Supporting Information

Determination of Optical Constants of Ligand-free Organic Lead Halide Perovskite Quantum Dots

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Tauc plots. Bandgap energy estimation.

In the case of direct bandgap semiconductors, the Tauc relation states that

$$(\alpha h\nu)^2 = C\left(h\nu - E_g\right), \qquad \text{(S1)}$$

where α is the absorption coefficient, h the Planck constant, ν the frequency of the photon, C is a constant and E_g the energy of the band-band transition of the semiconductor. E_g's extrapolation procedure consists of representing the quadratic dependence (in the case of direct bandgap semiconductors) of the absorption (αhν) with respect to the energy (hν) and intercepting the energies axis with a tangent to the inversion point of the curve. The inversion should in fact correspond to the linear region between the energy range where the absorption is zero (above the band edge) and the region where the material absorbs. The Tauc procedure is an approximation used mainly for bulk materials and which in any case does not provide an exact value of the band gap, but as already mentioned, the estimate of the Tauc gap, in this context, is a useful parameter to use as first approximation in the determination of the optical constants.

Brus model for the determination of perovskite NCs size

Brus approximation allows for the estrapolation of the radius (R) of a semiconductor nanocrystal by means of the following equation:[1]

$$E_{g,NC} \simeq E_{g,bulk} + \frac{h^2}{8\mu R^2} - \frac{1.8\, e^2}{4\pi\varepsilon_0\varepsilon_r R} \qquad \text{(S2)}$$

The dependence on the radius of the excitonic energy of the nanoparticle $E_{g,NC}$ is derived by adding two terms to the bandgap energy of the bulk material ($E_{g,bulk}$). The first term represents the quantization of the energy of a spherical particle-in-a-box system with infinite potential on the walls. h is the Planck constant and μ is the reduced mass of the exciton. The second term takes into consideration the electrostatic interaction between charges. In this term, e is the charge of the electron and ε_0 and ε_r the dielectric constants of the vacuum and that of the bulk semiconductor, respectively.,We used the Tauc gap as an approximation of the bandgap energy (Eg) of the NCs together with 4.2 and 17 as values for the dielectric constants of $MAPbBr_3$ and $MAPbI_3$, respectively, and $0.45m_0$ and $0.3m_0$ for their reduced masses.[2,3]

Experimental quantification of the filling fraction of perovskite nanocrystals

In order to study the spectral and size dependence of the optical constants of perovskite nanocrystals, a more precise quantitative investigation on the volume of perovskites contained within the porous matrix was necessary. In order to do so, lead determination was carried out through atomic emission spectroscopy with an inductively coupled plasma (ICP OES JASCO FT / IR-6200 IRT-5000). Porous films loaded with perovskite NCs synthesized in series at decreasing concentrations (in order to attain different NC sizes) were immersed in water to degrade CH_3PbX_3 perovskites to PbX_2, which solubilizes completely in the aqueous phase. Once the amount of lead element was obtained, it was possible to trace the mass of perovskite considering the weight proportion of the lead included in the perovskite composition. Then the volumetric ratio between silica and perovskite, was calculated taking into account the areas of the immersed samples, the thicknesses measured with a profilometer and density values reported in the literature for $MAPbBr_3$ and $MAPbI_3$: 3.83 gr/cm^3 and 4.15 gr/cm^3, respectively [4,5] Results are summarized in table S1. As a counter-test of the analysis, we performed a similar estimation on the amount of lead in bulk samples. The resulting volume for the thin film material corresponds to the volume obtained from direct measurements of area and thickness of the sample.

$MAPbI_3$	Pb ppm	$MAPbI_3$ mass mg	$MAPbI_3$ Volume mm^3	Total film Volume mm^3	$MAPbI_3$ v/v %
bulk	13.10	0.392	0.0945	0.091125	≈100
9 nm	11.11	0.332	0.08	0.1932	41.4 in SiO_2
7 nm	7.08	0.212	0.0511	0.1978	25.8 in SiO_2
6 nm	2.87	0.086	0.0207	0.2024	10.2 in SiO_2
$MAPbBr_3$	Pb ppm	$MAPbBr_3$mass mg	$MAPbBr_3$ Volume mm^3	Total film Volume mm^3	$MAPbBr_3$ v/v %
Bulk	31.29	0.723	0.1887	0.1518	≈100
2.40 nm	2.15	0.050	0.0131	0.2592	5.05 in SiO_2
2.30 nm	0.785	0.018	0.0047	0.2277	2.06 in SiO_2
2.20 nm	0.29	0.007	0.0018	0.23805	0.76 in SiO_2

Table S1. Quantitative analysis of iodide- and bromide-based perovskite inside the SiO_2 matrix from samples prepared with different precursor concentration. Columns from the left to the right correspond to the sample, Pb content from ICP, calculated perovskite mass and volume, total volume measured for the bulk film and SiO_2 matrix (considering that perovskite

is formed only inside the pores) and percentage of perovskite volume with respect the total volume of the composite system.

Modeling the Complex refractive index of perovskite NCs. Fitting parameters.

In order to obtain the spectral dependence of the complex refractive index of the perovskite nanocrystals (N_{NC}) synthesized in the porous matrices, we use a model that combines the transfer matrix method with a genetic algorithm to calculate the specular reflectance (R_{the}) and ballistic transmittance (T_{the}) of the films by fitting their experimental specular reflectance (R_{exp}) and ballistic transmittance (T_{exp}) with the least squares method. In particular, we find the set of parameters that fit the response of the films in the wavelength range comprised between λ=400 nm and λ =1000 nm for three different angles of incidence, i.e. θ=0 deg, 30 deg and 50 deg. Thus, we define the following Target

$$Target = \sum_{i,j} \left(R_{exp}(\theta_i, \lambda_j) - R_{the}(\theta_i, \lambda_j)\right)^2 + \left(T_{exp}(\theta_i, \lambda_j) - T_{the}(\theta_i, \lambda_j)\right)^2$$

To calculate the theoretical response, our model considers a layered system composed by a thin film (porous silica matrix loaded with NCs with a complex refractive index N_{eff} and thickness d) and a substrate (refractive index 1.51 and thickness 1 mm). Air (refractive index 1) is taken as incoming and outgoing media for light. We calculate the real (n_{eff}) and imaginary (k_{eff}) parts of N_{eff} of the porous silica film loaded with perovskite NCs using an effective medium approach (f_{EMA}) according to

$$N_{eff}(E) = f_{EMA}(N_{sil}, f_{sil}, N_{NC}, f_{NC})$$

where N_{sil} and N_{NC} are the complex refrractive indices of the silica matrix, which is considered only real and dispersionless as 1.4867, and the perovskite NCs, respectively; and f_{sil}, which is found to be 0.51, and f_{NC} are their volume fractions in the composite film. The spectral dependence of NNC is given by the Forouhi-Bloomer model in the parameterization of Jobin Yvon (new amorphous) as:

$$n_{NC}(E) = n_\infty + \sum_{j=1}^{N} \frac{B_j\left(E - E_j\right) + C_j}{\left(E - E_j\right)^2 + \Gamma_j^2}$$

$$k_{NC}(E) = \begin{cases} \sum_{j=1}^{N} \dfrac{a_j\left(E - E_j\right)^2}{\left(E - E_j\right)^2 + \Gamma_j^2}; for\ E > E_g \\ 0; for\ E < E_g \end{cases}$$

with

$$B_j = \frac{a_j}{\Gamma_j}\left(\Gamma_j^2 - \left(E - E_j\right)^2\right)$$

$$C_j = 2a_j\Gamma_j\left(E - E_j\right)$$

Where n_∞ is the refractive index in the high-energy limit, E is the energy of the light, Eg is the bandgap, and E_j, a_j, and Γ_j are, respectively, the spectral position, strength, and width of each of the oscillators employed to model the complex refractive index of the semiconductor.

$MAPbI_3$	ff_{pvk}	d (nm)	E_g (eV)	n_∞	E_1	a_1	Γ_1	E_2	a_2	Γ_2	E_3	a_3	Γ_3
bulk		200	1.55	1.800	1.58	0.127	0.082	2.29	0.028	0.357	3.20	0.003	1
9 nm	0.41	398	1.58	1.796	1.59	0.210	0.102	2.46	0.024	0.265	3.30	0.028	0.988
7 nm	0.26	401	1.59	1.748	1.60	0.305	0.250	2.52	0.214	0.658	3.30	0.011	0.96
6 nm	0.10	405	1.63	1.800	1.59	0.500	0.232	2.47	0.190	0.508	3.22	0.057	0.743

$MAPbBr_3$	ff_{pvk}	d (nm)	E_g (eV)	n_∞	E_1	a_1	Γ_1	E_2	a_2	Γ_2
Bulk		320	2.25	1.746	2.32	0.086	0.064	2.66	0.034	0.419
2.40 nm	0.05	433	2.28	1.807	2.34	0.313	0.077	2.65	0.567	0.692
2.30 nm	0.02	430	2.30	1.721	2.34	0.600	0.056	2.73	0.905	0.553
2.20 nm	0.01	460	2.32	1.722	2.33	0.891	0.074	2.77	0.808	0.490

Table S2. Fitting parameters attained for $MAPbX_3$ NCs assuming a Maxwell-Garnet EMA to account for the interaction between the NCs and the porous silica matrix.

Dielectric function of perovskite nanocrystals

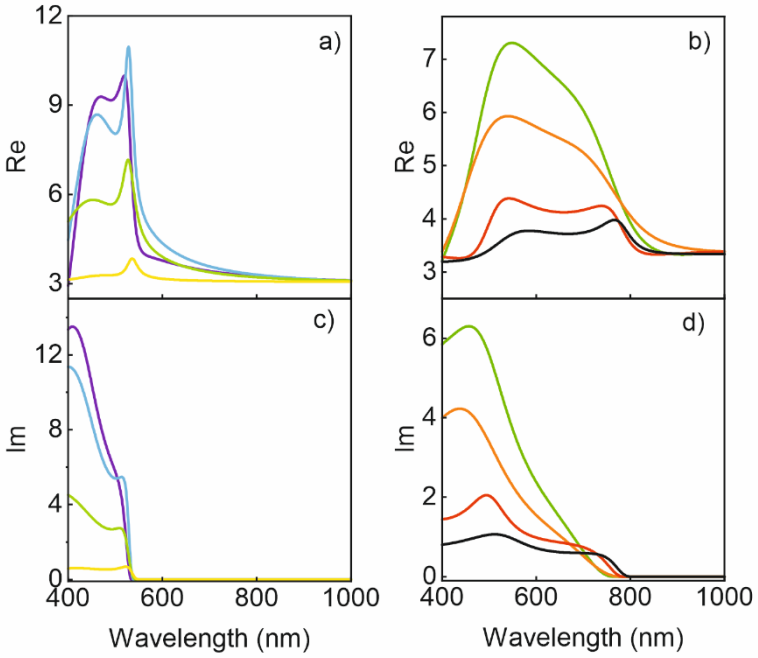

Figure S1. Real (a, b) and imaginary (c, d) parts of the dielectric function obtained for $MAPbBr_3$ NCs and polycrystalline film (a, c) and $MAPbI_3$ NCs and polycrystalline film (b, d). The same colour legend as in figure 4 is used.

Comparing effective medium approximation models

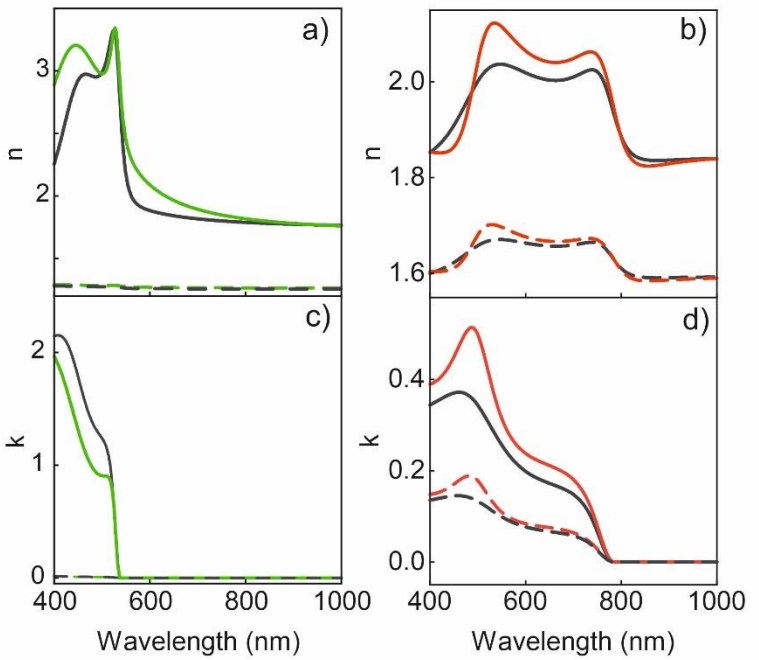

Figure S2. Comparative analysis of the real part of the complex refractive index (a, b) and extinction coefficient (c,d) calculated for $MAPbBr_3$-based samples (panels a and c) and $MAPbI_3$-based samples (panels b and d) with different effective medium approximation models. Color legend: Maxwell-Garnett (green and red lines in all panels); Maxwell-Garnett considering an effective index matrix (i.e, not assuming the pores as inclusions, but just the perovskite QDs; black lines in a and c for $MAPbBr_3$); Bruggeman (black lines in b and d for $MAPbI_3$). Solid lines correspond to $MAPbBr_3$ NCs (2.3 nm) and $MAPbI_3$ NCs (9 nm), dashed lines correspond to the effective complex refractive index of perovskite@silica layer containing that same perovkites NCs.

References

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