NIR Dynamic Light Scattering for Quantum Dots Size Measurement

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Abstract

Fluorescent semiconductor nanoparticles, known as *quantum dots* (QDs), have become a major field of research. Their applications range from the audiovisual to the biomedical imagery to the photovoltaic development. Since QD size (usually, $\leq$30 nm) is the key to their optical properties, a good grasp of their dimensions must be achieved. Dynamic Light Scattering (DLS) presents itself as an interesting candidate for such characterization, since it enables a representative size measurement of small nanoparticles (NPs) in suspensions. Nevertheless, the QDs absorption properties, in the range of classical DLS lasers, can represent a difficulty in such a measurement. In order to overcome these difficulties, we present here a DLS set-up developed specifically for Cd-based QD size measurement. The measurement, made directly in the suspension vial in order to limit the toxic QD handling, becomes possible, due to the replacement of the classical 635-nanometers laser by a near-infrared (NIR) 780-nanometers laser in the DLS apparatus. We were then able to determine the size of red-emitting QDs, even though their absorption band goes up to 650 nm.The analysis of a green-emitting QD suspension shows that such a set-up can also be used for more classical DLS size measurements, even when the NP size is quite small ($\simeq$ 9 nm) compared to the NIR wavelength. This study makes evidence that it is possible to extend the range of DLS uses for fluorescent particles with strong absorbance in the visible, making it a promising characterization technique for fluorophore-based system, especially in the biomedical field.

1 Context

1.1 Quantum Dots (QDs)

Quantum dots (QDs) are nanocrystals made from semiconductor materials (usually, transition metal selenides, sulfide, or tellurides such as CdSe, CdS, ZnS, CdTe) whose size induces unique optical properties[1, 2]. At the nanoscale, a quantum confinement appears in these particles, resulting in a discretization of the energy levels and, thus, in luminescent properties for the material. Especially, quantum dots exhibit fluorescence in the visible range of light, when excited with UV (*Figure 1 and 2*).

The wavelength of the emitted light is directly linked to the size of the nanoparticle (NP), since the gap between the conduction and the valence band depends on the NP size. It is then possible to tune the emission by changing the QD size, toward a very precise wavelength. The QD emission wavelength (*i.e.* the color of the produced light) will be directly linked to the size polydispersity in the suspension, for each class of size will generate a specific wavelength. Typical Cd-based QDs have a characteristic size between 5 and 25 nm, for an emission in the visible range of light. Therefore, QDs constitute a very interesting field of research, due to these properties, and can lead to a wide range of applications such as screen development, photovoltaic material, or biomedical imagery.

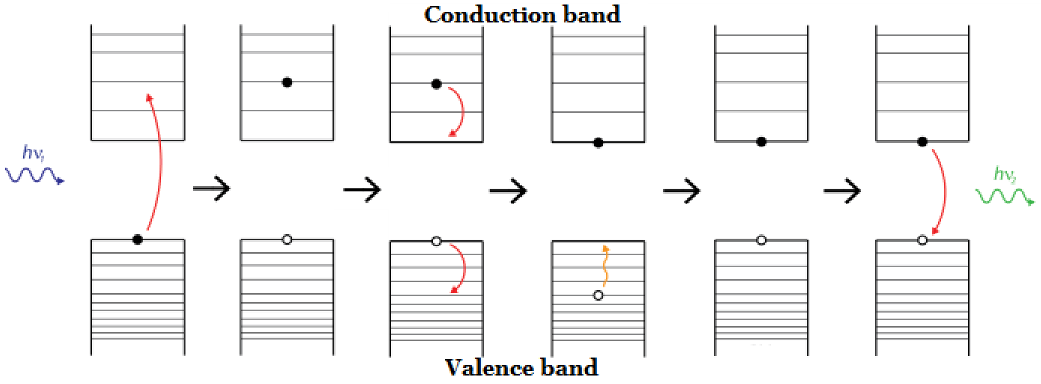


Figure 1: Scheme of the fluorescence process in quantum dots. An exciton (electron/hole pair) is formed with the UV excitation and, during its recombination, produces light in the visible range

1.2 Dynamic Light Scattering (DLS)

Dynamic Light Scattering (DLS) is a technique based on the measurement of the scattered light fluctuations through colloidal suspension, in order to get information on the NP size[3]. By analyzing the Brownian motion of the particles, it is possible to retrieve the NP diffusion coefficient (D) and therefore the hydrodynamic diameter (d) of the NPs, thanks to the Stokes-Einstein equation:

$$D = \frac{k.T}{3.\pi.\eta.\mathbf{d}} \tag{1}$$

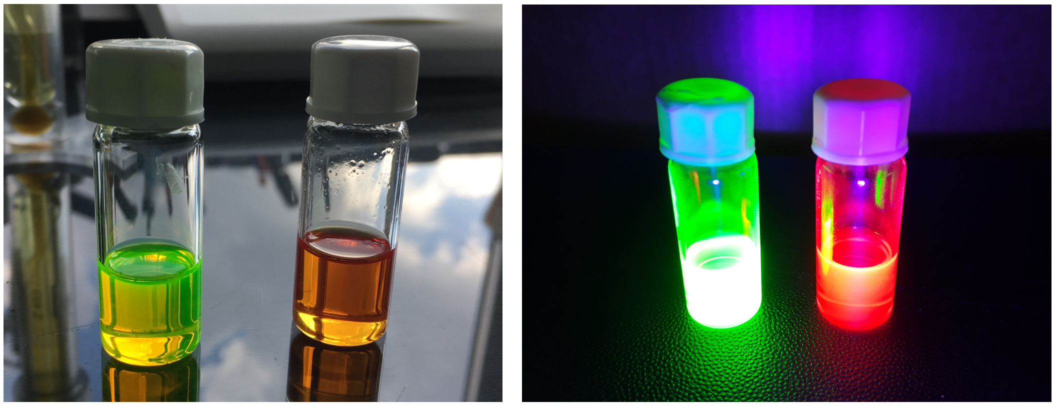
where D is expressed in $m^2.s^{-1}$, k is the Boltzmann constant (in $J.K^{-1}$), T is the medium temperature (in Kelvin), η is the medium viscosity (in $J.s.m^{-3}$) and d is the particle diameter (in m) DLS devices correlate fluctuations of the scattered laser light intensity with an exponential-like correlogram, whose decay rate can be linked to the diffusion coefficient and the scattering angle between the collected beam direction and the incident laser beam direction. Current DLS analysis can give a value of spherical NP size, as well as an idea of the polydispersity in sizes for a given colloidal suspension. As such, DLS technique has become an ideal characterization technique for NP size measurement, often associated with complementary imaging techniques, such as Electronic Microscopies (TEM, SEM). While electronic microscopy shows NP shapes and sizes at the local scale, DLS give an indication on the NP size and size polydispersity over the whole suspension.

1.3 DLS for QD size measurement

DLS has already proven to be valuable in the characterization of various nanosize species (metallic nanoparticles, vesicles, protein and polymeric compounds). However, its use for QDs raises some technical issues, despite the major advantages it could bring in the characterization of such nanocrystals. First, in DLS,in first approximation, the light scattering cross-section is proportional to d^6, so the smaller the particle, the less intense its signal will be. Therefore, the size of QDs, and especially the smaller ones (2-10 nm), can prove difficult to detect, especially if bigger objects (such as aggregates) are present in the suspension. Another point to take into account, is the high toxicity of Cd-based QDs. The manipulation of such species is, therefore, to be limited as possible and must constitute a safety concern. the last (but not least) issue is directly related to the QD optical properties. As they emit in the visible range of light, they also have a strong absorbance band, that also depends on the QD size. This band is shifted towards higher wavelengths with the size increase. For instance, in the case of red-emitting CdSe QDs (typical size around 15 nm), the absorbance band is located around 600-650 nm, that is typically the wavelength of a classical DLS laser (635 nm). A strong decrease in the collected signal is then related to this absorbance and, thus, a less easy size measurement. In order to tackle these issues, we propose an experimental set-up based on the use of a Near-Infrared (NIR) laser in a DLS equipped with a remoted head, as the core of our classical DLS experiment.

2 Experimental Protocol

2.1 *Colloidal suspensions*



(a) Natural light (b) UV-light

Figure 2: Pictures of both green- and red-emitting QDs suspensions in natural visible light and under UV exposition

Two batches of CdSe@CdS core/shell QDs have been studied: the first batch emits green-light fluorescence, while the second is red-emitting (*Figure* 2). For the following description, these batches will be called "green QDs" and "red QDS", respectively.
These QDs have been provided in powder form. QD suspensions (1 g/L) were prepared by dissolving the powders in toluene. Sonication (10 min, with an Emmi H22 sonicating bath; 120 W) was performed before DLS measurements.

2.2 *UV-visible and fluorescence spectroscopies*

QD suspension absorbance and fluorescence bands were analyzed at the Laboratoire de Chimie des Polymères Organiques (LCPO)(Pessac, France) with a Spectra Max M2 from Molecular Devices.

2.3 *Transmission Electronic Microscopy (TEM)*

TEM analysis was performed on a LVEM-5 bench top TEM (https://www.cordouan-tech.com/products/lvem5/), at the laboratoire d'applications de Cordouan Technologies.

2.4 *DLS set-up*

Dynamic Light Scattering measurements were made with a **Vasco Kin**^{TM} apparatus, developed by Cordouan Technologies (https://www.cordouan-tech.com/products/vasco-kin/), with either the "classical" 635-nanometers laser diode, or a 780-nanometers laser (NIR), for comparison sake. Measurements were made with the *in situ* head, at a scattering angle of 170 (back-scattering). The remoted head (*in situ* head) allows a DLS measurement directly into the NP container, without the need of transfering the species in a particular cell, thus preventing the extensive manipulation of the quite toxic Cd-based QDs. A continuous multimodal analysis algorithm (SBL), implemented by Cordouan Technologies, has been used to evaluate the size of the QDs. Some important features are given about the relevancy of the measure and analysis. The β parameter ($0 \leq \beta \leq 1$) is working as an indication of the ratio signal/noise. The closer β is from 1, the better the measure will be; while a β close to 0 indicates a strong noise in the signal, then a measure less easy to interpret. The residues are another features for the quality of the fit analysis. They correspond to the difference between the algorithm fitting curve and the correlogram obtained from the measure. The smaller the residues are (arbitrarily, residues are said "good" when $\leq$ 0.01), the better the quality of the size values given by DLS. With these tools, the quality of DLS characterization can be estimated.

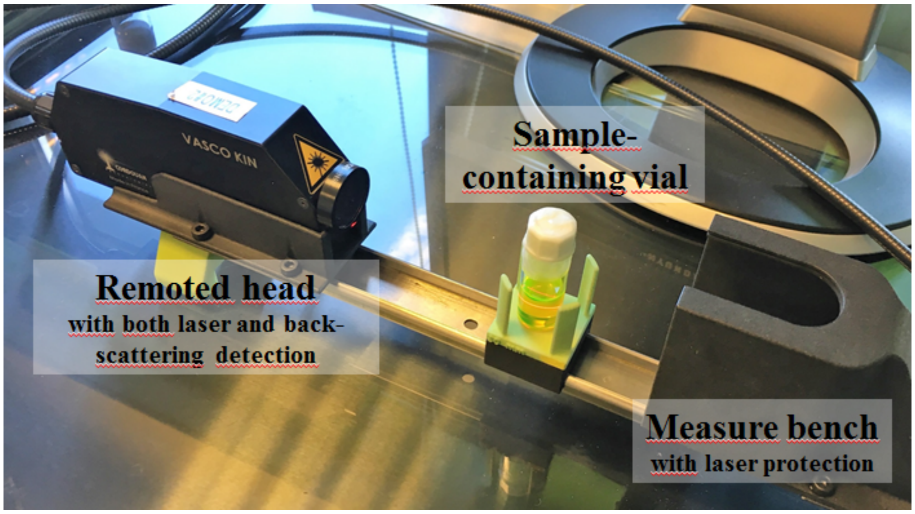
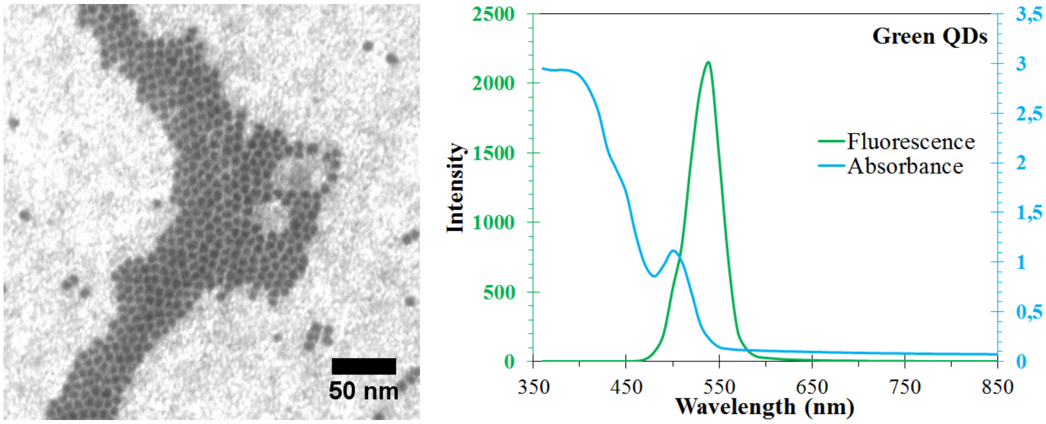


Figure 3: Picture of the DLS set-up, with the Vasco Kin *in situ* head, for green QD size measurement

3 Results

3.1 Green QDs

The first sample to be analyzed with this DLS set-up was a suspension of green-emitting CdSe@CdS quantum dots in toluene. The typical size of these particles was determined by TEM, around 7 nm (*Figure 4*).



(a) TEM (b) Absorbance and fluorescence spectra

Figure 4: Green QDs characterization

The absorbance band for this suspension is at 500 nm, which should not interfere too much with a classical DLS laser, even less with the 780-nanometers laser wavelength.

Figure 5 shows the correlogram obtained for the green QDs when analyzed with both 635-nanometers and 780-nanometers lasers. The classical Kin's laser (635 nm) has a better β, which come with no surprise since the higher wavelength laser is expected to have a stronger noise.

Table 1 summarizes the value of these β, as weel as the residues values. We can already notice that the measures made by DLS, whatever the laser wavelength, and the algorithm fits are relevant since the residues are very small ($\leq$0.007).

Size distribution analysis made with the 635-nanometers laser and the 780-nanometers laser (*Figure 6*) show similar results. It is worth noticing that a difference of 4 nm can be found with the TEM size measurements.

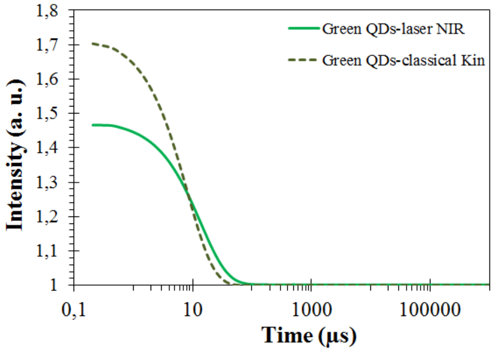


Figure 5: DLS correlograms for the green QDs analysis, either with the classical 635-nanometers laser or the 780-nanometers laser

	Laser 635 nm	**Laser 780 nm**
β	0.72	0.48
Residues	$\leq$0.005	$\leq$0.005

Table 1: β and residues values for the DLS measurements on the green QDs suspension, made with both laser wavelengths

These few nanometers can be attributed to the stabilizing agents surrounding the NPs. Indeed, such ligands can form a layer around the NPs, with a thickness up to 6 nm in diameter[4].

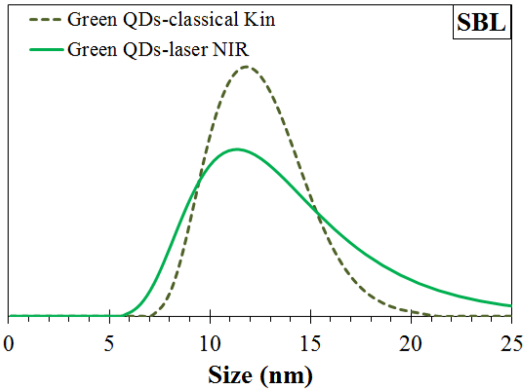


Figure 6: DLS size distribution of the green QDs either with the classical 635-nanometers laser or the 780-nanometers laser

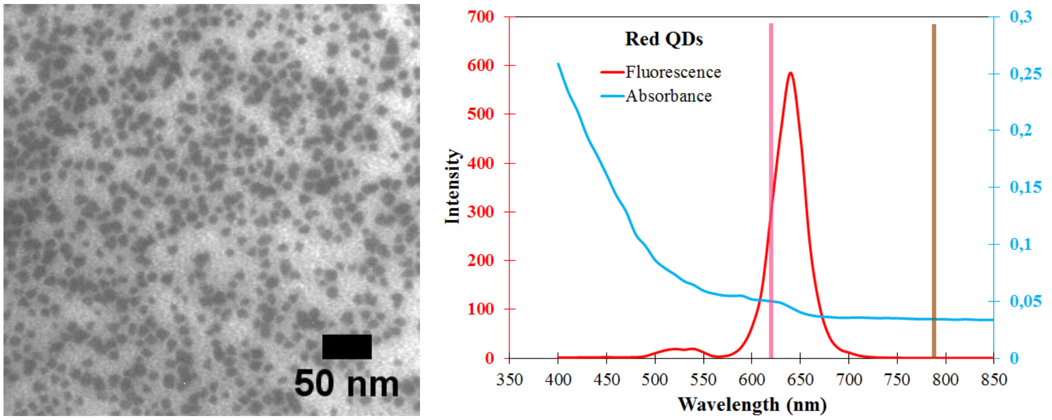
Intensity	**Laser 635 nm**	**Laser 780 nm**
QD size	11.7 nm	11.2 nm

Table 2: DLS size measurements for the green QDs for both laser wavelengths

3.2 Red QDs

Bigger red-emitting QDs have been investigated with the same NIR-laser DLS technique. Although their bigger size, seen in TEM around 12 nm, makes them easier to be detected, their absorbance band (600-650 nm) is now right in the usual DLS laser wavelength (*Figure 7*).

By using a higher wavelength, it is possible to prevent the absorption of the laser. The NIR-laser is then an adapted solution to tackle this absorption issue, although the collected signal stays very noisy. *Figure 8* shows the correlograms obtained with both kinds of laser. The β values (shown *Table 3*) show that the 635-nanometers laser cannot be used for the analysis of such QDs, due to a very high noise. The 780-nanometers laser, on the other side, shows a proper correlogram with a β quite acceptable, which can be analyzed for size measurement. The residues for both algorithms confirm this tendency, since no appropriate fit can be done on the measure with the 635-nanometers laser, and underline the pertinence of the measurement done with the NIR laser. The size distributions in intensity, for both lasers are shown in *Figure 9*. While it is not possible to recover any size values with the 365-nanometers laser measurement (*Table 4*), the one made with the 780-nanometers laser leads to a QD size of 15 nm, quite close to the size values obtained by TEM measurement, especially if the probable ligand layer surrounding the nanocrystals is taken into account.



(a) TEM

(b) Absorbance and fluorescence spectra (635 nm and 780 nm laser wavelengths are shown as pink and brown lines, respectively)

Figure 7: Red QDs characterization

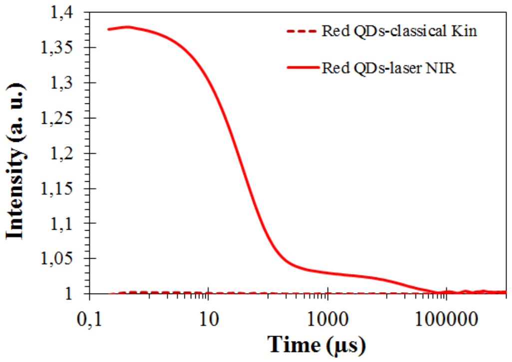


Figure 8: DLS correlograms for the red QDs analysis, either with the classical 635-nanometers laser or the 780-nanometers laser

	Laser 635 nm	**Laser 780 nm**
β	0.01	0.38
Residues	//	$\leq$0.005

Table 3: β and residues values for the DLS measurements on the red QDS suspension, made with both laser wavelengths

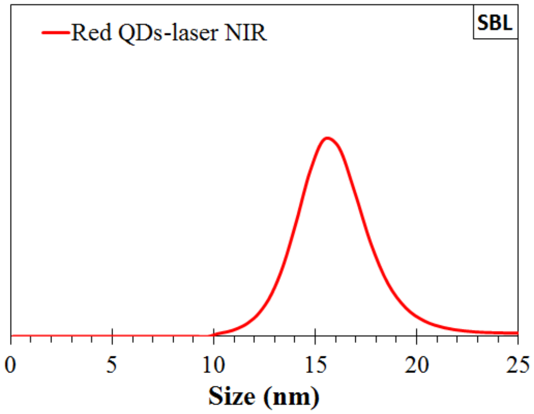


Figure 9: DLS size distribution of the red QDs with the 780-nanometers laser

Intensity	**Laser 635 nm**	**Laser 780 nm**
QD size	//	15.4 nm

Table 4: DLS size measurements for the red QDs for both laser wavelengths

4 Conclusion

We have shown here that the NIR-laser can be a valuable asset in the DLS measurement of Cd-based QDs. The laser wavelength at 780 nm prevents most of the absorption effects in the case of red-emitting QDs, in order to get a strong signal for size-retrieving, thanks to an adapted algorithm. although the values given by DLS are slightly bigger than the one seen in TEM (difference attributed to an organic layer of stabilizing agents, not seen in the TEM), the characteristic QD sizes have been retrieved. The comparison with the green-emitting QDs has shown that the DLS is already a potent instrument for characterizing small object ($\leq$10 nm) such as these nanocrystals and that the addition of the NIR laser can extend is potential towards absorbing materials. Furthermore, the set-up of the NanoKin^{TM} device, with its remoted head and the *in situ* measurement directly into the sample-containing vial, has also proven a powerful tool for limiting the handling of toxic materials

This study is but the first step in the DLS characterization of fluorescent nanoparticles. Already, the same methodology was applied on red-emitting gold nanoclusters (3 nm in size), with very promising results that would ensure the durability and viability of such a characterization technique. This would surely enlarge the field of applications for DLS to new domains, such as the bio-medical imagery/treatments, and to the characterization of strong visible-absorbing particles such as plasmonic NPs or various dyes/fluorophores used in the biological field.

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