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The complex optical index of PbS nanocrystal thin films and their use for short wave infrared sensor design†

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As nanocrystals (NCs) gain maturity, they become central building blocks for optoelectronics in devices such as solar cells and, more recently, infrared focal plane arrays. Now that the proof of concept of these devices has been established, their optimization requires a deeper understanding of their electronic and optical features to engineer their optoelectronic properties accurately. Though PbS NCs have been extensively investigated, the complex optical index of PbS NC thin films remains mostly unknown. Some previous works have unveiled the optical index for this type of material optimized for solar cells (excitonic peak at 940 nm), but longer wavelengths remain scarce and surface chemistry effects, which are known to be of central importance for layer doping, are simply unexplored. Here, we conduct a systematic investigation of the complex optical index of PbS NC thin films using broadband spectrally resolved ellipsometry. The obtained results are then compared with simulations combining tight-binding (TB) modeling at the NC level and the Bruggeman model to expand the results to the film scale. While TB calculation gives the NC optical indices, we extract the key NC film parameters such as the NC volume fraction and ligand indices by fitting the Bruggeman formula to ellipsometry measurements. We also bring evidence that this joint modeling method can be conducted without the need for ellipsometry data while preserving the main feature of the experimental results. Finally, the unveiled optical indices are used to model the absorption of short-wave infrared diode stacks based on PbS NCs and are relevant for state-of-the-art devices. Our electromagnetic modeling shows that the absorption within the contact is now a major limitation of the current device operated at the telecom wavelength.

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†Electronic supplementary information (ESI) available: (i) materials synthesis and characterization, (ii) details of the procedure to perform ellipsometry measurements and a full ellipsometry data set for all wavelengths and surface chemistries, (iii) tight binding simulations and (iv) the electromagnetic simulation procedure and additional results. See DOI: 10.1039/d1nr07770h

Introduction

Nanocrystals (NCs) initially developed for their bright tunable photoluminescence in the visible region appear to be equally promising for infrared optoelectronics.¹ PbS is certainly the most mature colloidal material in this spectral range.² It combines a strongly tunable cut-off wavelength from 800 to 2000 nm with a low polydispersity level favorable for the formation of high-quality films.

Integration of PbS NCs into a photodiode was initially motivated by the design of solar cells.³ Compared to bulk materials, PbS NCs enable the optimal optical gap for single-junction solar cells (≈ 1.3 eV) and benefit from the reduced threshold for multiexciton generation.^{4–7}

At this absorption energy, the diode structure has been extensively optimized, and a systematic investigation⁸ of the relationship between surface chemistry and the nature of the

majority carrier has allowed a rational design of a pn junction.⁹ The current best diode stack relies on ITO/ETL/PbS(n-type capped with a halide)/PbS(p-type capped with a thiol)/gold. Here, ITO stands for tin-doped indium oxide used as a transparent conductive contact, while ETL means electron transport layer and is generally based on either ZnO¹⁰ or TiO₂.¹¹ This diode stack achieves high internal quantum efficiency that suggests optimal charge separation and band alignment. This hypothesis was further supported by later uses of this structure for LED design.^{12,13}

Beyond solar cells, the PbS spectral range also matches other light-sensing applications in the short-wave infrared (SWIR) region, such as facial recognition for smartphones or industrial vision. In particular, in the SWIR region, water presents a strong absorption band (at 1400 nm), enhancing the contrast with respect to the visible region in which water is transparent.¹³ Thus, it appears meaningful to expand the spectral range of PbS NC based sensors beyond 1000 nm and explore wavelengths up to 1550 nm. Several reports in the literature already provide those types of diode stacks operated from 1200 to 1550 nm with impressive external quantum efficiency reaching 80%.^{10,14}

Further improvement requires a deep understanding of the current device performance to reveal the current bottlenecks and where future efforts must be focused. Here, we investigate the optical part of the device. So far and in contrast to II–VI compounds,^{15–17} the complex optical index of PbS NC films in the SWIR region has been studied in a small number of experimental works^{18–21} but an in-depth study of this quantity which is the main input of all electromagnetic simulations, remains absent. In this paper, we used spectroscopic ellipsometry measurements to provide a systematic investigation of the effect of the particle size and surface chemistry on the complex optical index of NC thin films. We show an increase in the indices by shortening the ligand length and increasing the NC diameter. We coupled these results with simulations based on the effective medium approximation (EMA) incorpo-

ating tight-binding (TB) electronic structure calculations to provide a better insight. EMA models were mainly used for dilute systems^{22–29} but they have recently shown great promise for NC thin films.^{18,30–32} However, to our knowledge, the coupling of electronic structure calculation with EMA models has not been reported. This joint modeling method reveals useful parameters of the NC film such as the NC volume fraction and the index of the surrounding medium which integrates the ligand shell. Assuming that the latter can be used for different film compositions as the ligand is unchanged, we demonstrate that the NC film complex optical index could be fully computed using a hard-sphere model.

Furthermore, we inject the unveiled complex optical indices into electromagnetic simulations of relevant PbS NC based diode stacks and map out their absorption properties.²⁰ We show that the calculated complex optical index as an input correctly describes the NC absorption. Thus, it would permit the probing of diverse composition photodiode performances. Moreover, we present evidence that the absorption loss within the contact is a major limitation and propose new directions to tackle it.

Results and discussion

We start by growing a series of PbS NCs with exciton peaks from 1000 to 1550 nm, see Fig. 1c. For this purpose, we used the procedure of Moreels *et al.*,^{22,33} in which PbCl₂ is reacted with sulfur in oleylamine (OLA). The reaction temperature and its duration are used as the main knobs to tune the particle size. A warmer and longer reaction leads to larger particles. As suggested by Moreels *et al.*,³³ TOP is introduced during the synthesis of the smallest particles to slow the growth rate. Though the exact shape is a truncated cube, the particles present a quasi-sphere shape for all particle sizes as revealed by transmission electron microscopy (TEM), see Fig. 1a, b and S1.† We thus assume a random close packing in all cases. The

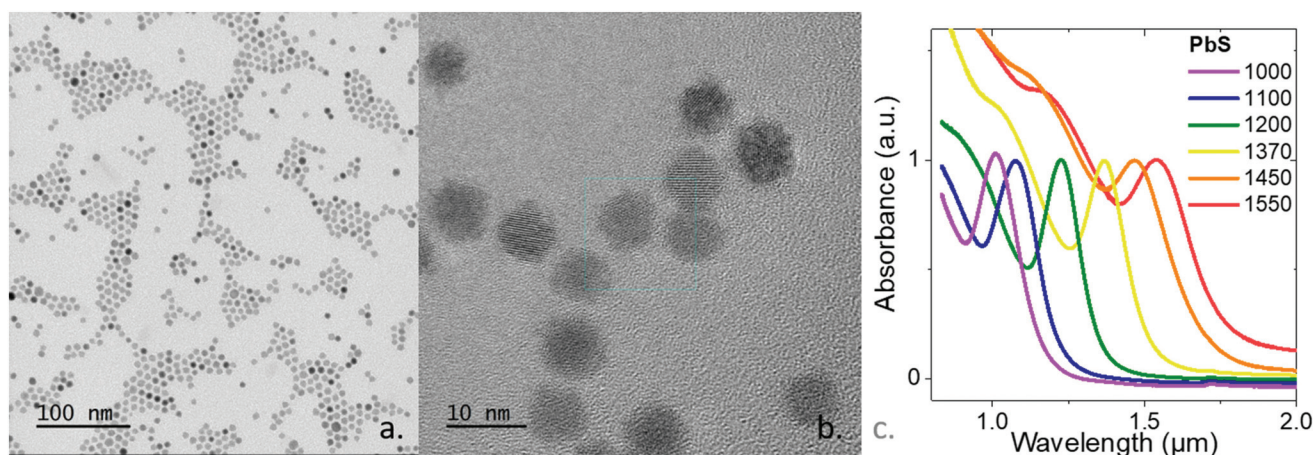


Fig. 1 PbS nanocrystals. TEM (a) and high resolution TEM images (b) of the PbS 1550 sample. (c) Absorption spectra of a series of PbS NCs with excitonic peaks from 1000 to 1550 nm.

NC diameter increases from 4.5 nm for a particle with an excitonic peak at 1000 nm, to 7.5 nm for a particle presenting an exciton at the telecom wavelength (1550 nm), see Tables 1 and S1.† Subsequently, in the rest of the article, each population of PbS will be referred to its peak wavelength (*i.e.*, PbS 1200 will refer to the population with an exciton feature at 1200 nm).

We deposit the PbS material to form a thin film onto a transparent glass substrate. In addition, for three particle sizes, we also perform ligand exchange to probe the effect of surface chemistry on the optical properties. We choose PbS 1200, PbS 1370, and PbS 1550. PbS 1200 and 1370 have been chosen because they are close to the water absorption edge and spectrally on each side of the absorption. PbS 1550 has been chosen to match the telecom wavelength and the associated broad range of source, which enables active imaging for example in an autonomous vehicle. Regarding the surface chemistry, we have focused on ethanedithiol (EDT) and an iodide ion (I^-), respectively, for their ability to form p- and n-type layers in the case of small-sized PbS NCs.

These films have been characterized by spectrally resolved ellipsometry in the 450 to 2000 nm range. Ellipsometry measured the change of the polarization of light upon its reflection on the NC film. The two angles (ψ ; Δ) associated with this change are measured. To retrieve these angles, the dielectric constant is then fitted by a sum of oscillators, see Fig. S2.† As a consequence, from this dielectric constant, one can estimate the values of ψ and Δ . Using a least-square fit procedure,

the parameters of the fit are optimized to minimize the difference between the measured and estimated (ψ ; Δ) values. To reduce possible errors, the measurements are conducted using three angles for incidence: 50°, 60°, and 70° (see Fig. S3†). In addition, we do not introduce oscillators at wavelengths beyond the exciton in order for k to converge to zero at a low energy. We provide in Fig. 2a–c the determined refractive index (n) and extinction coefficient (k) for the sample of PbS 1200 capped with the three ligands. Data for other wavelengths are presented in Fig. S4 (for size dependence) and S5† (for three surface chemistries), and all raw data spectra are provided in the ESI.†

Fig. 3a clearly shows an increase of the average refractive index of the NC film from 1.8 to 2.15 as the particle size is increased, which can be connected to the higher volume fraction (f_{NC}) of the NCs (Fig. 3c, see below). Another strategy to tune the volume fraction is to change the particle surface chemistry from oleic acid (OA) ligands to I^- . OA ligands are typically ≈ 1.5 nm long, while EDT is ≈ 0.5 nm and I^- is around ≈ 0.3 nm.³⁴ As a result, the refractive index increases from 1.95 for OA to 2.35 for EDT and finally to 2.7 for I^- (Fig. 2 and 3b). The same reason explains a drastic rise of the extinction coefficient, which almost triples as OA ligands are replaced by iodine (Fig. 3d). A similar trend is observed for all particle sizes (see Fig. S5†).

The importance of surface chemistry on the complex refractive index is shown in Fig. 4, in which we present the same

Table 1 Spectroscopic and structural parameters of the PbS NCs

	PbS 1000	PbS 1100	PbS 1200	PbS 1370	PbS 1450	PbS 1550
Particle diameter (nm)	4.5 ± 1.5	4.6 ± 1.1	5.2 ± 0.8	6.1 ± 1.4	6.6 ± 1.3	6.7 ± 1.1
Exciton peak ($\text{nm cm}^{-1} \text{ meV}^{-1}$)	1012 nm 9880 cm^{-1} 1225 meV	1078 nm 9270 cm^{-1} 1150 meV	1223 nm 8172 cm^{-1} 1013 meV	1370 nm 7300 cm^{-1} 905 meV	1465 nm 6825 cm^{-1} 846 meV	1533 nm 6520 cm^{-1} 808 meV
Average refractive index (OA capping)	1.84 ± 0.1	1.81 ± 0.1	1.95 ± 0.1	2.04 ± 0.1	2.17 ± 0.1	2.04 ± 0.1

The average refractive index is calculated over the wavelength range of 750–2000 nm.

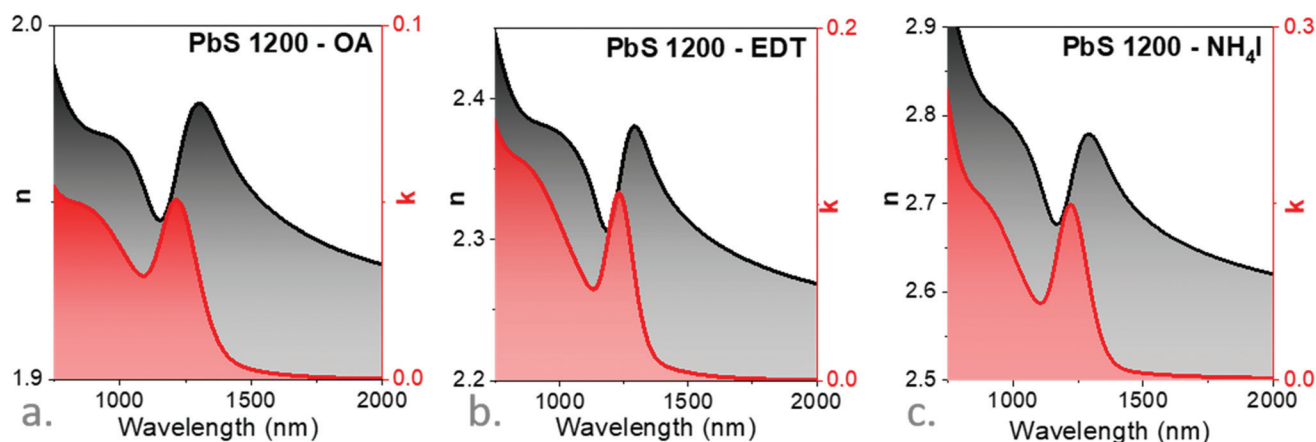


Fig. 2 Refractive indexes and extinction coefficient spectra of PbS 1200 capped with oleic acid (a), EDT (b) and NH_4I (c). Data for PbS 1370 and 1550 are provided in Fig. S5.†

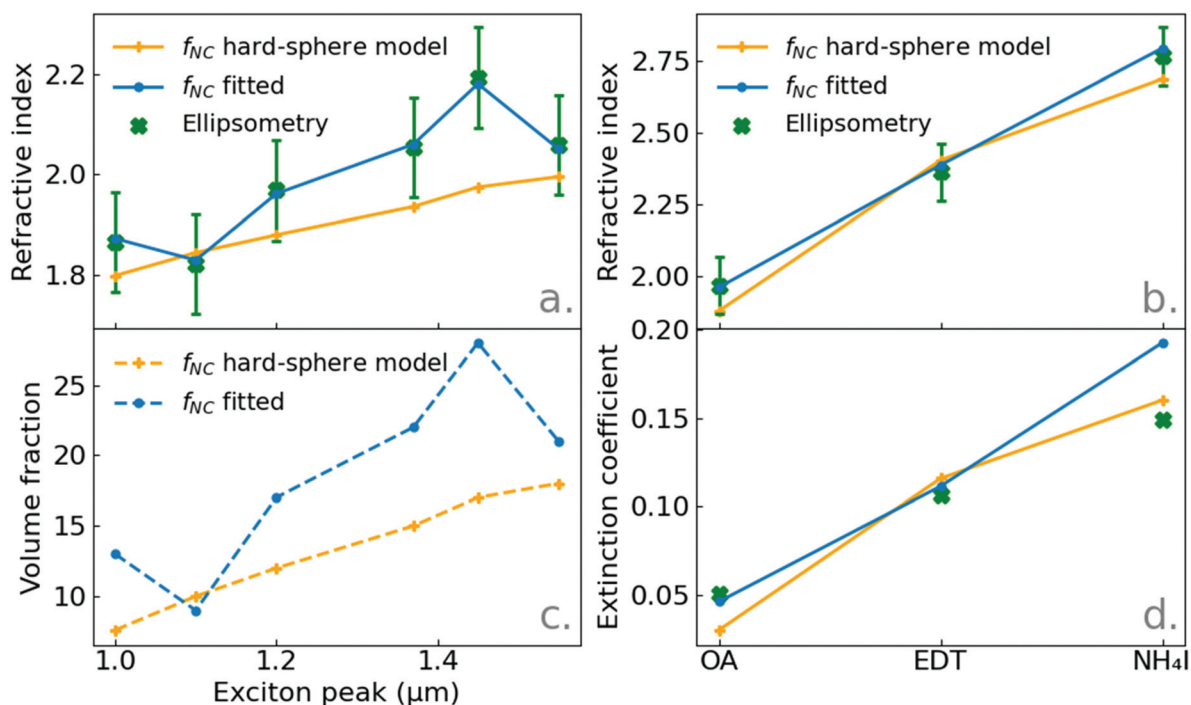


Fig. 3 Comparison between the data extracted from ellipsometry measurements (green crosses) and Bruggeman simulations, in which the NC volume fraction was either fitted (blue) or computed with a hard-sphere model (orange), as a function of exciton peak wavelength for OA capping (a and c) or as a function of capping for PbS 1200 nm (b and d). (a) and (b) Refractive index averaged over the 750 to 2000 nm range. (c) NC volume fraction. (d) Extinction coefficient.

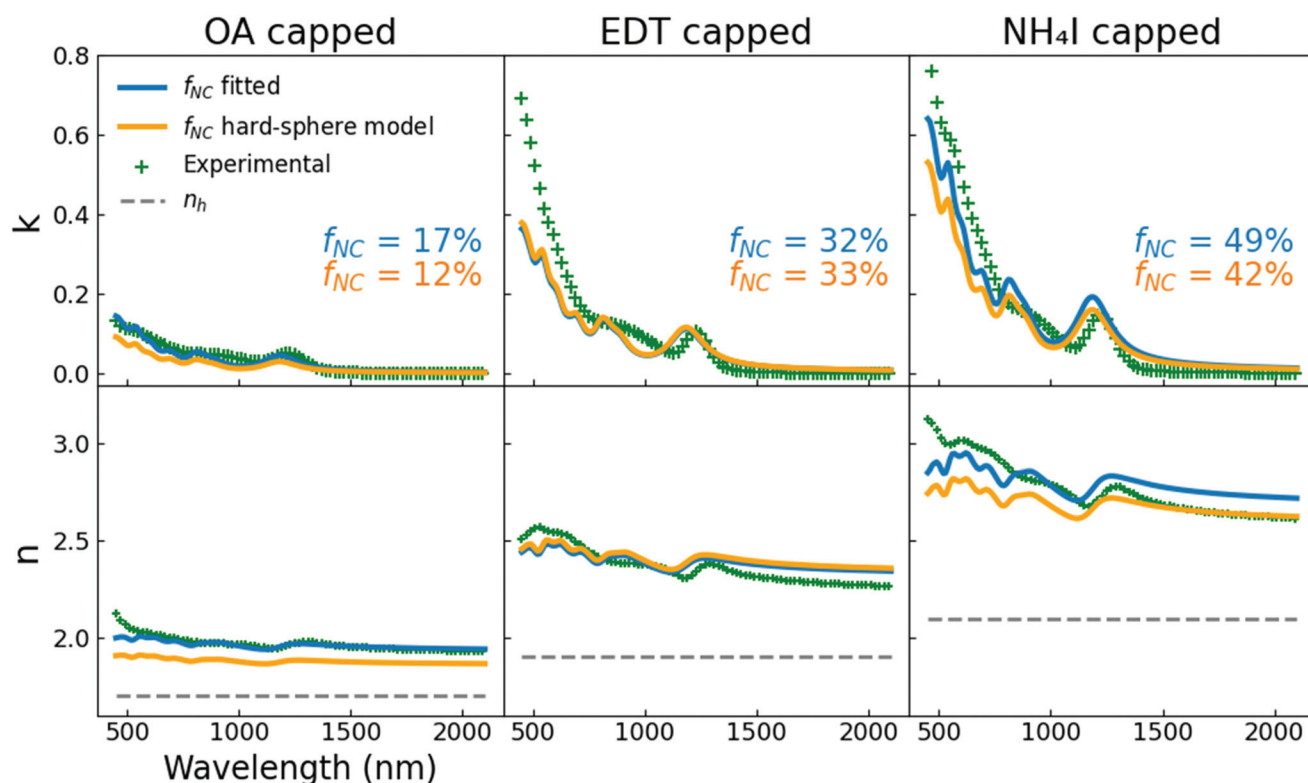


Fig. 4 Refractive indexes (n) and extinction coefficients (k) of PbS 1200 capped with OA, EDT, and NH₄I. The theoretical indices (full lines) obtained with the Bruggeman approximation, in which the NC volume fraction (f_{NC}) is either fitted (blue) or computed by a hard-sphere model (orange), are compared with the ellipsometry measurements (green crosses). The grey dashed line denotes the host refractive index: 1.7, 1.9 and 2.1 for OA, EDT, and NH₄I, respectively.

data as Fig. 2 for PbS 1200 (Fig. S5† for other particle sizes) but using common vertical axes allowing direct comparison. In order to have a deeper insight into these evolutions, we used an effective medium approximation (EMA) coupled with TB calculations to simulate the complex refractive index and compare it with ellipsometry measurements. Two EMAs, the Maxwell Garnett approximation and the Bruggeman approximation,^{35,36} are compared in the ESI,† while the latter is presented in the main text. Indeed, due to its symmetry, the Bruggeman formula is better suited when the NC volume fraction f_{NC} approaches the host one. The Bruggeman formula is given by:

$$f_{\text{NC}} \frac{\varepsilon_{\text{NC}} - \varepsilon}{\varepsilon_{\text{NC}} + 2\varepsilon} + (1 - f_{\text{NC}}) \frac{\varepsilon_{\text{h}} - \varepsilon}{\varepsilon_{\text{h}} + 2\varepsilon} = 0 \quad (1)$$

where ε_{NC} , ε_{h} , and ε are the complex dielectric functions for the NC, the host, and the medium, respectively ($n + ik = \sqrt{\varepsilon}$). ε_{NC} is the computed from TB calculations (Method section), while ε_{h} and f_{NC} are used as fitting parameters to reproduce ellipsometry measurements. Note that ε_{NC} , the dielectric constant of the pristine NC in Fig. 5, presents much larger values of the refractive index ($n > 3.4$) than the one observed from the film.

The method of extraction of ε_{NC} , ε_{h} and f_{NC} to solve the film permittivity ε is detailed in the Method section. We also considered an alternative approach by taking the NC volume fraction (f_{NC}) given by the hard-sphere model (eqn (3), Method section). Fig. 4 compares the complex refractive index of the PbS 1200 film measured by ellipsometry and computed with the Bruggeman approximation. The data for PbS 1370 and 1550 are given in the ESI.† The refractive index of ligands (n_{h}) obtained for OA, EDT, and NH_4I are 1.7, 1.9, and 2.1, respectively. As n_{h} mainly depends on the host, we assume that these values are transposable to any NC thin film, as the ligands keep unchanged, allowing to remove one free parameter. The

fitted (hard-sphere model) volume fractions f_{NC} are 17(12), 32(33), and 49(42) percentage for OA, EDT, and NH_4I , respectively. In accordance with the experimental results, the volume fraction of NCs increases with the shortening of the length of the ligand. This leads to an increase of the complex refractive index due to the inorganic matter quantity growing in the film (Fig. 3b, d and 4).

As found by Dement *et al.*,³¹ the volume fractions obtained with the hard-sphere model match those fitted from experiments using the Bruggeman model (Fig. 3c and 4). However, we observe a slight underestimation for the hard-sphere model, also visible when we vary the NC size. As suggested by Diroll *et al.*,¹⁶ a picture of hard cores with rigid organic shells overestimates the denominator term of eqn (3) (Method section), leading to an underestimation of f_{NC} . Despite this, both theoretical calculations (fitted and hard-sphere model) give spectral features, excitonic and higher-order peaks, in reasonable agreement with experiments. Moreover, the quantitative evolution of the extinction coefficient and the average refractive index with surface chemistry and size (Fig. 3 and 4) follows the ellipsometry data. Here, we bring evidence that the EMA models coupled with electronic structure calculations allow to unveil film parameters such as the NC volume fraction. Adding another theory layer with the analytical hard-sphere model and using known ligand optical indices, this parameter-free model (see eqn (1)) allows direct film optical index calculation.

Thereafter, we aim to use the complex optical indices to reveal the absorption properties of a diode stack used for SWIR sensing. We consider the most typical stack^{9,14} based on ITO/ TiO_2 /PbS(n-type capped with a halide)/PbS(p-type capped with a thiol)/gold. Geometrical parameters are provided in the ESI.† To vary the optical gap of the diode, we tune the cut-off wavelength of the PbS n-type layer, while keeping for all diodes the same type of NC, and in particular the p-type layer (PbS 1200 with EDT capping). Indeed, PbS capped with a thiol experiences a crossover from p-doped to n-doped with size.³⁷ As for ellipsometry data, Fig. 6 focuses on PbS 1200, and similar data are provided in the ESI† for diodes at 1370 nm (Fig. S13†) and 1550 nm (Fig. S14†).

In all that follows, the spectral dependence of both n and k has been included in our simulation. Nevertheless, we notice that the spectral dependence of the refractive index is weak, $\Delta n(\lambda)/\langle n(\lambda) \rangle \approx 5\text{--}10\%$ where $\langle n(\lambda) \rangle$ is the spectrally averaged value of n and $\Delta n(\lambda) = n(\lambda) - \langle n(\lambda) \rangle$. In Fig. 6b and S11,† we have simulated the absorption spectra for the three diodes, either accounting for entire spectral dependence or using the average spectral value of n instead. It appears that the spectra remain primarily unchanged. In particular, the features close to the optical gap are well reproduced. This observation may ease future measurements since spectrally resolved measurement of the refractive index may not be required unless high accuracy simulations are targeted. Additionally, we have simulated the absorption spectrum of the full diode stack while using the $(n; k)$ values obtained directly from the TB simulation, assuming for simplicity the hard-sphere model

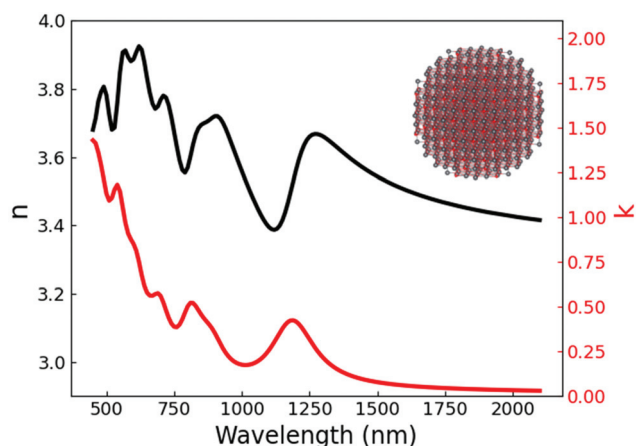


Fig. 5 Optical indices calculated in TB for a single PbS NC with the lowest exciton at 1200 nm. The refractive index (black line) and extinction coefficient (red line) are computed using the TB electronic structure of a 2 nm-diameter NC (upper right insert).

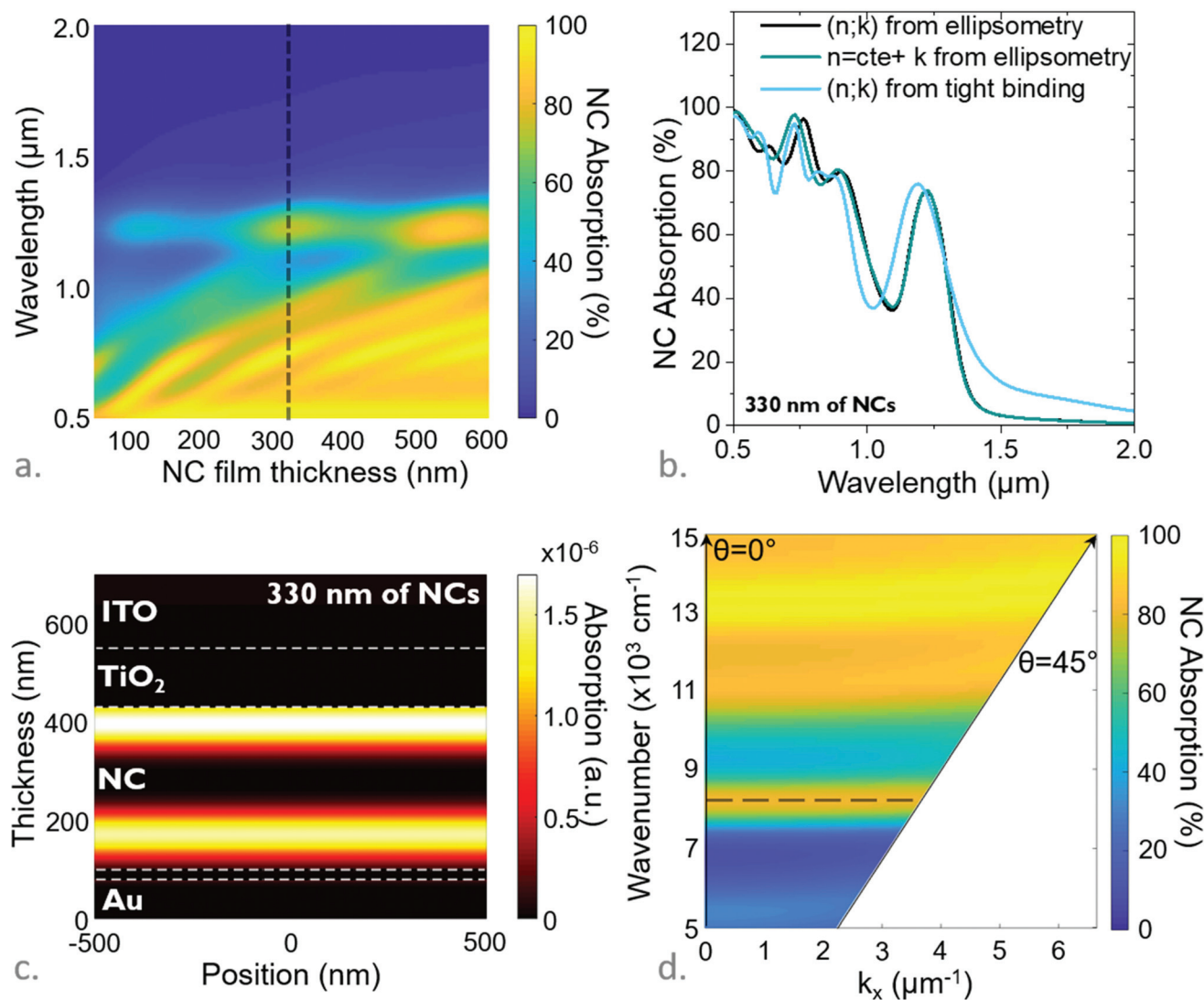


Fig. 6 Simulation of diode absorption based on the refractive index and extinction coefficient revealed by ellipsometry and modelling. (a) Absorption within the NCs for a diode made of PbS 1200 as a function of the wavelength and thickness of the n-type NH₄I capped with a PbS layer. (b) Absorption spectra within the NCs for a diode made of PbS 1200 for a 330 nm thickness of the n-type NH₄I capped with a PbS layer. (c) Absorption spatial map for a diode made of PbS 1200. (d) Dispersion relation (the wavenumber as a function of k_x wavevector) for a diode made of PbS 1200.

(Fig. 6b). In this case, even though the agreement is not as good, it remains very reasonable, meaning that TB calculations can be used for the scaling rule of design.

In Fig. 6a, we have plotted the absorption (taken equal to $1 - R$, with R the reflection, since the transmission is null due to the gold mirror) spectra within the NC film (*i.e.*, excluding the loss in the contact) as a function of the thickness of the I⁻ capped PbS layer. We observe a modulated horizontal line at ≈ 1200 nm corresponding to the exciton, while a series of tilted lines result from resonances. As these resonances reach the exciton energy, a strong modulation of the absorption amplitude is observed for the energy corresponding to the exciton. The nature of the resonances is better revealed by the dispersion map, see Fig. 6d. There is almost no dispersion (*i.e.*,

no k_x dependence) which is typical of a Fabry-Pérot resonance. Such resonances may have been anticipated given the simplicity of the structure (no grating or any subwavelength resonator).

The presence of this resonance makes the absorption at the exciton non-monotonic with thickness. As a result, a 330 nm thick layer is more absorbing than a 400 nm layer, while it also enables a better charge collection since the thickness better matches the short carrier diffusion length induced by hopping. With 75% of absorption, a 330 nm thick layer typically absorbs twice as much as the same layer not included in the diode structure ($1 - \exp(-\frac{4\pi k_i t}{\lambda})$ with t the device thickness and λ the wavelength). The absorption map (Fig. 6c) better explains why we observe a non-monotonic increase of the

absorption with thickness. In this stack, the absorption appears as a standing wave with the core and node, and the period D of this wave is given by $\lambda = 2nD$. For a resonance at ≈ 1200 nm and $n = 2.7$ as measured for Γ^- capped PbS, this leads to $D = 230$ nm. Thus, if the thickness is increased but only includes an area corresponding to a node of the absorption, the increase of absorption is very weak. We observe a significant increase of absorption only when the thickness is increased by $\approx D$. However, building thicker devices may become challenging and may not lead to an efficient charge collection. Finally, it is worth pointing that, at 1200 nm, the absorption is spatially located within the NCs, and losses in ITO and metal remain weak.

An interesting question to ask at this point: would there be any optical benefit of tuning the relative thickness of the n- and p-type layers? Fig. S12† shows a map of the absorption in the NCs as a function of n- and p-type layer thicknesses. The resonance lines of the exciton exactly follow the iso-thickness curve, meaning that increasing the p-type layer brings no benefit and that only the total thickness plays an actual role. Thus, the relative choice of thickness between the two layers will be rather dictated by electrostatic (formation of the pn junction) and technological (building a thick p layer from the solid-state ligand exchange is likely more difficult) considerations.

As the cut off wavelength of the diode is increased (*i.e.*, the one from the n-type layer with Γ^- capping, see Fig. S13 and S14†), some results remain unchanged: (i) we keep observing a series of non-dispersive resonances which can be attributed to a Fabry-Pérot cavity within the diode stack and (ii) the absorption map is still the result of a standing wave. However, there are also some apparent differences. Thin devices are only poorly absorbing, and only devices thicker than 500 nm can achieve absorption above 50%. This makes the recent development of μm thick films of utmost interest.³⁸ Second, losses in the contacts become non-negligible, both in gold and ITO. For the sake of illustration, we have estimated the loss in the ITO layer for the diode based on PbS 1550, see Fig. S15.† In this case, 15% of the total absorption occurs in ITO. This makes the recent report of 80% of external quantum efficiency on a similar diode operating at 1.55 μm even more impressive.¹⁴ Because absorption is already large, there will be only a limited benefit to introduce light resonators³⁹ to increase the light absorption (+25% at best). Resonators might still be interesting from a transport point of view since charge collection is also more efficient in thin devices.¹⁵ Reducing the loss in contacts is probably the next important challenge. Gold remains a moderate problem at this wavelength, and its use as both the hole extractor and mirror makes it difficult to reduce the thickness. Thus, a first obvious optimization strategy will be to reduce the ITO thickness, but this will come at the price of higher contact resistance. The optimizing conditions of ITO growth has also been proposed as a possible strategy.⁴⁰ We probably reach a point where an alternative material for contact will have to be explored. Graphene^{41,42} or silver nanowire arrays⁴³ are certainly possible strategies combining high

infrared transparency, high conductivity, and large-scale availability.

Conclusion

We have conducted a systematic investigation of the complex optical index of PbS NC films as a function of their size and surface chemistry, which is of utmost interest for the later optical design of devices based on these materials. The results are compared with simulations where the tight-binding method is used to determine the effective parameters at the particle level and where the Bruggeman model is also used to expand the results up to the macroscopic scale. This joint approach is useful to extract the essential parameters of NC films, such as the NC volume fraction or the refractive index of the host. Moreover, we demonstrate that using a hard-sphere model (*i.e.*, without free parameters) and a fixed n_h (transferable to any size of NCs), optical indices with a reasonable match with experimental data can be obtained. These indices can then be used as inputs for electromagnetic simulations to predict photonic device performance and propose new directions for experimental works.

Method section

Chemicals

Triethylphosphine (TOP, Alfa Aesar, 90%), oleylamine (Alfa Aesar, 80–90%), lead chloride (PbCl_2 , Alfa Aesar, 99%), sulfur powder (S, Alfa Aesar, 99.5%), oleic acid (OA, Alfa Aesar, 90%), 1,2 ethanedithiol (EDT, Fluka, 98.0%), ethanol absolute anhydrous (VWR), methanol (VWR, 99.8%), acetone (VWR), *n*-hexane (VWR), *n*-octane (SDS, 99%), toluene (VWR, 99.3%), *N,N*-dimethylformamide (DMF, VWR), ammonium iodide (NH_4I , Alfa Aesar, $\geq 99\%$), acetonitrile (VWR, ACS), and butylamine (Alfa Aesar, 99%). All chemicals are used as received, except oleylamine which is centrifuged before use.

PbS NC synthesis

In a three-neck flask, 300 mg of PbCl_2 and 7.5 mL of OLA are degassed, first at room temperature and then at 110 °C for 30 min. For the smallest particles (*ie*, with an exciton peak below or equal to 1200 nm), 100 μL of TOP is also introduced. Meanwhile 30 mg of S powder are mixed with 7.5 mL of OLA until full dissolution and a clear orange solution is obtained. Then under N_2 at a temperature between 80 and 150 °C, this solution of S is quickly added to the flask. After 0.5 to 15 minutes, the reaction is quickly quenched by the addition of 1 mL of oleic acid and 9 mL of hexane. The NCs are precipitated with ethanol and redispersed in toluene. This washing step is repeated one more time. The solution is then centrifuged to remove the unstable phase. The supernatant is precipitated with methanol and redispersed in toluene. The exact procedures for each size of particle are given in the ESI.†

Film deposition for ellipsometry measurements

After the synthesis, the NC solutions are filtered with a PTFE filter. A glass slide is cut (12×15 mm) and washed using an acetone bath in ultrasound for 5 min. The substrates are then rinsed with acetone and isopropanol and dried using an N_2 gun. The pristine samples are deposited on a glass substrate by spin coating (1500 rpm, 500 rpm s^{-1} , 45 s). For the EDT ligand exchange the NC solution is diluted at 30 mg mL^{-1} in toluene. A layer is then deposited onto the substrate by spin coating (2000 rpm, 1000 rpm s^{-1} , 45 s). The sample is then dipped into an EDT exchange solution (0.1%vol EDT in ACN) for 1 min and rinsed in pure ACN for 30 s. This process is repeated one more time. For NH_4I ligand exchange, an ink is made. 1 mL of a saturated solution of NH_4I in DMF is added to 1 mL of the NC solution (in toluene). Hexane is added to help the phase dissociation. The apolar phase is discarded. Cleaning with hexane 3 times is conducted. The NCs are precipitated using acetone. After centrifugation, the liquid phase is discarded and the NCs are dispersed in a mixture of 140 μL of DMF, 60 μL of ACN and 5 μL of butylamine. The ink is then spin coated onto the substrate (2000 rpm, 200 rpm s^{-1} , 120 s). This ink is used for PbS with an excitonic peaks at 1200 nm and 1300 nm.

For the NCs with a peak at $1.5 \mu\text{m}$, a solid-state ligand exchange is conducted. The NC solution is diluted at 30 mg mL^{-1} in toluene. A layer is then deposited onto the substrate by spin coating (2000 rpm, 1000 rpm s^{-1} , 45 s). The sample is then dipped into an NH_4I exchange solution (60 mg of NH_4I in EtOH) for 1 min and rinsed in pure EtOH for 30 s. This process is repeated one more time.

Infrared spectroscopy

The solution of NCs is dropcast on the diamond cell of a Fourier Transform Infrared spectrometer (FTIR, Thermo Fischer iS50) in the ATR mode. The source is a halogen lamp, the beam splitters are made of CaF_2 and the detector is a DTGS sensor. In all cases, the background uses the same optical configuration but without the sample onto the substrate. Spectra are typically acquired with a 4 cm^{-1} resolution and typically averaged 32 times.

Transmission electron microscopy

A drop of diluted NC solution was dropcast onto a copper grid covered with an amorphous carbon film. The grid was degassed overnight under secondary vacuum. Imaging was conducted using a JEOL 2010 transmission electron microscope operated at 200 kV.

Optical ellipsometry

Spectroscopic ellipsometry measures the changes in the polarization state between the incident and reflected light and is characterized by the angles ψ and Δ .

$$\rho = \frac{r_p}{r_s} = \left| \frac{r_p}{r_s} \right| e^{i(\delta_p - \delta_s)} = \tan \psi e^{i\Delta}$$

where r_p and r_s are the reflection coefficients of p and s polarized light, respectively, and δ_p and δ_s are the phase shifts in reflection in p and s polarizations, respectively. The measurements are performed on a V-VASE ellipsometer (J.A. Woollam) in the 450–2100 nm range with steps of 10 nm and with angles of incidence of 50° , 60° and 70° .

Tight-binding simulation

The Hamiltonian matrix, including the spin-orbit coupling, is constructed in an $sp^3d^5s^*$ basis. The TB parameters are listed in Table S1.† The resulting TB bulk band structure is in good agreement with *ab initio* calculations (Fig. S6†). Under appropriate boundary conditions, the TB parameters are the same, from bulk to NCs. We used excitonic peak position to calibrate NC diameters and compare them to TEM measurements, Fig. S7.†

Nanocrystal complex dielectric function

The NC complex dielectric function is given by:⁴⁴

$$\epsilon_{\text{NC}} = 1 - \sum_{i,j} \frac{e^2 |u_{c,i}|^2 |r \cdot e| |u_{v,j}|^2}{\epsilon_0 \Omega} \left(\frac{1}{\hbar\omega - E_{c,i} - E_{v,j} + i\sigma} - \frac{1}{\hbar\omega + E_{c,i} - E_{v,j} + i\sigma} \right) [f_{v,j} - f_{c,i}] \quad (2)$$

where $u_{c,i}$ and $u_{v,j}$ are the conduction and valence wave functions of energies $E_{c,i}$ and $E_{v,j}$ with the equilibrium population given by $f_{c,i}$ and $f_{v,j}$ provided a Fermi–Dirac distribution. σ is a parameter accounting for the experimental broadening due to electron–phonon interactions and size polydispersity. It is obtained by fitting a Lorentzian function to the excitonic peak of experimental data (PbS 1200 OA) and transferred without any change to the other NC films (see Fig. S8†). Ω is the volume of the NCs, e is the polarization vector of light and r is the electron position.

The Bruggeman model and parameter extraction

To solve ϵ from eqn (1), the three following parameters need to be extracted: f_{NC} , ϵ_h , and ϵ_{NC} . The latter is determined *via* TB calculation using the eqn (2). We consider that the imaginary part of ϵ_h equals zero because the host is assumed to be non-absorbing at the wavelength of interest. The real part ($\epsilon_h = nh^2$) is supposed to be constant over the spectral range as its frequency dependence is weak. Moreover, n_h is a NC independent parameter; in other words, it only depends on the host, including ligands, air, and any residual organics in a solid-state form. Thus, for each passivation type, we estimated it as the overall best value to fit the Bruggeman optical indexes to PbS 1200, 1370, and 1550 ellipsometry measurements. Once we determined ϵ_{NC} and n_h , we fitted f_{NC} by a least-squares minimization procedure on experimental data.

The f_{NC} value has also been calculated by the hard-sphere model:

$$f_{\text{NC}} = \text{PF} \frac{r_{\text{NC}}^3}{r_{\text{NC+ligand}}^3} \quad (3)$$

where a random close-packed distribution assumes 64% packing fraction (PF). It has shown reasonable packing estimates for the glassy films of CdSe NCs.⁴⁵ The length of the ligands in the films is taken close to the literature, including the interparticle spacing measured by Weidman *et al.*:³⁴ 1.5, 0.5, and 0.3 nm for OA, EDT, and NH₄I, and the NCs radii r_{NC} are those calibrated by TB.

Electromagnetic simulation

Calculations are achieved with the Matlab library based on RCWA.⁴⁶ The Maxwell equations are solved in each layer and interface conditions are applied to find the final solution of the whole structure. We consider incoming plane waves under normal incidence, either with transverse magnetic (TM) or transverse electric (TE) polarizations, *i.e.* with a magnetic field or electric field parallel to the slits of the gratings, respectively.

Author contributions

B. Chehaibou, G. Mugny, A. Arnaud, and C. Delerue performed the modelling part. M. Cavallo, A. Khalili, T. H. Dang, and C. Gréboval grew the particles under the supervision of E. Lhuillier and S. Ithurria. E. Izquierdo conducted the ellipsometry measurements and analyzed the results under the supervision of B. Gallas. X. Z. Xu performed TEM imaging. A. Chu and C. Abadie conducted the electromagnetic simulations under the supervision of G. Vincent.

Conflicts of interest

The authors declare no competing financial interest.

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