

Supporting information for:

**Elemental Mass Spectrometry: a powerful tool for an
accurate characterisation at elemental level of
Quantum Dots**

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Experimental Section:

Chemicals and Materials:

All chemical reagents were of analytical grade and used as received without further purification. Cadmium oxide (99.99%), trioctylphosphine oxide (TOPO, 99%), trioctylphosphine (TOP, 90%), selenium (powder, 100 mesh, 99.99%), hexamethyldisilathiane, diethylzinc solution 1.0 M in hexanes, anhydrous methanol and anhydrous chloroform were purchased from Aldrich (Milwaukee, WIS, USA). Hexylphosphonic acid (HPA) was obtained from Alfa Aesar (Karlsruhe, Germany). Nitric acid and chloridic acid were obtained from Merck (Darmstadt, Germany),

Enriched ^{111}Cd (96.48% abundance for ^{111}Cd), ^{77}Se (93.13 % abundance for ^{77}Se) and ^{67}Zn (94.01 % abundance for ^{67}Zn) were prepared from solid materials supplied by Cambridge Isotope Laboratories (Andover, MA, USA). The concentrations of cadmium, selenium and zinc in these solutions were established by reverse isotope dilution analysis using a natural abundance Merck certified standard (Merck, Darmstadt, Germany) as described elsewhere.¹ Ultrapure water (resistivity 18.2 M Ω cm) was used throughout the work.

Instrumentation:

Absorbance measurements were performed with a UV/VIS/NIR Spectrophotometer (Lambda 900, Perkin Elmer). Luminescence spectra measurements were performed with a Varian Cary Eclipse spectrometer (Varian Iberica, Madrid, Spain).

Transmission electron microscopy (TEM) was conducted on high-resolution transmission electron microscope (2000 EXII, JEOL, Tokyo, Japan).

In order to carry out the synthesis a heating mantle with energy heater control (Jp Selecta, Barcelona, Spain) with simultaneous stirring was employed. To keep a constant argon atmosphere inside the flask, a needle with argon flow was used. This flow was set to 25 mL min⁻¹ by means of a rotameter (Serv' Instrumentation, Irigny, France).

Elemental measurements were carried out on a quadrupole ICP-MS Agilent model 7500ce (Agilent Technologies, Tokyo, Japan) was used. The instrument consists of an ICP source with plasma-shield torch, and enclosed octapole ion guide operated in the RF mode and a quadrupole mass analyser with a SEM detector. A flow of 4.5 mL min⁻¹ of hydrogen was used to pressurise the octapole chamber for Se and Zn determinations. The sample introduction system consisted of a Meinhard nebuliser with double-pass glass spray chamber cooled down to 2 °C.

Procedures:

Synthesis of CdSe(ZnS) Quantum Dots: The synthesis of the nanoparticles was done following procedures described in the literature with slight modifications. Selenium stock solution was prepared in an Ar-filled dry-box by dissolving 1.63 mmol of selenium powder in 7.5 ml of TOP, to produce a solution of trioctylphosphine selenide (SeTOP). Zinc sulfide (Zn/S/TOP) stock solution was also prepared in Ar atmosphere by mixing 1.18 mmol of hexamethyldisilathiane, 8.34 mmol of diethylzinc and 10.25 mL of TOP. CdSe/ZnS quantum dots were synthesized using CdO as precursor via the procedure described by Peng's group.² Briefly, 1.23 mmol of CdO, 0.6 g of HPA and 17.5 g of TOPO were loaded into a 250 mL glass three-necked flask. The mixture was heated up to 300–320 °C under argon flow for 15–20 min to allow the complete dissolution of CdO in HPA and TOPO. After cooling the temperature of the solution down to 270 °C, 6 mL of the SeTOP solution was swiftly injected. After injection, nanocrystals were left to grow for about 11 min at 250 °C. Once the growth process has reached de desirable core size, 7.5 mL of Zn/S/TOP solution was added slowly at 230 °C in order to allow the generation of the shell, and then it was cooled down to 100 °C for an hour. Afterwards the solution was cooled down to room

temperature, and the QDs solution was transferred to a glass vial and diluted with chloroform anhydrous.

In order to study the synthesis evolution, aliquots of the reacting mixture were taken out of the flask throughout the synthetic process. The amount of extracted liquid was measured by weighting the loaded and unloaded syringes (in a range within 0.70 and 1.05 g). Then, aliquots were quickly dispersed in 1 mL chloroform (also weighed) to produce a fast decrease of the temperature, avoiding evaporation of solvents.

Purification of CdSe(ZnS) Quantum Dots: The purification process of the aliquots was done by mixing the QDs solution dispersed in 1 mL chloroform, with 1 mL of methanol. Then the mixture was centrifuged at 5000 rpm during 5 minutes in order to separate the QDs by precipitation. The supernatant liquid phase was decanted to remove any excess of reagents. This procedure was repeated two times more.

Sample preparation: Afterwards, purified QD nanocrystals were then re-dispersed in 1.5 mL of anhydrous chloroform.

Optical properties measurements: In order to carry out the absorption and fluorescence measurements, 100 μL of sample were diluted in 4 mL of chloroform (both were exactly weighed). For fluorescence measurements the excitation wavelength was fixed at 350 nm. Absorbance spectra were employed for QDs size and concentration estimation by means of application equation of Peng.³

Transmission Electron Microscopy (TEM). Samples for TEM were deposited onto copper TEM grids (3mm of diameter) coated with thin carbon films. 10 μL of nanocrystal dissolved in anhydrous chloroform were placed on a grid followed by solvent evaporation at room temperature. The grids were examined in a JEOL 2000 EXII high-resolution electron microscope operating at 160 kV. Nanocrystal sizes were measured by counting HRTEM images by digital analysis employing the ImageJ software of image processing.

Elemental mass spectrometry (ICPMS) measurements: For elemental content measurements 0.35 mL of sample solution in chloroform was first evaporated under argon flow, and the resulting dried solid was digested with 1 mL of aqua regia (subboiled nitric acid/ chloridic acid 1:3 v/v) and then diluted with 1% v/v subboiled nitric acid to 40 mL. In order to quantify Cd, Se and Zn present in QDs using Isotope Dilution Analysis, accurately weighed amounts ranging from 50 to 100 μL of diluted digested samples were spiked with appropriate amounts of the

enriched ^{111}Cd , ^{77}Se and ^{67}Zn spikes. Then, all samples were diluted with 1% v/v subboiled nitric acid to 6 mL.

Three cadmium isotopes (111, 112 and 114), five selenium isotopes (76, 77, 78, 80 and 82) and three zinc isotopes (66, 67 and 68) were monitored by ICP-MS. For daily optimization of ICPMS operation conditions and acquisition parameters, a solution of 10 ng g^{-1} of Li, Co, Y and Tl (prepared from 1000 mg L^{-1} natural abundance Merck certified standards) in 1% v/v subboiled nitric acid was used. A solution of 1% v/v subboiled nitric acid was also used to check the background level caused for polyatomic Ar interferences. The cadmium was measured without reaction cell. On the hand, H_2 was used as collision gas to minimise the Ar_2^+ interferences on the most abundant Se isotopes. The correction for SeH^+ formation was carried out using mathematical corrections, by monitoring the signals at masses 76, 82 and 83 for (SeH^+) as described elsewhere.⁴ All isotope ratio measurements were corrected for dead time (49 ns) and mass bias using the bracketing technique.¹

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- (1) J. Ruiz Encinar, J.I. García Alonso, A. Sanz-Medel, S. Main, P. J. Turner, *J. Anal. At. Spectrom.*, **2001**, 16, 315-321.
 - (2) Z.A. Peng, X. Peng, *J. Am. Chem. Soc.*, **2001**, 123, 183-184.
 - (3) W. W. Yu, L. Qu, W. Guo, X. Peng, *Chem. Mater.*, **2003**, 15, 2854-2860.
 - (4) L. Hinojosa Reyes, J.M. Marchante Gayón, J.I. García Alonso, A. Sanz-Medel, *J. Anal. At. Spectrom.*, **2003**, 18, 11-16.

Figures:

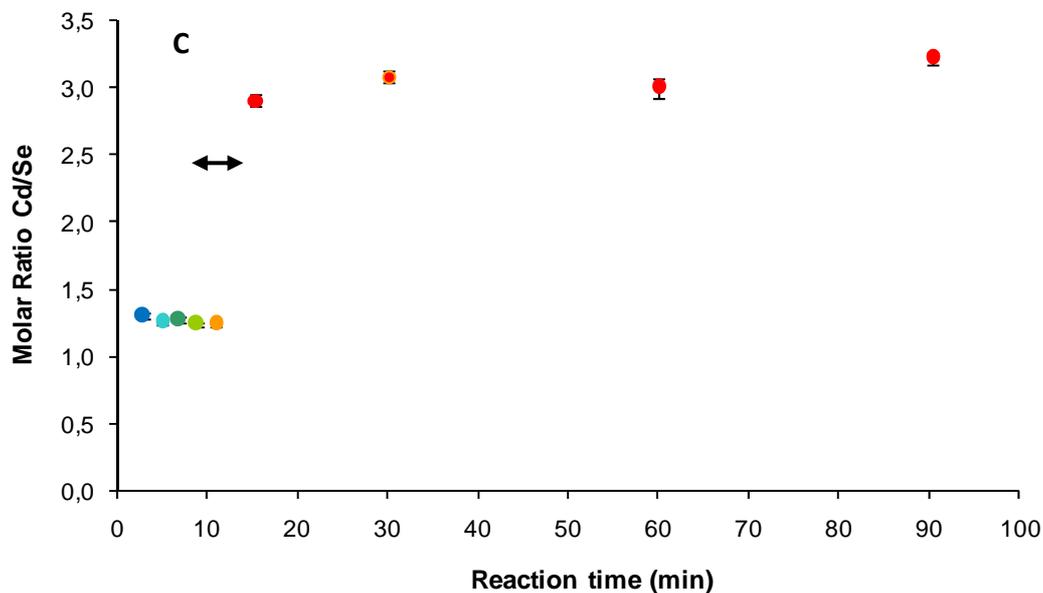


Figure S1. Molar ratio Cd/Se obtained from their independent quantification by isotope dilution analysis throughout the synthesis reaction. Uncertainty bars corresponds to 1 standard deviation. Double arrow indicates the time of addition of ZnS precursors.

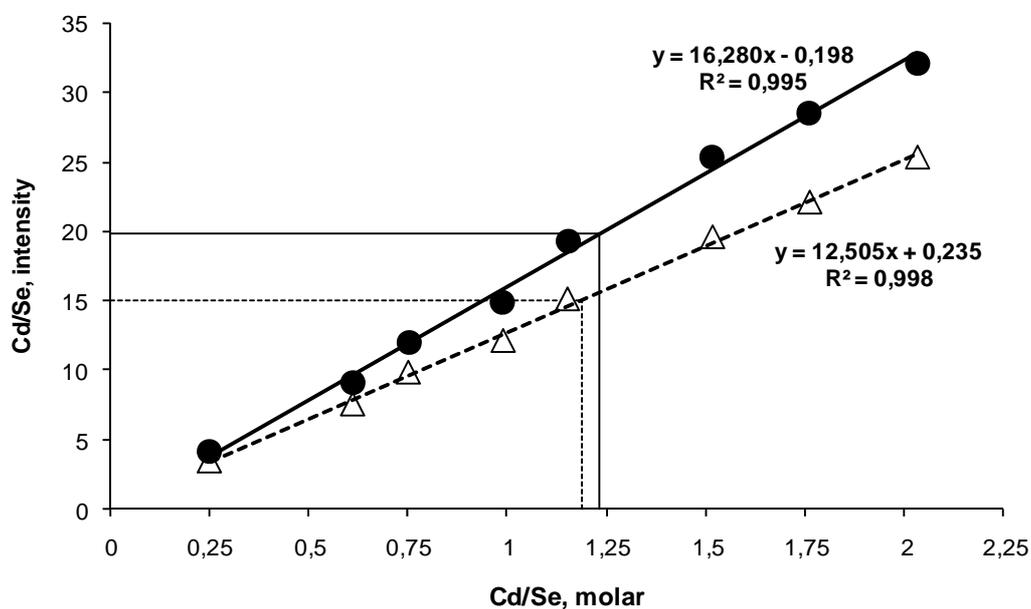


Figure S2. Plot of the Cd/Se intensity ratio experimentally obtained by ICPMS versus the theoretical Cd/Se molar ratio for the eight elemental standards mixtures prepared. Two independent intensity elemental ratios were measured : (●) $^{110}\text{Cd}/^{77}\text{Se}$ and (Δ) $^{111}\text{Cd}/^{82}\text{Se}$.