emission spectra were acquired between 485 nm and 700 nm. The band pass for the emission monochromator was 2 nm and was 1 nm for the excitation. The calibration of the emission monochromator and detector was done in factory by Jobin Yvon and the conversion from intensity to photons was achieved by multiplying the wavelength with the intensity at each wavelength. The quantum yields were calculated using:

where the subscripts ST and X denote standard and test respectively, Φ is the fluorescence quantum yield, $Grad$ the gradient from the plot of integrated fluorescence intensity vs absorbance, and η the refractive index of the solvent.

A cross-calibration of the two standards was made using this equation. The values of the two quantum yields obtained should match the literature values within ±5%. If the QY for the standard samples are an acceptable match, the quantum yield values for the test samples can be calculated, using the same equation above. For each test sample, two Φx values will be obtained, one relative to fluoresceine standard, the other to rhodamine B standard. The average of these two values represents the quantum yield of the test sample. The acceptable error is ±5%.

Reference:

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Sample	Solvent	Refraction index	Gradient	Quantum yield (%)
Fluoresceine	NaOH 0.1 M	1.3576	3.8879E+13	91
Rhodamine B	Absolute ethanol	1.361	2.8136E+13	67
CdSe/CdS/Cd$_{0.5}$Zn$_{0.5}$S/ZnS	Hexane	1.3727	2.4798E+13	60
CdSe	Hexane	1.3727	4.5556E+11	1.0
CdSe/CdS/Cd$_{0.5}$Zn$_{0.5}$S/ZnS with DHLA	Water	1.3333	1.00845E+13	23