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Probing the fluorescence dipoles of single cubic CdSe/CdS nanoplatelets with vertical or horizontal orientations

Fu Feng1, Loan Thu NGuyen1,2, Michel Nasilowski3, Brice Nadal3, Benoît Dubertret3, Agnès Maître1, Laurent Coolen1

1Sorbonne Universités, UPMC Univ Paris 06, CNRS-UMR 7588, Institut des NanoSciences de Paris, F-75005, Paris, France
2Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay Dist., 100000 Hanoi, Vietnam
3Laboratoire de Physique et d'Etude des Matériaux, ESPCI, UPMC Univ Paris 6, CNRS, 10 rue Vauquelin, Paris, France

Abstract

Measuring the orientation of a single fluorescent nano-emitter and obtaining emitters with a desired orientation is of highest importance for nanophotonics, especially in plasmonics where an emitting dipole close to a metallic surface will couple efficiently to plasmonic modes only if it is deposited vertically. Control of the orientation of a nano-object remains a challenge. Achieving vertical orientation, or having an information on the dipole orientation are key steps for efficient plasmonic excitation. We consider here cubic-shaped nanoplatelets with a thin CdSe core sandwiched in a thick CdS shell. By a combination of polarization measurement and radiation pattern Fourier analysis, we show that each single platelet behaves with excellent precision as a 2D dipole (sum of 2 orthogonal incoherent dipoles) and having only two possible orientations: either they lie horizontally on the substrate or they stand vertically on the edge. The cubic shape allows some platelets to deposit vertically so that they present a deterministic vertical dipole component.

Key words: single fluorescent emitter, nanoplatelet, emission polarization, radiation pattern

Colloidal semiconductor nanoparticles offer a wide range of applications in optics and opto-electronics. Spherical II-VI quantum dots are already commercially used for light-emitting diode (LED) displays and bio-imaging labels. Elongated or tetrapod structures have been synthesized, and recently flat nanoplatelets with atomically controlled and monodisperse thickness1 have been produced, showing great potential for LEDs2-3, photovoltaics4, lasers5-6 or photodetection7. For many applications, emission enhancement is sought thanks to a plasmonic structure. The coupling of the emitter to plasmonic modes is then strongly dependent on the dipole orientation and significantly enhanced for a dipole orthogonal to the metallic substrate8-9. Moreover a precise understanding of the photophysics of these light emitters is necessary in order to optimize their synthesis protocol and optical properties. The radiation of the electron-hole pair states responsible for light emission is dependent on the quantum-confinement properties of these states, but may also involve dielectric antenna effects of the surrounding protection shell and environment, trapped charges in the vicinity of the emitter, ligands, etc.
The emission from a nanorod\textsuperscript{10} or a dot-in-rod\textsuperscript{11} can be described as originating from a linear radiating dipole\textsuperscript{12} (« 1D dipole »). Spherical quantum dots, on the other hand, behave as an incoherent sum of 2 orthogonal dipoles (« 2D dipole »)\textsuperscript{13-15}. Some results however suggest an intermediate behavior (sum of 1D and 2D dipoles) for dots-in-rods\textsuperscript{16} and quantum dots\textsuperscript{17}, while 1D-dipole emission has also been reported for quantum dots and attributed to ligand effects\textsuperscript{18}.

While spherical quantum dots deposit with random orientations on substrates, a deterministic deposition of single emitters with horizontal dipole has been shown with either 1D (nanorod\textsuperscript{19}) or 2D (dot-in-plate\textsuperscript{20}) dipole natures. However, horizontal dipoles have very low interaction with the intense field close to the metallic surface and cannot benefit from surface-plasmonic enhancement as vertical ones do. Ensemble polarization measurements have shown that layers of fluorescent dye molecules with an overall vertical orientation could be deposited by using a liquid-crystal matrix\textsuperscript{21-23}, with possibilities of orientation control by an applied voltage\textsuperscript{23} and of applications for luminescent solar concentrators\textsuperscript{21}. However deposition with deterministic vertical dipole component has not to our knowledge been demonstrated at the single emitter level. Single-emitter radiation analysis is of importance in the context of fundamental photophysics study as well as for quantum optics experiments such as single-photon generation. Single-emitter manipulation by a plasmonic structure crucially depends on the presence of a vertical dipole.

In this paper, we demonstrate that by using single CdSe nanoplatelets with a thick CdS shell, it is possible to deposit some emitting dipoles orthogonal to metallic substrate which can benefit the most of plasmonic interaction. To this purpose, in order to evidence the orthogonal dipole, we use a method combining polarimetry and Fourier-plane analysis of a single nanoplatelet shell in order to obtain a precise determination of both the dipole nature (1D, 2D and potential existence of a third dipole) and the dipolar orientation.

In the first part of the paper, we present the experimental method. We then discuss the nature and orientation of the 2D emitting dipole. In the last part, we demonstrate that the contribution of a third linear dipole can be excluded, so that eventually some nanoplatelet emitters are shown to behave deterministically as 2D dipoles with the same vertical component.
Figure 1 (a) Schematic presentation of a cubic nanoplatelet. (b) TEM image of the nanoplatelets. (c) distribution of the aspect ratio b/a measured on the TEM image (b). (d) Schematic of the optical setup.

Experimental protocol

The nanoplatelets studied consist of a core CdSe square layer of 16x16 nm² lateral dimensions and 1.2 nm thickness, sandwiched between two layers of shell CdS which passivate its dangling bonds and improve its optical properties\(^2\) (fig. 1(a)). The nanoplatelets were synthesized following modifications of a protocol published in\(^2\) as described in the Supporting Information (S.I.). Unlike in previous reports\(^2\), we consider here thick shells of 8.5 ± 1 nm, so that the overall dimensions of the nanoplatelets are 18 nm in thickness and 29 ± 3 nm lateral dimensions (with aspect ratio b/a between 1 and 1.18 where a and b are the lateral dimensions (fig 1(c)), which makes them closer to a cubic shape. Because of the cubic shape of these emitters, it is seen on transmission electron microscopy (TEM) images (fig. 1(b)) that the emitters can deposit both horizontally and vertically.

The cubic nanoplatelets are spin coated on a substrate with a density around 1 emitter per 10 µm\(^2\). The substrate is a glass coverslip covered by a 200-nm layer of gold with 50 nm of SiO\(_2\) on top (see S.I. for sample fabrication). 50 nm of PMMA are added on top of the sample in order to protect the sample from the environment (fig. 1(d)). An oil immersion objective is used (N.A. 1.4) so that for calculations the nanoplatelets can be considered embedded in a homogenous medium of index 1.5. The distance of the core or emitting dipole can be estimated at a distance of 62 nm (which accounts for the 50-nm silica and the shell thickness) from a thick gold layer. The platelets are excited by a blue laser beam (450 nm with 3.2 µW power) and the emission is collected by the same objective.

The radiation pattern and emission polarization are analyzed simultaneously to characterize the emission dipole nature and orientation from each single emitter. On the one hand the sample Fourier plane (rear
focus plane of the objective) is imaged onto an EMCCD to perform the radiation pattern analysis: the image in the Fourier plane gives access to the distribution of the emitter’s radiation into the ($\theta$,$\phi$) angular coordinates (the z-axis being normal to the substrate). On the other hand, the emission polarization is analyzed by putting a rotating half wave plate followed by a polarized beam splitter (equivalent to a polarizer of angle $\alpha$) on the emission path. Two avalanche photodiodes are placed on the outputs of the cube and the normalized intensity $I = I_1/(I_1+I_2)$ is plotted as a function of $\alpha$. The setup was shown to modify polarization less than 5% (see discussion in S.I.).

The intensity of the emission of a given dipole analyzed by a rotating polarizer along angle $\alpha$ can be expressed in the form:

$$I(\alpha) = I_{\text{min}} + (I_{\text{max}} - I_{\text{min}}) \cos^2 \left( \Phi_{\text{max}} - \alpha \right)$$  \hspace{1cm} \text{(equation 1)}$$

It was shown in$^{12}$ that this curve can be used to obtain the ($\Theta$,$\Phi$) angular coordinates of the emitting dipole orientation (note that ($\Theta$,$\Phi$) coordinates are used to describe the dipole orientation while ($\theta$,$\phi$) coordinates are used to describe the radiation pattern ; ($\Theta$,$\Phi$) is the orientation of the dipole for a 1D dipole and the orientation normal to the dipole plane for a 2D dipole). The in-plane orientation $\Phi$ is obtained as $\Phi = \Phi_{\text{max}}$ for a 1D dipole and $\Phi = \Phi_{\text{max}} + 90^\circ$ for a 2D dipole. The degree of polarization $\delta$ is defined as $\delta = (I_{\text{max}} - I_{\text{min}}) / (I_{\text{max}} + I_{\text{min}})$. Its value depends on the measurement conditions (substrate index, objective numerical aperture, 1D or 2D dipole) and on the zenithal (out-of-plane) orientation $\Theta$ of the dipole. Figure 2(a) plots, for the experimental conditions described before, the theoretical relation between the degree of polarization $\delta$ and orientation $\Theta$ following$^{12}$. For $\Theta \sim 0^\circ$, the degree of polarization for both 1D and 2D dipoles is close to 0 as the system then presents axial symmetry. For $\Theta \sim 90^\circ$, the degree of polarization reaches its maximum (0.87 for a 2D dipole and 0.97 for a 1D dipole). Given this curve, the orientation $\Theta$ can be extracted from a measured value of $\delta$, however this requires that the 1D or 2D nature of the dipole is already known. The polarization analysis is not sufficient to determine both the dipole 1D/2D nature and its orientation.

The emission Fourier image can provide the necessary information to discriminate between 1D and 2D dipoles. Figure 2(b) plots the Fourier image of the emission from a 1D or 2D dipole with $\Theta = 0^\circ$ and $90^\circ$, calculated for the same measurement conditions following$^{26}$. For the two orientations considered, the Fourier images are qualitatively very different for the 1D and 2D dipoles (let us note that the gold+silica layer substrate is a key element at this point: a glass substrate would lead to more similar Fourier patterns for the 1D and 2D cases) (see S.I.). It is thus possible to fully determine the emission dipole nature and its associated orientation by analyzing the emission polarization and radiation pattern simultaneously. In the next section, we apply this method to the case of the cubic nanoplatelets.
Figure 2 (a) Theoretical emission degree of polarization ($\delta$) with respect to the dipole orientation $\Theta$ for 1D and 2D dipoles ($\lambda = 650$ nm, PMMA index 1.5, gold index 0.15 + 3.32i, distance dipole-gold 62 nm). (b) Theoretical radiation pattern for 1D or 2D dipoles with orientations 0 or 90° (see S.I. for calculation details).

Experimental results: horizontal and vertical 2D dipoles

Figure 3 (a) shows the polarization analysis curve $l(\alpha)$ for two typical nanoplatelets. The first platelet is representative of the main population of platelets, for which the degree of polarization is very close to 0 (a fit by eq. 1 gives for this platelet $\delta = 0.08$). The second platelet belongs to a second population for which a much higher degree of polarization (here $\delta = 0.79$) is obtained. Figure 3(c) shows in red (resp. green) a histogram of values of the degrees of polarization $\delta$ measured to the first (resp. second) population of platelets (note that the second population represents about 10% of the total platelets population). The emission degree of polarization is between 0 and 0.08 for the red population and between 0.77 to 0.88 for the green population. It is remarkable that no platelet was found with a degree of polarization between these two intervals: all platelets belonged to either one of the two very distinct populations.

As discussed in the first section, it is necessary to combine polarization with Fourier image analysis in order to fully characterize the emission dipole. For the first platelet, the very low degree of polarization suggests a 1D or 2D dipole with $\Theta = 0$ in either case. The measured Fourier image (fig. 3(b)) is qualitatively in agreement with the theoretical data calculated for a 2D dipole at $\Theta = 0^\circ$ and very different from a 1D dipole at $\Theta = 0^\circ$ (plotted in fig. 2(b)). From this data, figure 3(d) extracts the measured radiation patterns along directions $\phi = 0$ and $90^\circ$ and compares them with the calculated radiation pattern from a 1D or 2D dipole at $\Theta = 0^\circ$ (left and right figure respectively). These comparisons further confirm that the emission cannot be described by a 1D dipole but is on the other hand very well described by a 2D dipole at $\Theta = 0^\circ$. Similar results were found for all nanoplatelets of the first population. The slightly non-zero value of $\delta$ for
The presence of two distinct populations is then an indication of nanoplatelets deposited either horizontally ($\Theta = 0^\circ$) or on their side ($\Theta = 90^\circ$), as observed on the TEM images (fig. 1(b)). In this latter case,
the 2D-dipole emitter exhibits a dipole which is vertical to the metallic surface, which permits a maximum interaction with plasmons enhanced fields.

Figure 3: Polarization analysis curves (a) and Fourier images (b) measured for two typical nanoplatelets. (c) Histogram of the measured degree of polarization for the two populations of platelets with almost-zero (red) and high (green) degree of polarization. (d) Dots: experimental radiation patterns of the two platelets, extracted from fig. 3(b), along two $\phi$ directions (indicated in red and blue on fig. 3(b)); lines: tentative fits by the theoretical curve of a 1D (left) or 2D (right) dipole.

Further analysis of the dipolar transition

For the moment, we have considered that the nanoplatelet dipole could be modeled either by pure 1D and 2D dipoles, and finally excluded the 1D case. However, for other semiconductor nanoparticles, it has been reported that the emission might be a sum of a 2D dipole and a third orthogonal 1D dipole with different oscillator strengths\textsuperscript{16-17}. However these discussions relied either on the assumption that the dipole orientation was known\textsuperscript{16} or on very delicate quantitative analysis of the polarization and defocused image\textsuperscript{17}. In the following section, we will demonstrate that, for these nanoplatelets, we can exclude the emission from a third dipole to less than 5%.

Assuming the presence of a third dipole $d_3$ with a smaller oscillation strength, orthogonal to the 2D-dipole plane, we define the factor $\varepsilon$ to describe the relation of oscillation strengths for these three dipoles by

$$\frac{|d_3|^2}{|d_1|^2 + |d_2|^2} = \varepsilon$$

(with $d_1 = d_2$ here for a 2D dipole). The relation between the degree of emission polarization and the factor $\varepsilon$ in the case $\Theta = 90^\circ$ is plotted in Figure 4(a). When $\varepsilon = 0$, the degree of emission...
polarization in this case is thus 0.87 as shown in Figure 2(a) (2D dipole). When $\varepsilon = 0.5$, all three dipoles have equal oscillator strengths and the emission is unpolarized (“3D dipole”). The measured degrees of emission of the green population (histogram of fig. 3(c)) are just in the range 0.77 – 0.88, which corresponds theoretically to $\varepsilon = 0 - 0.03$. For a value of $\varepsilon = 0.05$, even by taking into account the elongated shape of the platelets, the theoretical value of the degree of polarization gets to 0.74, which remains below the experimental values.

We now consider the Fourier image data, for instance for the same emitter as in Figure 3(c). Figure 4(b-e) presents fits of the measured radiation patterns (same as fig. 3(d)) with the theoretical calculation for different values of factor $\varepsilon$. The value $\varepsilon = 0$ gives the best fit of the data, and $\varepsilon = 0.05$ is also very close. Starting from $\varepsilon = 0.1$, and more clearly at $\varepsilon = 0.25$, a difference between theory and experiment begins to be distinguishable. To conclude this study, the contribution from the third dipole $d_3$ for a nanoplatelet can be deduced from both measurements to be very small: less than 10 % from Fourier images and even less than 5 % from polarization data. The method thus provides an excellent precision for the dipole analysis of nanoemitters. The very fine control over the nanoplatelets synthesis provides emitters with very good agreement to theory.

**Figure 4**

(a) Calculated relation between emission degree of polarization $\delta$ and factor $\varepsilon$. (b-e) Comparison between the measured emission pattern along $\phi = \Phi_{max}$ (red dots) and $\phi = \Phi_{max} + 90^\circ$ (blue dots) and the calculated emission pattern from an incoherent sum of a 2D dipole and a 1D dipole at $\Theta = 90^\circ$, $\Phi = \Phi_{max} + 90^\circ$ for different values of $\varepsilon$.

**Conclusion**

It has been demonstrated that by combining the emission polarization analysis and radiation pattern analysis, the emission dipole nature and orientation of a single nanoemitter can be fully determined. The excellent agreement between the experiment data and the calculations further demonstrate the relevance of the method developed here. We demonstrated that the emission from cubic-shaped (thick-shell) nanoplatelet present perfect (better than 95 %) 2D-dipole behavior. Thanks to the independent analysis
of single emitters and to the combination of polarimetric and emission diagram measurement, we have demonstrated two single different orientations of deposition of the platelets; either horizontally or vertically. The occurrence of vertical platelets deposition, due to their cubic shape, allows for a vertical dipole component which can be of major interest for efficient surface plasmon coupling and emission optimization. This latter feature remains for other conventional emitters very challenging and even for spherical nanocrystals the occurrence of dipoles perpendicular to the surface by spin coating deposition is very low. Therefore, the use of cubic colloidal nanoplatelets, offering just 2 orientations for the dipoles, and quite high probability to obtain vertical orientation, is an important improvement for plasmonics. The easy operation of such colloidal nanoplatelets, their optical quality, and their semi deterministic orientation make them appropriate objects in photonic devices.

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Supporting information

Nanoplatelets synthesis and spectral properties; micro-photoluminescence setup, polarization and Fourier plane measurements; sample preparation; theoretical radiation pattern calculations.

Reference


