Assembling nanocrystal superstructures

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Claims that cannot be tested, assertions immune to disproof are veridi-
cally worthless, whatever value the may have in inspiring us or in excit-
ing our sense of wonder.

— Carl Sagan

In this chapter, we review the main experimental techniques and sample preparation methods used in this thesis. We use a broad range of experimental techniques to study the structure, optical and electric properties of nanocrystals and their aggregates. These include electron microscopy, X-ray and light scattering to determine the structure; light absorption, emission and quantum yield measurements to gain insight into the energetic structure and light-matter interaction of nanocrystals; time-resolved microwave conductivity and field-effect transistors to measure the micro- and macro-
spic electrical conductivities of nanocrystal assemblies. Finally, we review the synthetic protocols mostly used in this thesis, including those concerning the preparation of nearly monodisperse CdSe quantum dots and nanoplatelets of various aspect ratios.
2.1 Main experimental techniques

2.1.1 Light absorption

The interaction of light with matter provides a powerful probe to gain insight into the structure and morphology of nanoparticles and their aggregates, as well as their optoelectronic performance. In general, light can interact with matter through absorption or scattering. Measuring the absorption spectrum of a dispersion of nanoparticles offers a unique tool to probe the energetic structure and uniformity of the ensemble, also allowing to measure nanoparticle concentration.

Consider an incident beam of intensity $I_0$ propagating along the $z$-direction and impinging on a uniform medium. The medium can absorb light, and as a result the intensity of the incident beam decreases with $z$. If we consider a small slice of thickness $dz$, then it is reasonable to assume that the drop in incident intensity between $z$ and $z + dz$ is proportional to the thickness of the slice:

$$dI = I(z + dz) - I(z) = -\alpha I(z) dz$$

By integrating this expression we obtain the well-known Lambert-Beer law:

$$I(z) = I_0 e^{-\alpha z}$$  \hspace{1cm} (2.1)

where $\alpha$ is known as the absorption coefficient and has the units of inverse length, typically $cm^{-1}$. It is often useful to work with a quantity proportional to the absorption coefficient, the absorbance:

$$A(z) = \log \frac{I_0}{I} = 0.434 \alpha z$$

expressed in optical density units.

In direct-bandgap semiconductors such as CdSe, the absorption coefficient, and therefore the absorbance, is proportional to the joint density of states $g(\hbar \omega)$, where $\hbar \omega$ is the energy of the incident photons. Therefore:

$$\alpha(\hbar \omega) = \begin{cases} 0 & \text{if } \hbar \omega < E_g \\ \propto g(\hbar \omega) & \text{if } \hbar \omega \geq E_g \end{cases}$$

While in bulk semiconductors $g(\hbar \omega) \propto \sqrt{\hbar \omega - E_g}$, in quantum dots the density of states is a collection of discrete states described as $\sum_{n,l,\sigma} \delta(\hbar \omega - E_{nl}(\sigma))$; however, because of the polydispersity of the sample, the $\delta$-peaks appear broadened (equation 1.11). For this reason, the width of the peaks in the absorption spectrum is usually related to the sample polydispersity, with sharper peaks indicating a more uniform sample.
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Since the absorbance of isolated colloidal nanocrystals is usually measured from a dilute dispersion, it is important that the dispersing solvent shows a negligible absorption in the energy range of interest. For instance, hexane is an excellent choice in the wavelength regime \(300 < \lambda = 2\pi c/\omega < 1000\text{nm}\), where \(c\) is the speed of light in vacuum. However when measuring in the near infrared, \(1\mu m < \lambda < 10\mu m\), tetrachloroethylene is a much better choice.

Nanocrystals are usually measured as a dispersion with molar concentration \(c\); it is therefore useful to work with the molar extinction coefficient \(\epsilon\), defined as \(\epsilon = \alpha/c\), expressed in units of \(M^{-1}cm^{-1}\) where \(M = \text{moles/L}\) indicates the number of moles per liter. A greatly appreciated contribution in the literature relates the absorbance \(A_1 = 0.434\alpha_1 z\) at the spectral position \(\lambda_1\) of the first peak in the absorption spectrum for CdS, CdSe, and CdTe quantum dots to the dot diameter \(\sigma\) and molar concentration \(c\). [48] In this case, \(z\) is the optical path of the cuvette used for the measurement. We report here the empiric relation obtained in the mentioned reference for CdSe that has been used throughout this thesis to approximately determine \(c\) and \(\sigma\):

\[
\begin{align*}
\sigma (\text{nm}) &= 1.6122 \times 10^{-9} \lambda_1^4 - 2.6575 \times 10^{-6} \lambda_1^2 + 1.6242 \times 10^{-3} \lambda_1^2 - 0.4277 \lambda_1 + 41.57 \\
\epsilon (M^{-1}cm^{-1}) &= 5.857 \times 10^3 \sigma^{2.65}
\end{align*}
\]

(2.2)

from which we can then extract the concentration: \(c = \alpha_1/\epsilon = A_1/(0.434z\epsilon)\).

2.1.2 Light scattering

Light can also interact with matter through scattering. Imagine an electric field \(\mathbf{E}\) of wavelength \(\lambda\) incident on a particle of diameter \(\sigma \ll \lambda\) and refractive index \(n\) suspended in a medium of refractive index \(n_0\). The incident electric field will induce a dipole \(\mathbf{\delta} = \varrho \mathbf{E}\) oscillating at the same frequency as the electric field, where \(\varrho\) is the polarizability. Since oscillating dipoles produce radiation, the dipole will emit light. The intensity of the scattered light at a distance \(d\) from the scattering particle scales as

\[
\frac{I}{I_0} = \frac{16\pi^4}{d^2\lambda^4} \left(\frac{\varrho V}{4\pi\epsilon_0}\right)^2
\]

where

\[
\varrho V = 3\epsilon_0 \left(\frac{(n/n_0)^2 - 1}{(n/n_0)^2 + 2}\right) V
\]

is the polarizability of the particle and \(V = 4\pi(\sigma/2)^3/3\) is the particle volume. Substituting \(\varrho V\) we obtain:

\[
\frac{I}{I_0} = \frac{\pi^4}{4} \frac{\sigma^6}{d^2\lambda^4} \left(\frac{n^2 - n_0^2}{n^2 + 2n_0^2}\right)^2
\]

(2.3)

Key consequences descend from this expression:
• the scattered intensity grows with $\sigma^6$, therefore a particle twice as large will scatter $2^6 = 64$ times more. Consequently, it is extremely important to minimize the amount of dust when working with scattering techniques, as a few dust particles may easily shadow the signal of millions of nanoparticles;

• the scattered intensity decreases with $\lambda^4$, meaning that radiation at smaller wavelengths will be scattered more efficiently;

• the scattered intensity grows with the square of the difference of the squares of the refractive index of the scattering object and that of the surrounding medium. Therefore for instance, teflon particles, $n = 1.315$, will scatter very weakly in water, $n_0 = 1.330$.

With this preamble we will now proceed to describe the two main scattering techniques used in this thesis: Dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS).

**Dynamic light scattering**

Light scattering is an invaluable tool in Soft Matter and Nanoscience, being able to determine the structure and dynamic correlation of objects of sizes ranging from the nanometer to the micrometer scale. Specifically, static light scattering can extract information concerning the shape, size, and assembly structure of scattering objects; instead, dynamic light scattering exploits the Brownian motion of objects to study their dynamic behavior in solution. For a dispersion of particles in solution, dynamic light scattering is able to extract the distribution of particle sizes from their diffusion in the solvent.

Let a coherent excitation source of wavelength $\lambda$, such as a laser, impinge on a dispersion of particles of diameter $\sigma$ in a solvent of refractive index $n_0$. The particles can scatter light, as shown by equation [2.3] for the case of small particles, $\sigma \ll \lambda$. The sum of the scattering wavefronts projected onto a screen at a distance $d$ from the sample will result in a speckle pattern due to constructive (high intensity regions) and destructive (low intensity regions) interference. Since the particles are subject to Brownian motion, the interparticle distance, and therefore the phase difference between the scattering wavefronts, will change as a function of time. When detecting at a scattering angle $\theta$, we observe that the scattered light intensity fluctuates around a mean value. The nature of these fluctuations is directly linked to the Brownian motion of the particles, and it is possible to harness this information by calculating the autocorrelation function of the scattered light intensity, which correlates the intensity $I$ of the scattered light at times $t + \tau$ and $t$. Intuitively, we can suppose that if $\tau$ is very small, $\tau \to 0$, the values of $I(t + \tau)$ and $I(t)$ will be very similar to one another and we say that $I(t + \tau)$ is correlated with $I(t)$; instead, for $\tau \to +\infty$ the value of $I$ has significantly changed in time as a consequence of Brownian motion, and we say that...
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the two intensity values are no longer correlated. The correlation function of the scattered light is a direct measure of the probability of a particle moving a given distance in a time \( \tau \). We can formalize these concepts by defining the intensity autocorrelation function as:

\[
\langle I(0)I(\tau) \rangle = \lim_{T \to +\infty} \frac{1}{T} \int_0^T I(t)I(t+\tau)dt \tag{2.4}
\]

where \( \tau \) is the delay time. The products \( I(t)I(t+\tau) \) can be positive or negative; since \( I(t)I(t) = I(t)^2 \geq 0 \) we must conclude that \( \langle I(0)^2 \rangle \geq \langle I(0)I(\tau) \rangle \). For delay times \( \tau \) large respect to the characteristic time of the fluctuations we expect that \( I(t) \) and \( I(t+\tau) \) become completely uncorrelated so that \( \lim_{\tau \to +\infty} \langle I(0)I(\tau) \rangle = \langle I(0) \rangle \langle I(\tau) \rangle = \langle I \rangle^2 \). Therefore the quantity \( \langle I(0)I(\tau) \rangle \) decays from \( \langle I \rangle^2 \) to \( \langle I \rangle^2 \) as a function of the delay time \( \tau \). In the case of Brownian motion this decay is exponential with a characteristic time \( \tau_c \) so that:

\[
\langle I(0)I(\tau) \rangle = \langle I \rangle^2 + (\langle I^2 \rangle - \langle I \rangle^2) e^{-\tau/\tau_c} \tag{2.5}
\]

which we can rearrange to give:

\[
g_2(\tau) \equiv \frac{\langle I(0)I(\tau) \rangle}{\langle I \rangle^2} = 1 + \frac{(\langle I^2 \rangle - \langle I \rangle^2) e^{-\tau/\tau_c}}{\langle I \rangle^2} \equiv 1 + \zeta e^{-\tau/\tau_c} \tag{2.6}
\]

which is the normalized correlation function of the scattered light intensity. The decay time \( \tau_c \) is inversely proportional to the diffusion coefficient of the particles:

\[
\tau_c = \frac{1}{Dq^2} \tag{2.7}
\]

which allows the diffusion coefficient to be determined by taking the slope of the plot of \( 1/\tau_c \) against \( q^2 \), where \( q \) is the scattering wavevector

\[
q = \frac{4\pi n_0}{\lambda} \sin \left( \frac{\theta}{2} \right) \tag{2.8}
\]

Using the *Einstein-Smoluchowski relation* we can write:

\[
D = \frac{k_B T}{3\pi \eta \sigma_H} \tag{2.9}
\]

where \( \eta \) is the viscosity of the solvent and \( \sigma_H \) is the hydrodynamic diameter of the diffusing particles. In general \( \sigma_H > \sigma \) as, for the diffusion through the solvent, also the ligands and other surface-bound moieties count. By combining (2.7) and (2.9) we can write:

\[
\sigma_H = \frac{k_B T}{3\pi \eta q^2 \tau_c} \tag{2.10}
\]
which allows us to determine in practice the hydrodynamic diameter from the decay time $\tau_c$, solvent viscosity $\eta$, temperature $T$ and scattering angle. The larger the particle, the slower the diffusion and therefore the larger the decay time. In the case of the coexistence of $N$ populations of different sizes we will have multiple exponential decays overlapping, so that:

$$\frac{g_2(\tau) - 1}{\zeta} = \sum_{i=1}^{N} A_i \exp\left(-\tau / \tau_c^i\right)$$

(2.11)

The excitation source used for dynamic light scattering is typically a He–Ne laser with wavelength $\lambda = 632.8\,nm$. Considering that the scattering angles that can be achieved lie in the range of $10^\circ \leq \theta \leq 150^\circ$, this leaves us with a range of $q$ of $0.002\,nm^{-1} \leq q \leq 0.02\,nm^{-1}$ for water, and therefore for nanoparticles $q \sigma \ll 1$. However, interesting effects arise when $q \sigma \sim 1$, as we will see in the next section. From [2.8] we can conclude that to increase $q$ enough to reach this regime, $\lambda$ must decrease by a factor of at least 100, which brings us to X-rays scattering.

**Small-angle X-ray scattering**

Suppose to have an X-ray beam of wavelength $\lambda = 0.154\,nm \ll \sigma$ impinging on a dilute dispersion of nanoparticles. The medium is isotropic, the interparticle distance $d \gg \sigma$, and therefore we can describe the scattered light intensity according to: [50,51]

$$\frac{I(q)}{I_0} = V \int \langle \Delta \rho(r_1)\Delta \rho(r_2) \rangle \frac{\sin qr}{qr} 4\pi r^2 dr$$

(2.12)

where $V$ is the irradiated volume, $\Delta \rho(r) = \rho(r) - \langle \rho \rangle$ is the electronic contrast, that is, the difference between the density of electrons at $r$ and its average value measured at $r \to +\infty$. In the case of particles dispersed in a solvent, $\langle \rho \rangle$ corresponds to the electronic density of the solvent. The solution of this integral for the case of a sphere of diameter $\sigma$ has been given by Lord Rayleigh:

$$\frac{I_1(q)}{I_0} = (\Delta \rho)^2 V_1^2 \left[ \frac{3 \sin (q\sigma/2) - (q\sigma/2) \cos (q\sigma/2)}{(q\sigma/2)^3} \right]^2$$

(2.13)

where $V_1$ is the volume of the sphere. In the case of $N$ particles in the dilute limite, where particles have no correlation with each other, we simply sum the intensity of the scattered light over all the particles:

$$\frac{I_N(q)}{I_0} = NI_1(q)$$

In the case of more dense dispersions, correlations in the particle positions arise, and we need to take into account the interference between all of the wavefronts scattered.
by all the particles, and we obtain:

\[ I(q) = I_1(q) \left[ N + 2 \left( \sum_i \sum_j \frac{\sin q r_{ij}}{q r_{ij}} \right) \right] \quad (2.14) \]

This expression can be summarized in the product:

\[ I(q) = P(q) S(q) \quad (2.15) \]

where \( P(q) = I_1(q) \) is the form factor, and the interference term the structure factor \( S(q) \). The form factor is sensitive to the intrinsic properties of the particles, their shape and size, while the structure factor describes the presence of correlation in the positions of the particles in space, if any. In the case of non-interacting particles, \( S(q) \to 1 \) over the whole \( q \)-range. This is the typical case for the scattering pattern from a dilute dispersion of particles, or a gas. In the presence of short- or long-range order, \( S(q) \neq 1 \). We distinguish two cases:

- **Dense fluids and disordered solids**: In this case there is no long-range correlation in the particle positions and most terms in equation 2.14 cancel out. However, at short distances there is a certain degree of correlation due to the fact that the distance between the particle centers must satisfy \( d \geq \sigma \). This yields a broad peak in \( S(q) \) at \( q_{nn} = 2\pi / r_{nn} \), where \( r_{nn} \) is the average nearest neighbor spacing. \[52\]

- **Ordered solid**: In the case of an ordered arrangement of nanoparticles, the long-range spatial correlation will result in multiple peaks in \( S(q) \) the position of which is determined by Bragg’s law:

\[ 2a \sin \theta = n \lambda \quad (2.16) \]

where \( a \) is the spacing between the diffracting planes and \( n \) is an integer. We therefore see that we need \( \lambda \) to be the same order of magnitude as \( a \) to observe diffraction peaks, which illustrates the need for X-rays.

### 2.1.3 Light emission

Electron and holes excited in a material can recombine through the emission of a photon. If the material is excited optically with a photon of energy \( \hbar \omega = h c / \lambda_{exc} > E_g \), then the recombination process is known as photoluminescence. Usually, electrons and holes lose their excess energy \( \hbar \omega - E_g \) quickly with the emission of phonons, and only recombine when they have reached their lowest energy state in the conduction and valence band, respectively. The emission spectrum can be described by a single band centered around \( \lambda_{em} \), the width of which is influenced by the polydispersity.
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of the sample: more polydisperse samples will result in a broader emission band. The efficiency of photoluminescence can be quantified by the photoluminescence quantum yield, \( PLQY \), defined as the ratio of the number of emitted and absorbed photons:

\[
PLQY = \frac{N_{em}}{N_{abs}}
\]

Quantifying the efficiency of the emission process in nanomaterials is fundamentally important since it provides an insight into the microscopic mechanisms governing the release of energy at the nanoscale. For instance, a high \( PLQY \) may suggest a well-passivated sample, or a high crystallinity of the nanocrystals, while a low \( PLQY \) may suggest the presence of traps and/or structural defects. Two main techniques exist to determine the \( PLQY \): an absolute and a relative measurement. \( N_{em} \) and \( N_{abs} \) can be accurately determined using the absolute measurement, while the relative measurement relies on the use of an emission standard. However, since the absolute measurement is experimentally more challenging and time-consuming, the relative measurement is still the most popular method. We hereby describe a relative measurement. For details concerning the absolute measurement we refer the reader to more comprehensive texts. \([53,54]\) The photon flux of emitted photons can be calculated as

\[
F = \int_{\lambda_{em}} I_c(\lambda_{em}) \frac{\lambda_{em}}{hc} d\lambda_{em}
\]

where the integration is over the whole emission spectrum \( I_c \) after subtraction of the blank spectrum \( I_b \) from the uncorrected spectrum \( I_{uc} \) and dividing by the spectral responsivity of the instrument \( s(\lambda) \):

\[
I_c(\lambda) = \frac{I_{uc}(\lambda) - I_b(\lambda)}{s(\lambda)}
\]

Instead, the fraction of light absorbed by the sample can be calculated as:

\[
f = \frac{I_0(\lambda_{exc}) - I(\lambda_{exc})}{I_0(\lambda_{exc})} = 1 - 10^{-A(\lambda_{exc})}
\]

(2.17)

By using a quantum yield standard, absorbing and emitting in the same spectral window as the sample, we can determine the relative \( PLQY \) through:

\[
PLQY_{sample} = PLQY_{standard} \left( \frac{F_{sample}}{F_{standard}} \right) \left( \frac{f_{standard}}{f_{sample}} \right) \left( \frac{n^2_{sample}(\lambda_{em})}{n^2_{standard}(\lambda_{em})} \right)
\]

where \( n \) is the refractive index of the solvent used. A typical quantum yield standard for the visible range is Rhodamine 6G dispersed in ethanol, with a nominal \( PLQY \) of 91 ± 4%. \([53]\)
2.1.4 Electron microscopy

Electron microscopy is a key imaging technique in Nanoscience, since it allows for the direct observation of objects with sizes from the micrometer to the angstrom scale. At these length scales, using electron microscopy is indispensable, since the resolution of imaging systems is fundamentally limited by the diffraction of light to a resolution limit comparable to the wavelength used.

An ideal optical system would image an object point perfectly as a point. However, the diffraction of light of wavelength $\lambda$ at the aperture used to collect light results in a blur, also known as Airy disk. The size of the Airy disk is proportional to $\lambda$, and therefore it can become the limiting factor in the resolution of the instrument. We can define the resolution limit of an imaging system as:

\[ \Delta \ell = \frac{\lambda}{2NA} \]  

where $NA = n \sin \theta$ is the numerical aperture. If we consider visible light at $\lambda = 500 \text{nm}$ with an aperture of $NA = 1$ we obtain a resolution limit of $\Delta \ell = 250 \text{nm}$.

To decrease the resolution limit, and therefore increase the resolution power of the imaging system, we need to use smaller $\lambda$. This is easily done by using an electron gun as source, since the wavelength of electrons can be decreased by increasing their kinetic energy through $\lambda(\text{nm}) = \frac{hc}{E} \approx \frac{1240}{E(\text{eV})}$. Reaching a sub-nanometer resolution of $\Delta \ell \leq 0.1 \text{nm}$ is therefore possible by using energies $hc/\lambda = 0.61hc/\Delta \ell \geq 7564 \text{eV}$. Electron microscopy exploits these simple ideas to image objects at the nanoscale, such as nanoparticles, and subnanoscale, atoms.

In this thesis we have used an scanning electron microscope (SEM) to image nanoparticle assemblies on a substrate, as well as a transmission electron microscope (TEM) to image details at higher resolution of nanoparticles deposited on a carbon-coated TEM grid. In this instrument, a beam of monochromatic electrons of energy $E$ is accelerated and ejected from an electron gun, and focused by means of electric and magnetic fields. The electron beam can interact with the bound electrons in the sample and lose energy via several mechanisms, resulting in the emission of secondary electrons, X-rays or even visible light. A variety of detectors positioned in transmission, reflection, or at an angle, can harvest the scattered or emitted electrons and photons. As a result, the transmitted beam is attenuated. By scanning the electron beam across the sample and detecting the number of electrons transmitted, we can obtain a map of the electron density of the sample. The substrate, typically a thin carbon layer in TEM, has a small electronic contrast and therefore it will result in a bright background (bright-field imaging); the sample instead will result in darker areas which describe its thickness and morphology. When collecting the electrons which have been forward-scattered at an angle $\theta$, we obtain a dark background with a bright signal from the sample (dark-field imaging).
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2.1.5 Electron conductivity

One of the central quantities that describe the electrical performance of a material is the conductivity of charge carriers. The mobility of charge carriers is proportional to the conductivity, and represents the figure of merit of reference. Given an electric field $E$, charge carriers will gain a drift velocity defined by:

$$v_{e,h} = \mu_{e,h} E$$ (2.19)

where $e, h$ specifies the mobility values of electrons and holes, respectively. We can then define the total conductivity $\gamma$ as:

$$\gamma = e(n_e\mu_e + n_h\mu_h)$$ (2.20)

where $n_{e,h}$ indicates the concentration of electrons and holes, respectively.

Probing the conductivity of a material on different length scales can yield useful insights into the microscopic processes behind charge transport. Consider for instance a two-dimensional superstructure of average crystalline domain size $\xi$, composed of nanoparticles of diameter $\sigma$. The ordered arrangement of nanoparticles is expected to yield improved conductivity since the average number of nearest neighbors is higher. The conductive properties of the sample related to the ordered arrangement of nanoparticles can be studied when probing a length scale $\delta$ so that $\sigma < \delta < \xi$; however, when considering larger length scales $\delta > \xi$, the conductivity will rather depend on the macroscopic sample morphology, for instance on the connection between the crystalline domains.

In this thesis we have used two different techniques to probe the conductive properties of nanocrystal assemblies on two different length scales, see Figure 2.1:

- To probe conductivity on the short length scale limit of a few nanoparticles, we used time-resolved microwave conductivity (TRMC). We can estimate that for CdSe the probed length scale is $\delta_{TRMC} = 28 \text{nm}$; [55][56]
- To probe conductivity on a longer length scale, we use field-effect transistors. In this case the length scale probed is given by the separation between the source and drain electrodes, typically $\delta_{FET} = 2.5 \mu\text{m}$.

The schematics for these two techniques are shown in Figure 2.1

Time-resolved microwave conductivity

This technique exploits the fact that free charges moving in an oscillating electric field absorb energy, leading an attenuation of the incident field. Optically exciting a film of nanoparticles of bandgap $E_g$ with a laser pulse of wavelength $\lambda \leq hc/E_g$ results in the generation of electron-hole pairs. The charge carriers can move in the microwave field, and therefore dissipate the power reflected by the microwave. Let $\Delta \Pi$
be the decrease in reflected power due to the presence of the photoexcited conductive sample. For small photoinduced changes in the conductance, we can write:

\[
\frac{\Pi_{\text{light}}(t) - \Pi_{\text{dark}}}{\Pi_{\text{dark}}} = \frac{\Delta \Pi(t)}{\Pi} = -K \Delta G(t)
\]

where \( K \) is a factor dependent on the resonance characteristics of the cavity and dielectric properties of the sample and \( \Delta G = G_{\text{light}}(t) - G_{\text{dark}} \) is the change in conductance. The time-dependence derives from the fact that eventually the charge carriers will recombine, and therefore \( \Delta G \to 0 \) in time. By definition, conductance and conductivity are related through:

\[
\Delta G = \beta t \Delta \gamma
\]

where \( \beta \) is the ratio between the broad and narrow dimensions of the waveguide and \( t \) is the sample thickness. [57] Assuming \( n_e = n_h = n \), since we are generating electrons and holes in pairs, and following equation 2.20, we can write:

\[
\Delta G(t) = \beta t e \Sigma \mu n(t)
\]

there \( \Sigma \mu = \mu_e + \mu_h \). We can now express the concentration of photoexcited pairs \( n \) as

\[
n(t) = I_0 f \Phi(t) / t
\]

where \( I_0 \) in the incident photon fluence, \( f \) is the fraction of absorbed light by the sample described according to equation 2.17, and \( \Phi(t) \) is the number of electron-hole pairs generated per absorbed photon at time \( t \). [58] We can then write:

\[
\frac{\Delta G(t)}{e \beta I_0 f} = \Phi(t) \Sigma \mu \quad (2.21)
\]

At \( t = 0 \) the change in photoconductance reaches the maximum \( \Delta G(0) = \Delta G_0 = \Phi_0 \Sigma \mu \) and then decreases as a consequence of charge recombination. Since in general
\[\Phi_0 \leq 1, \Phi_0 \Sigma \mu \leq \Sigma \mu\] provides a lower limit to the sum of the mobilities of electrons and holes in the material. By increasing photon fluence \(I_0\), the decay time of the change in photoconductance decreases; this can be explained as follows. The photon fluence is proportional the number of electron-hole pairs generated in a nanocrystal; when this number rises above unity, additional recombination pathways that involve three or more carriers can be activated, therefore increasing the probability of recombination and decreasing decay time of carriers. One of the most investigated mechanisms is the \textit{Auger effect}, a three-body interaction where one electron and a hole recombine and the excess energy is transferred to second electron. To exclude the presence of multi-body effects, we extrapolate to \(I_0 \rightarrow 0\), and estimate the sample mobility in conditions of non-photoexcitation.

**Field-effect transistors**

Field-effect transistors probe charge transport over a length scale of several micrometers, by directly contacting the material and subjecting it to an applied voltage. Typically, two contacts separated by a distance \(d\) and positioned on an insulating substrate confine the semiconductor material to be probed. The two contacts are addressed as source and drain, and the volume comprised between them as the \textit{channel}. The channel can be filled with a semiconductor material, such as a film of nanoparticles. When applying a voltage difference between source and drain \(V_D\), a current \(I_D\) will result. We can add a third contact below the insulating layer, which we will address as the \textit{gate}, Figure 2.1. We can now apply a voltage difference between the gate and the source, which we will call \(V_G\). Let’s now choose \(V_D > 0\) and \(V_G > 0\). If the material filling the channel behaves as a n-type semiconductor, namely electrons are the majority carriers, \(I_D\) will increase if the gate voltage exceeds a threshold \(V_{th}\), since the electrons responsible for the conduction will be attracted into the conductive channel. Conversely, for \(V_G < 0\) the electrons will be repelled and \(I_D\) will go to zero. This is the basic idea of a field-effect transistor.

To measure the field-effect mobility, we can either work in the linear regime, for small \(V_D\) so that \(I_D \propto V_G\), or in the saturation regime. In the latter case, for each value of \(V_G\) we increase \(V_D\) until \(I_D\) saturates to a value \(I_{D,\text{sat}}(V_G)\). Under these conditions, we have that:

\[I_{D,\text{sat}}(V_G) = \mu_e \frac{C W}{2L} (V_G - V_{th})^2\]

where \(L\) and \(W\) are the length and the width of the channel, and \(C\) is the capacitance per unit area of the insulator. By plotting \(\sqrt{I_{D,\text{sat}}(V_G)}\) against \(V_G\), we measure the slope \(m_{\text{sat}}\) which is related to the mobility via:

\[\mu_e = m_{\text{sat}}^2 \frac{2L}{WC}\]  

(2.22)
2.2 Sample preparation

In first approximation, the conductivity of a thin film of nanoparticles is dictated by the average number of nearest neighbors. [60] Close-packed crystalline structures satisfy best this requirement. However, the nanoparticle polydispersity plays a huge role in allowing the formation of these dense structures. A proper sample preparation is therefore crucial, as we will see in the next section.

2.2 Sample preparation

The phase behaviour of hard-sphere colloidal particles predicts that increasing the polydispersity suppresses crystallization. [61] This observation illustrates that to obtain close-packed ordered nanoparticle superstructures, it is crucial to start with a monodisperse sample. After analyzing a number of synthetic protocols in the literature, we found a recipe that allowed for the production of low polydispersity CdSe quantum dots and nanoplatelets. We hereby report these protocols. Figure 2.2 shows a schematic of the experimental setup needed for the protocols.

2.2.1 Synthesis of CdSe quantum dots

We have followed the protocol reported by Chernomordik et al. [62] This synthetic protocol is made of several parts outlined below in detail.

1. Preparation of the reaction flask. A 100mL three-neck round-bottom flask was cleaned by brushing in soapy water, followed by sonication in Hellmanex solution (Hellma) and drying in the oven at 100°C by means of a heating mantle. A 4mmoles = 512mg amount of cadmium oxide (CdO) was added to the flask, together with 22mmoles = 7mL of oleic acid (OAH) and 99mmoles = 32mL of 1-octadecene (ODE). A stir bar was added, and the dispersion was brought to a temperature of 100°C under vacuum, and kept for half hour. This step is to ensure the removal of dissolved air and water, which can be confirmed by the visible bubbling. Afterwards, the temperature was raised to 260°C and the atmosphere is switched to N2. As CdO reacted with OAH to form cadmium oleate (Cd(OA)2), the reaction flask went from a maroon color to colourless. Care should be taken in making sure all of the CdO is collected from the walls of the flask. The reaction can be described as: CdO+2 OAH \( \rightarrow \) Cd(OA)2 + H2O. After the contents of the flask were completely clear and no residues of CdO were visible, the temperature was lowered to 100°C and the flask was placed under vacuum for 20 minutes to remove the extra water produced. Afterwards, the atmosphere was switched again to N2 and the temperature raised to 260°C.

2. Preparation of the injection syringe. An amount of 0.8mmoles = 63mg of selenium powder (Se) was added to 5mL of ODE in a vial. The capped vial
was then sonicated for 15 minutes. The Se powder did not dissolve, but formed a metastable dispersion. Care should be taken that the cap of the vial does not unscrew as a result of sonication. Before the injection, the dispersion was transferred to a 20\text{mL} disposable syringe equipped with a 16 gauge needle.

3. **Preparation of the slow-addition syringe.** A 1\text{M} solution of Se in trioctylphosphine, TOP, was prepared by adding 10\text{mmoles} is Se to 10\text{mL} of TOP. Care should be taken to ensure that the transfer of TOP is under an oxygen-free atmosphere, since this chemical is prone to oxidation to trioctylphosphine oxide (white powder). These conditions can be ensured by using a glovebox or a glovebag filled with N\textsubscript{2}. After adding a stir bar, the vial containing the reagents was capped under N\textsubscript{2} by means of a cap with setpum. The dispersion was stirred at room temperature until the Se powder dissolved to form a transparent, slightly yellow, solution. 3\text{mL} of the solution were added to 7\text{mL} ODE.
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and transferred to a glass syringe which was placed on a syringe pump with injection rate set to 10mL/hr.

4. Injection. The dispersion of Se in ODE was swiftly injected into the reaction flask and the set temperature was decreased to 240°C. The contents of the glass syringe were slowly added to the reaction flask by using the syringe pump. The first droplet reached the reaction mixture ∼ 1min after injection. The reaction was continued for a time Δt during which the nanocrystals grow.

5. Quenching and purification. To quickly stop the reaction, the set temperature was decreased to below room temperature, the mantle was removed and the flask was surrounded with a crystallization plate full of water at room temperature under stirring. The nanocrystals were isolated from ODE and unreacted precursors by adding 5mL of reaction mixture to a 50mL centrifuge tube, followed by 20mL of hexanes, shaking, and 25mL of ethanol. The dispersion quickly became turbid as a result of the scattering from nanocrystal aggregation in solution. The tube was centrifuged at 3000g for 30 minutes. Afterwards, the clear supernatant was discarded and 25mL of hexanes were added to the pellet. After redispersing, the nanocrystals were again precipitated by adding 25mL of ethanol and centrifuging. The procedure was repeated in total 3 times, at the end of which the nanocrystals were dispersed in 10mL of hexanes, filtered through a 200nm syringe filter and stored in a capped vial.

To monitor the growth of nanocrystals, we have taken 0.5mL aliquots as a function of ΔT. These aliquots were quenched in 4.5mL hexane vials and their absorption spectra were recorded. From the position of the lowest-energy peak in absorption we have determined the average size of nanocrystals using 2.2. We also extracted the half-width at half-maximum (HWHM) of the lowest energy peak which is a measure of the polydispersity of the sample. The results are reported in Figure 2.3. We can clearly observe that the absorption spectrum of nanocrystals shifts towards longer wavelengths, and therefore lower energy, during growth (Figure 2.3b). As discussed in the previous chapter, the position of the lowest-energy peak is a measure of the nanocrystal size, while the width of the peak is a measure of the polydispersity of the sample. The average nanocrystal size increases as a function of growth time, to plateau around σ = 6nm at 70min ≤ Δt = 130min, and then increase further (Figure 2.3b). At the same time, the HWHM markedly decreases to reach a minimum of $HWHM = 38meV$ around ΔT = 60min. At nanocrystal nucleation, which corresponds to the injection of the dispersion of Se in ODE at Δt < 0, the ratio of Cd : Se = 4/0.8 = 5, while at the end of the slow addition of we have Cd : Se = 4/(0.8 + 3) = 1.05. Since the growing crystallites should have a ratio close to stochiometric, Cd : Se ∼ 1, we argue that the reaction kinetics proceed slowly thanks to the excess of metal precursor present in solution, therefore allowing for size
Figure 2.3: Ex-situ measurement of nanocrystal growth kinetics. (a) Absorption spectra of nanocrystals during growth. Data measured from aliquots removed from the reaction flask. (b) Nanocrystal diameter values during growth, as extracted using 2.2. (c) Half-width at half-maximum of the lowest energy peak in absorption during growth.

focusing. Once all the extra Se precursor has been added and the ratio becomes near stochiometric, the nanocrystals may grow further via Ostwald ripening, leading to size defocusing. Therefore we estimate that the best choice of $\Delta t$ to obtain the least polydisperse sample is $60\text{min}$. We illustrate the effect of polydispersity on the absorption features of nanocrystals with figure 2.4. Here we show the absorption spectra of four samples of CdSe nanocrystals with similar peak position, corresponding to similar average sizes, differing instead in peak width or polydispersity (Figure 2.4).

We have used small-angle X-ray scattering to relate the HWHM of the lowest energy absorption peak of CdSe nanocrystals to their polydispersity value. The polydispersity of each sample was obtained by fitting the scattering pattern to the spherical form factor reported in modulated by a gaussian distribution $G(\sigma, \sigma_0, \Delta \sigma)$ of sizes $\sigma$ centered around a mean value $\sigma_0$ and of width $\Delta \sigma$:

$$I_G(q, \sigma_0, \Delta \sigma) \propto \int_{0}^{+\infty} \frac{I_1(q, \sigma)}{I_0} G(\sigma, \sigma_0, \Delta \sigma) d\sigma$$ (2.23)
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The polydispersity value was then obtained by \( PD = \Delta \sigma / \sigma_0 \). This procedure also allowed us to compare the mean diameter values to the ones predicted by [2.2]. The results are shown in figure 2.5. We notice that the nanocrystal diameter values extracted from the absorption spectrum through [2.2] compare well to the values measured with SAXS; the results may point to an underestimation of diameters for smaller nanocrystals and an overestimation for larger nanocrystals. Instead, the polydispersity results suggest a linear relation between absorption and SAXS data for higher polydispersity values, \( PD \geq 6.5\% \), which seems to becomes more uncertain for more monodisperse samples. These results show that using [2.2] to determine size and polydispersity of nanocrystals yields satisfactory results, although it would be interesting to investigate any deviation from the expected trends by measuring further.
Figure 2.5: Relation between absorption and scattering measurements to determine size and polydispersity of CdSe nanocrystal ensemble. (Left) Comparison of the diameter extracted from the lowest energy peak in the absorption spectra using Eq. 2.2 and the values measured from fitting the scattering pattern of nanocrystals to 2.23. (Right) Comparison of the HWHM of the lowest energy peak in the absorption spectra of CdSe nanocrystals to the polydispersity values extracted from SAXS using 2.23.

2.2.2 Synthesis of CdSe nanoplatelets

To synthesize CdSe nanoplatelets we followed the protocol reported by She et al. [64].

1. Preparation of the reaction flask. A 100 mL three-neck round-bottom flask was cleaned as described in the previous section. A 1.1 mmole = 510 mg amount of cadmium myristate (Cd(myr)₂) was added together with 131 mmole = 42 mL of ODE. A stir bar was added, and the dispersion was brought to 100°C while under vacuum by means of a heating mantle. The temperature was kept for half hour. The atmosphere was then switched to N₂ and the temperature was increased to 240°C. At this stage, it is important to make sure that the set temperature does not overshoot to ≥ 260°C; when this would happen, the dispersion turned to a gray colour which we ascribed to the nucleation of cadmium metal nanoparticles.

2. Preparation of the injection syringe. A 0.45 mmole = 36 mg amount of Se powder was added to 3 mL of ODE and sonicated for 15 minutes to form a metastable dispersion. Prior to injection, the dispersion was transferred to a 10 mL disposable syringe equipped with a 18 gauge needle.
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Figure 2.6: Nanoplatelets with different aspect ratios (a) Absorption spectra of NPs with different aspect ratios dispersed in hexane. The reaction time is indicated in the legend. (b) Measured length and aspect ratio of NPs synthesized with different reaction times. Error bars represent the standard deviation values obtained by sampling > 100 NPs for each reaction time.

3. Preparation of the second addition. A 60mg = 0.8mmoles of finely ground cadmium acetate (Cd(Ac)$_2$) was placed on a spoon that would fit through the neck of the round-bottom flask for swift addition. Here it is important that the Cd(Ac)$_2$ is finely ground to ensure fast dissolution in the reaction mixture. At the end of the reaction there should be no solids precipitates.

4. Injection. Once the temperature of the reaction flask stabilized, the dispersion of Se/ODE was swiftly injected. After 20s of delay, the Cd(Ac)$_2$ was swiftly introduced. The solution was held at 240$^\circ$C for a time $\Delta t$.

5. Quenching and purification. The temperature of the reaction flask was rapidly reduced by removing the heating mantle and replacing it with a water bath. When the temperature reached 100$^\circ$C, 24mmoles = 6mL of OAH were added; at 70$^\circ$C 45mL of hexanes were added. The mixture was transferred to two 50mL centrifuge tubes and centrifuged at 4000g for 1 hour, yielding a colored supernatant (dispersion of quantum dots) and a dark precipitate (NPs). The supernatant was discarded and the precipitate was dispersed in 10mL of hexane. Depending on the size of the NPs, 220nm (PTFE), 450nm (PTFE) or 800nm (MCE) pore sized filters were used to filter the dispersion.

By varying the reaction time $\Delta t$ between 5 and 30 minutes, nanoplatelets with the same thickness and different aspect ratios (length/width) can be synthesized (Figure 2.6b, 2.7): The sharp absorption transition at $\lambda = 514nm$ is indicative of a thickness of 4.5 atomic monolayers, corresponding to 1.2nm, Figure 2.6a. [65][66].
Figure 2.7: Bright field STEM images of NPs synthesized with increasing reaction times. Scale bars indicate 50 nm.