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Diameter Distribution by Deconvolution (DdD): Absorption spectra as a practical tool for semiconductor nanoparticle PSD determination

Diego Onna^{1,2}, Ignacio Perez Ipiña³, Agustina Fernández Casafuz³, Álvaro Mayoral^{4,5}, M. Ricardo Ibarra García⁶, Sara A. Bilmes², María Luz Martínez Ricci^{2*}

¹Instituto de Nanosistemas, Universidad Nacional de San Martín, Av. 25 de Mayo 1021, San Martín, Buenos Aires, Argentina

² Instituto de Química, Física de los Materiales, Medioambiente y Energía (INQUIMAE-CONICET),

DQIAQF, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón II, Ciudad Universitaria, C1428EHA-Buenos Aires, Argentina

³Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón I, Ciudad Universitaria, C1428EHA-Buenos Aires, Argentina

⁴ Center for High-resolution Electron Microscopy (CħEM), School of Physical Science and Technology ShanghaiTech University, 393 Middle Huaxia Road, Pudong, Shanghai, 201210

⁵ Laboratorio de Microscopías Avanzadas (LMA), Aragon Institute of Nanoscience (INA), University of Zaragoza, Mariano Esquillor, Edificio I+D, 50018, Zaragoza, Spain

⁶ Aragon Nanoscience Institute (INA) University of Zaragoza Pedro Cerbuna 12, 50009 Zaragoza (Spain)

S1. Experimental and characterization of SiO₂ MTFs

S1.1 Chemicals

Tetraethoxysilane (TEOS, 99.999%, trace metal basis), triblock copolymer Pluronics F-127 (F127, PEO106-PPO70-PEO106, MW \approx 13 800), cadmium (II) acetate (Cd(Ac)₂, puriss. p. a.), sodium sulfide (Na₂S, 98%), hydrochloric acid (HCl, 37%, ACS reagent), and ethanol (EtOH, absolute) were purchased from Sigma Aldrich and used without further purification. Millipore water was used for the preparation of all precursor solutions. Glass substrates were purchased from Marienfield (Germany).

S1.2 Preparation of Mesoporous SiO₂ Thin Films.

Mesoporous silica films (MSF)ⁱ were prepared on glass substrates by a sol-gel method based on the oxide precursor tetraethoxysilane (TEOS) using Pluronic F-127 as templating agent.

Prior to deposition, the substrates were washed with Dextran or other suitable surfactantbased cleaning agents, followed by rinsing with water, ethanol and acetone. Precursor films were prepared by dip-coating with a withdrawing speed of 2 mm s⁻¹ under 40–50% relative humidity (RH) at room temperature. The precursor solution was prepared using the following molar ratios: 1 TEOS: 0.0055 F127: 40 EtOH: 10 H2O: 0.009 HCl. Deposited films were stored immediately in a chamber with 50% RH for 24hs followed by a stabilizing thermal treatment of 24hs at 60 °C and 24hs at 130 °C. The final calcination was carried out at 350 °C for 2 h. After this treatment, transparent, crack-free and robust SiO₂ films with a well-defined mesoporous structure of 150nm thickness were obtained.

S1.3 Loading of the MTF with SNPs by SILAR route.

To infiltrate the mesoporous SiO₂ films with CdS (CdS@SiO₂), we used a successive ionic layer adsorption and reaction (SILAR) process^{ii,iii}. Each infiltration cycle consisted of a total of four steps divided in two main stages as represented in Fig. S1. *Stage 1*: In the first step the SiO₂ film is placed for 1 min in a 0.01 M ethanolic solution of Cd(Ac)₂. Cd(II) species are adsorbed on the silica surface, forming an electrical double layer with the Ac⁻ anions. In the second step, the substrate is rinsed with distilled water to remove unadsorbed Cd²⁺ and Ac⁻ ions from the diffuse layer. After these two steps, the Cd_j stage will be ended (where j identifies the cycle number). *Stage 2*: In the third step the substrate is immersed into a 0.025 M ethanolic solution of Na₂S solution for 1 min leading to the replacement of the Ac⁻ ions with S²⁻ ions. In the last step, the substrate is washed again with H₂O to remove Na₂S in excess. This second stage will be named as S_j. Hence, after the two stages, the reaction between the Cd²⁺ and S²⁻ ions occurs, leading to the formation of insoluble CdS nanoparticles. The cycle can be repeated j times, in order to obtain higher pore loading of CdS.

The cycle can be repeated j-l times, in order to obtain higher pore loading of CdS. To exemplify terminology: two complete cycles will be identified as Cd2S2, while Cd2S1 will refer to one complete cycle and a second Stage 1.



Fig. S1: Schematic illustration of the Successive Ionic Layer Adsorption and Reaction (SILAR) method for the synthesis of CdS SNPs in MSFs.

S1.4 Characterization Techniques

UV-Vis optical characterization of the films was performed with a Shimadzu UV3101PC spectrophotometer. Environmental Ellipsometric Porosimetry (EEP) measurements were performed on a UV–visible (190–1000 nm, MgF₂ optics) variable angle spectroscopic ellipsometer (VASE) from SOPRA (GES5A), and analyzed with the WVase 32 software. Dynamic in situ monitoring of the film parameters (index of refraction and thickness) was realized by varying of the relative vapor pressures between 0% and 100% inside the analysis chamber. Also the accessible volume was calculated as reported elsewhere^{iv}.

The morphology of films was studied using scanning electron microscopy (SEM) with an SUPRATM 40 field emission SEM (Carl Zeiss SMT AG) working at an electron beam energy of 5 keV.

For high resolution scanning transmission electron microscopy (HRSTEM), the samples were dispersed in ethanol and placed onto a carbon coated copper microgrid and left to dry before observation. Spherical aberration (C_s) corrected scanning transmission electron microscopy high-angle annular field (STEM-HAADF) imaging analyses were performed in a XFEG FEI Titan microscope operated at 300 kV. The microscope was equipped with a CEOS aberration corrector for the electron probe, achieving a point resolution of 0.8 Å, an EDAX EDS detector and Gatan Energy Filter Tridiem HR865 for electron energy loss spectroscopy (EELS).

Analysis of the nanoparticle size distribution in HRSTEM images was made with the ImageJ software (http://rsb.info.nih.gov/ij/).

S1.5 SiO₂ MTF structural description

Fig. S2 shows SEM and poroelipsometry data for SiO₂-F127 thin films. From SEM image (Fig. S2(a) and (b)) it is possible to observe a pore-ordered sample in a Im3m arrangement. From the absorption branch, poroelipsometry data shows pores of 8-9nm approx. Desorption branch exhibits a bimodal distribution of necks of 3nm and 5nm diameter (Fig. S2(c) and (d)) that leads to a complete connected nanostructure.



Figure S2: (a) Top view and (b) side view from SEM micrographs of SiO₂ MTF. (c) Adsorption isotherm of water from Environmental Ellipsometric Porosimetry of SiO₂ MTF. (d) Pore size distribution of SiO₂ MTF calculated from the isotherm.

S2. Database

S2.1 About the chosen Database

Nowadays, there are two main approaches to obtain the chosen base: (i) colloids synthetized with a constrain for nanoparticle growth (e.g. micelles)^v and/or (ii) a post synthesis separation^{vi,vii,viii}.

In optimal conditions, these pathways allow a minimum size deviation of $\approx 10\%$, implying that the chosen bases present greater error for lower sizes than bigger sizes. It is worth mentioning that the quality of the PSD determination depends to a large extent in the quality of the chosen base. This means that a narrower size distribution of the base would lead to a PSD with neater features. In case the database corresponds to SNPs with capping shell, λ_e would be shifted a fixed quantity respect its corresponding bare SNPs wavelength position; if it is an unavoidable condition DdD method must be executed and the shift must be calculated once relying on HRTEM images.

S2.2 Sampling criteria of the Database

To resolve the matrix system detailed in Eq. 1, a double discretization has to be done. The spectroscopic measurement $Abs^{SNP}(\lambda)$, is discretized in M elements according to the spectrometer resolution. A good wavelength resolution in each curve is required to obtain a detailed spectrum which will lead to an appropriate deconvolution. Row size M of matrix $X^{DB}(\lambda_m, \lambda_{en})$ is determined by the same resolution in each spectroscopic spectrum of the database. Column size N of matrix $X^{DB}(\lambda_m, \lambda_{en})$ is determined by the number of curves selected for the absorption spectra database. Fig. S3 shows how the PSD of Cd2S1@SiO₂ changes according the sampling distance between curves of the database is decreased. Upper row of Fig S3, illustrates the separation between two contiguous curves of the database in the vicinities of λ_e^i (i = 1,...,N). Sampling distance was defined through the variable $\Delta \lambda_e = \lambda^{i+1}, \min_{e_i} - \lambda_e^i$, where i and i+1 indicate two contiguous curves of the database, $\lambda_e^{i+1,min}$ corresponds to the left minima next to the exciton position of *i*+*1*-*th* curve while λ_e^i is the exciton position of *i* -*th* curve. Variable Δe controls the superposition of curves of the database. Curves λ_e^i , λ_e^{i+1} and the minimum $\lambda_e^{i+1,min}$ are indicated in the upper graphs of Fig. S3.



Fig. S3: Different PSD for Cd2S1@SiO₂ obtained with 3 kind of sampling distance ($\Delta \lambda_e > 0$, $\Delta \lambda_e \approx 0$ and $\Delta \lambda_e < 0$)

The sampling distance defines the amount of curves from the database, in which each curve represents a different diameter. The obtained mean diameter for the three types of sample distances is $D^{DdD} = (3,1 \pm 0,8)$, however each PSD distribution is different. For $\Delta \lambda_e > 0$ (low sampling density), the obtained histogram shows a poor description of the distribution probably due to a low number of curves of the database which do not properly describe all possible SNP diameters D since not enough wavelength positions λ_e are included. Central distribution in the lower row of Fig. S3 corresponds an intermediate sample density where $\Delta \lambda_e \approx 0$. In this case, the number of curves allows a well-defined PSD which has a very good accordance with the HRTEM of Fig 4(c). For a sample density that fulfills the condition of high sampling density ($\Delta \lambda_e < 0$), there is a clear superposition of curves of λ_e^i and λ_e^{i+1} . This excess of elements in the

database leads to empty diameter values and a rough PSD as it is shown in the left distribution in the lower row of Fig. S3(c). In each distribution, column bin sizes have been defined according to $\Delta D(\Delta \lambda_e)$ which indicates the resolution for each sample density selection.

S2.3 CdS and CdSe functions and databases for DdD execution

-CdS SNPs: To carry out the DdD method for the CdS cases, the used bibliographic data^{ix} shown in Figure S4(a) was taken as the database to build the $X^{DB}(\lambda_{en},\lambda_m)$ matrix. The molar absorption^x $\epsilon(\lambda_e) = 21536(D(\lambda_e))^{2.3}$ was taken under consideration as well as the empiric

function^x $D(\lambda_e) = a\lambda_e^3 + b\lambda_e^2 - c\lambda_e + d$, where $\begin{cases} a = (-6.6521 \times 10^{-8})nm^{-2} \\ b = (1.9557 \times 10^{-4})nm^{-1} \\ c = (-9.2352 \times 10^{-2}) \\ d = (13.29)nm \end{cases}$ was used for the jacobian.

-CdSe SNPs: for the CdSe examples, Figure S4(b) shows the bibliographic data^{xi} used to build the $X^{DB}(\lambda_{en},\lambda_m)$ matrix. The molar absorption^x defined by $\epsilon(\lambda_e) = 5857(D(\lambda_e))^{2.65}$ was used while the employed empiric function^x was $D(\lambda_e) = a\lambda_e^4 + b\lambda_e^3 + c\lambda_e^2 - d\lambda_e + e$, where $\begin{pmatrix} a = (1.6122 \times 10^{-9})nm^{-3} \\ b = (-2.6575 \times 10^{-6})nm^{-2} \\ c = (1.6242 \times 10^{-3})nm^{-1} \\ d = (-0.4277) \\ e = (41.57)nm \end{pmatrix}$



Figure S4: (a) CdS and (b) CdSe database used for DdD calculation in this work.

S3. Lognormal Distribution Fitting

The histograms were fitted using a Lognormal Distribution (Eq. S1) in order to extract the mean μ and standard deviation σ from the asymmetric particle size distribution.

$$y = y_0 + \frac{A}{\sqrt{2\pi}wx}e^{-\frac{\left[\ln x - \ln x_c\right]^2}{2w^2}},$$
 (Eq. S1)

where y_0 represents the offset; x_c corresponds to the center of the distribution; w is the log standard deviation and A denotes the area. In general, the figures required to inform the characteristics of a distribution are the mean and the standard deviation. Eq. S2 and Eq. S3 correspond to the mean (μ) and standard deviation (σ) of the LogNormal distribution, while Eq. S4 and Eq. S5 represent the mean (\bar{x}) and standard deviation (\tilde{w}) of the associated normal distribution

Log-Normal Distribution	Associated Normal Distribution
Parameters	Parameters
$\mu = e^{\left(ln(x_c) + 0.5w^2\right)}$, (Eq. S2)	$\bar{x} = \ln x_{c'} \qquad (Eq. S4)$

$$\sigma = e^{\left(ln(x_c) + 0.5w^2\right)} \sqrt{e^{w^2} - 1}, \text{ (Eq. S3)}$$
 $\tilde{w} = w, \quad (Eq. S5)$

It is worth noting that the proposed LogNormal function fits well for a nanoparticles growth in a transport process due to diffusion and drift^{xii}. Figure S5 shows as an example Cd2S1 SILAR cycle histogram for (Fig 4(e)), and its fitting using the LogNormal distribution (dash line).



Figure S5: DdD Particle size distribution of SiO₂ MTF with CdS NPs fitted by a LogNormal function.

S4 Web App



Diameter Distribution by Deconvolution

Web app for determining the size of nanoparticles from absorption spectra. DOI:10.XXXX/XXXXXXXX



(4) J Threshold filter	ar the results
(3) EXI	ECUTE NNLS
(1) ABSORPTION SPECTRUM	(2) ABSORPTION DATABASE
Diego Onna <u>dieg</u>	o.onna@qi.fcen.uba.ar
Ins	tructions
he Absorption Spectrum	

Load the Absorption Spectrum
Load the Absorption Database
Execute NNLS
Load the Jacobian
Apply a threshold filter for eliminating the numeric error in lower sizes

Figure S6: Screenshot of the Web App before using it.



Diameter Distribution by Deconvolution





Figure S7: Screenshot of the Web App after using it.

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