

Evaluation of oscillator strength in colloidal CdSe/CdS dots-in-rods

Ferruccio Pisanello^{*1,2}, Godefroy Leménager¹, Luigi Martiradonna³, Piernicola Spinicelli¹, Angela Fiore², Alberto Amo¹, Elisabeth Giacobino¹, Roberto Cingolani^{2,3}, Massimo De Vittorio^{2,3}, and Alberto Bramati¹

¹ Université Pierre et Marie Curie, Laboratoire Kastler Brossel, CNRS UMR8552, Ecole Normale Supérieure, 4 place Jussieu, 75005 Paris, France

² National Nanotechnology Laboratory of CNR/INFM, Scuola superiore ISUFI, Università del Salento, 16 Via Arnesano, 73100 Lecce, Italy

³ Istituto Italiano di Tecnologia (IIT), Center for Bio-Molecular Nanotechnology, Via Barsanti 1, Arnesano, 73010 Lecce, Italy

Received 19 October 2009, accepted 20 February 2010

Published online 9 August 2010

Keywords CdSe/CdS core/shell structures, cavity electrostatics, photonic crystals, polaritons

* Corresponding author: e-mail pisanello@spectro.jussieu.fr, Phone: +33 1 44 27 72 66, Fax: +33 1 44 27 38 45

The oscillator strength in CdSe/CdS colloidal dot-in-rods is evaluated and assessed to be of ~ 1.5 . On the basis of this finding, the possibility to reach the strong coupling regime with photonic crystals nanocavities is discussed. In spite that carefully choosing the cavity parameters the

strong coupling regime could be analytically achieved at room temperature, theoretical considerations show that the typical Rabi doublet cannot be resolved. The work draws also a viable strategy toward the observation of the strong coupling at cryogenic temperatures.

© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Light-matter coupling in nano- and micro-cavities is a fundamental research field which allows the investigation of intriguing Quantum Electro Dynamic (QED) phenomena, such as exciton-polaritons [1] and the generation of non-classical light fluxes [2]. When an optical emitter is placed in a resonant cavity and the energetic distributions of the two systems allow an interaction between the two oscillators, two different phenomena, known as *weak* and *strong coupling*, can be observed [3]. In the *weak coupling regime*, the spontaneous emission rate of an emitter X interacting with an optical mode C is modified by a factor which depends on how the energy is confined inside the cavity [4]. Instead, in the *strong coupling* condition the interaction between X and C leads to a coherent exchange of energy between them, thus resulting in vacuum Rabi oscillations [3].

Both these types of interactions have been widely investigated in the infrared spectral region by using epitaxially grown materials, such as quantum wells, quantum wires and quantum dots (QDs) and advanced optical resonators such as Bragg reflectors based microcavities photonic crystals (PhC) defects and microdisks [1, 5-8]. On the other hand, an emerging technology is based on the

chemical synthesis of high luminescent QDs, so called colloidal nanocrystals (NCs). These emitters are crystalline structures with a size smaller than the Bohr radius, thus allowing discrete energy levels and the investigation of quantum mechanisms also at room temperature. Moreover, the low cost synthesis procedure and their versatility make them appealing materials for several fields, such as non classical quantum communications and biology [2, 9]. In order to rule their emission properties, several NCs compositions and shapes have been proposed in past years, allowing polarized emission and very high quantum yields [10, 11]. If colloidal NCs applications are still limited by several drawbacks, such as blinking, spectral diffusion, low oscillator strength and short coherence times, it has been recently demonstrated that by engineering the environment surrounding the quantized levels the blinking phenomenon can be overtaken [12, 13]. Among the proposed strategies to realize asymmetric core/shell structures, the dot-in-rod (DR) configuration, in which the CdSe spherical core is surrounded by an elongated CdS rod-like shell [14], presents several properties that make it very promising to reach the strong coupling regime. It has been demonstrated that such nanosystems are characterized by a shorter ex-

© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

cited state lifetime compared to spherical nanocrystals and that the elongated shape leads to a strong electric field inside them [15]. These two parameters are strictly linked to the so called *oscillator strength*, which plays a key role in the dynamic of strongly coupled systems [16]. Indeed, with elongated-core NCs, so called nanorods (NRs) [17] the strong coupling regime has been reached at cryogenic temperature by coupling them with dielectric nanospheres [18].

The goal of this paper is to evaluate if CdSe/CdS DRs are suitable quantum emitters for strongly coupled systems. In the following, the concept of strong coupling will be introduced and the fundamental parameters which must be ruled to reach this regime will be discussed with particular attention to the strong coupling of a single colloidal NC in a PhC cavity. The oscillator strength of an isolated DR will be measured by means of time resolved spectroscopy in order to understand if these nanoclusters are suitable to reach the strong coupling regime.

2 The strong coupling regime A system constituted by a QD (emitting at $\hbar\omega_X$) strongly coupled to an optical mode in a photonic cavity (at energy $\hbar\omega_C$) is described by the Hamiltonian [19]

$$H = \hbar\omega_C a^\dagger a + \hbar\omega_X b^\dagger b + g(a^\dagger b + ab^\dagger), \quad (1)$$

where a and b are the cavity and exciton operators, respectively. The last term describes the linear coupling between X and C. The coupling constant g is a fundamental parameter to design a strongly coupled system and is bound to the properties of both X and C. By taking into account the relaxation terms of both X and C and if the detuning between X and C is zero ($\hbar\omega_X = \hbar\omega_C = \hbar\omega_0$) the eigen-energies of a strongly coupled system are given by the following expression:

$$E_{\pm} = \hbar\omega_0 - i\frac{\gamma_X + \gamma_C}{2} \pm \sqrt{g^2 - \left(\frac{\gamma_C - \gamma_X}{4}\right)^2} \quad (2)$$

where γ_C and γ_X are the linewidths (full width at half maximum) of C and X, respectively. When the X-C interaction becomes larger than the combined X-C decay rate (assumed as threshold t), i.e.

$$g^2 > \frac{(\gamma_C - \gamma_X)^2}{16} = t, \quad (3)$$

the real part of E_+ and E_- are different [$Re(E_+) \neq Re(E_-)$] and the two oscillators allowed to coherent exchange energy. In this picture the coupling constant g is related to the oscillator strength of X (f) and to the modal volume (V) of C by Eq. (3):

$$g^2 = \frac{1}{4\epsilon_0\epsilon_r} \frac{e^2 f}{mV}, \quad (4)$$

where m is the free-electron mass and ϵ_0 and ϵ_r are the dielectric constant of the vacuum and of the relative dielectric constant of the medium. The photoluminescence (PL) spectrum of this system, according with Ref. [3], is:

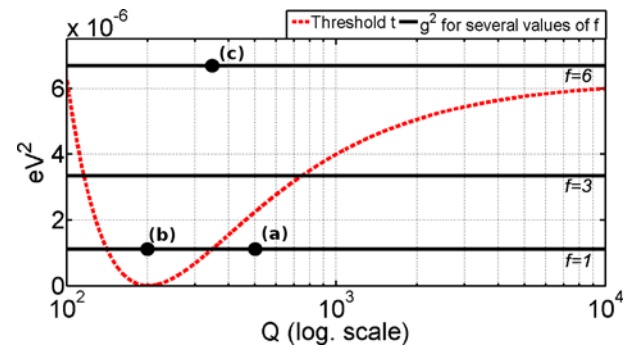


Figure 1 Threshold t as a function of the cavity Q-factor (red dashed line) and coupling constants g^2 for several values of f and a modal volume $V=0.48(\lambda/n)^3$. Black dots refer to the graphs of Fig. 2.

$$S(\hbar\omega) \propto \left| \frac{E_+ - \hbar\omega_0 + i\frac{\gamma_C}{2}}{\hbar\omega - E_+} - \frac{E_- - \hbar\omega_0 + i\frac{\gamma_C}{2}}{\hbar\omega - E_-} \right|^2 \quad (5)$$

From Eq. (3) it is clear that the higher the cavity modal volume, the lower the coupling constant between X and C. The best way to obtain a low modal volume is to use a PhC based nanocavity [20]. In the visible spectral range these resonators present lower quality factors with respect to the infrared wavelengths because of the low refractive index of transparent materials between 500 nm and 700 nm [21]. However, V is preserved and the modal function can be confined in a volume lower than the cubic wavelength. In particular, the nanocavity proposed in Ref. [22] gives the possibility to work with resonant modes having a modal volume from $V=0.48(\lambda/n)^3$ to $V=0.7(\lambda/n)^3$ and, importantly, a quality-factor (Q-factor) tunable over a broad range in a simple way, with a maximum value of $Q \sim 800$. Let's suppose that a single colloidal DR emitting at $\hbar\omega_X = 2.072 eV$ with a room temperature linewidth of $\gamma_X = 10 meV$ [15] is localized in the center of a PhC cavity with a quality factor $Q = (\hbar\omega_C) / \gamma_C$. Figure 1 reports the behaviour of the threshold $t = (\hbar\omega_C / Q - \gamma_X)^2 / 16$ as a function of the cavity Q-factor. When the cavity linewidth approaches γ_X the threshold t is minimized and the condition (3) achievable also for lower oscillator strength. For example, as shown by the continuous lines in Fig. 1, the higher f the wider the interval of Q for which $g^2 > t$. However t is an asymptotic threshold in respect to Q , i.e. $\lim_{Q \rightarrow \infty} t = \gamma_X^2 / 16$, and t can be overtaken also for high Q and $g > \gamma_X / 4$. This is justifiable in a simple way: if f is not enough to allow a coherent exchange of energy between X and C this could be compensated by approaching the two energy configurations themselves.

An experimental evidence that the strong coupling condition regime is reached is represented by a doublet in the PL spectrum. However, because of the relation between Eq. (4) and Eq. (2), a non-zero difference between $Re(E_+)$ and $Re(E_-)$ is not a sufficient condition for the observation of two different peaks in $S(\hbar\omega)$. Some examples

of the possible situations are reported in Fig. 2 with reference to the points evidenced in Fig. 1. Figure 2 shows that below the threshold t (i.e. $Re(E_+) = Re(E_-)$) the two eigenstates are frequency-degenerate leading to a single PL peak. The point (b) is instead just above the threshold t and the non-degeneracy of the eigenstates is clearly visible. However, a single peak in the spectrum is still present because the vacuum Rabi splitting is significantly smaller than the spectral width of each peak. This is not the case of Fig. 2(c), in which the PL spectrum is modified by the presence of the vacuum Rabi oscillations by virtue of a stronger oscillator strength (i.e. $g^2 \gg t$).

As we will discuss in the following, the oscillator strength of colloidal NCs at room temperature is extremely low. In spite of that, for low f , the condition $Re(E_+) \neq Re(E_-)$ is fulfilled, and the strong coupling is theoretically reached. However, as in the case of Fig. 2(b), the observation of strong coupling features would not be possible by PL measurements because the doublet state is not evident in $S(\hbar\omega)$.

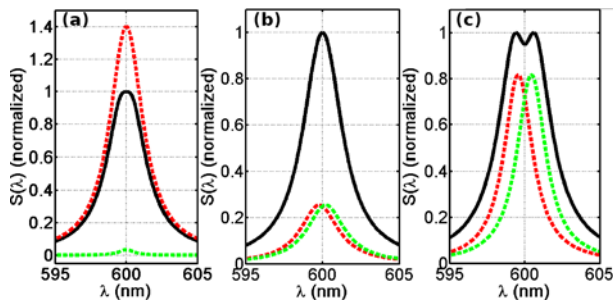


Figure 2 Photoluminescence spectra (black continuous lines) computed via Eq. (5) for the points (a), (b) and (c) of Fig. 1. Coloured dashed line represents the eigenstates.

3 Methods and techniques

3.1 Colloidal dot-in-rods synthesis

The CdSe/CdS DRs were synthesized using the procedure reported in Ref. [14]. The CdSe cores were prepared by mixing TOPO (3.0g), OHPA (0.280g) and CdO (0.060g) in a 50 mL flask, heated to ca. 150 °C and exposed to vacuum for ca. 1 hour. Then, under nitrogen, the solution temperature was increased to above 300 °C to dissolve the CdO until it turns optically clear and colorless. Then 1.5 g of TOP was injected in the flask and heated to 360 °C. After that, a Se solution in TOP (0.058 g Se + 0.360 g TOP) was quickly injected in the flask and the reaction was stopped after 1 min by removing the heating mantle. CdSe seeds were precipitated with methanol, redissolved in toluene, reprecipitated with methanol, and finally dissolved in 1mL of TOP.

In order to obtain a preferred axis growth for the CdS shell, OHPA (0.290 g), HPA (0.080 g), TOPO (3.0 g) and CdO (0.060 g) were mixed in a three-neck flask, heated at 150 °C, and pumped to vacuum for ca. 1 hour. The temperature was first increased up to 300 °C and stabilized at 350 °C after the injection of 1.5 g of TOP. Then a solution of S in TOP (0.120 g S + 1.5 g TOP) containing 8×10^{-8} mol

of readily prepared CdSe nanocrystals (diameter $c \sim 2.7$ nm) dissolved in TOP was quickly injected in the flask. The shells were allowed to grow for about 6-8 minutes after the injection, after which the heating mantle was removed. The resulting nanocrystals (mean length 30 nm) were precipitated with methanol, washed by repeated re-dissolution in toluene and precipitation with the addition of methanol. At the end they were dissolved in toluene.

3.2 Optical characterization A nanomolar solution of DRs diluted in toluene was dropcasted on a microscope coverslip. A circularly-polarized picosecond-pulsed laser (at a wavelength of 404 nm) was focused on the sample by means of a microscope air objective. The single DR emission was collected through the same objective and sent into a Hanbury-Brown and Twiss setup based on two avalanche photodiodes. The collected signals were elaborated by means of a time-resolved data acquisition card (Time-Harp200, Picoquant). By triggering the acquisition with the laser pulses individual photon-detection events with their absolute arrival time and their delay from the laser pulse were recorded, thus allowing to analyze the PL time traces and the radiative decay behavior of the system under investigation, up to a time-resolution of 36ps. In order to confirm that the measurements were carried out on a single nanoparticle, antibunched measurements were performed as explained in Ref. [23]. All measurements were performed at room temperature in air at the single NC level.

4 Experimental results and discussions

Equation (4) and Fig. 1 show that the emission oscillator strength f is one of the parameters which define the regime of the coupled system. f can be expressed as a function of the radiative decay rate $1/\tau_{Xr}$, i.e.

$$f = \frac{6m\epsilon_0\pi c \lambda^2}{q^2 n} \frac{1}{\tau_{Xr}}, \quad (6)$$

where q is the electron charge. The average lifetime of the transition X (τ_X) can be estimated by fitting the decay curve obtained by the delays histogram between the laser pulses and the received photons. A typical decay behaviour measured on a single DR is reported in Fig. 3; the experimental data are well fitted by a mono-exponential decay function e^{-t/τ_X} and τ_X has been assessed to be ~ 11 ns. It is evident that this method estimates the total decay rate ($1/\tau_X$), which is the sum of the radiative recombination rate and the non radiative one ($1/\tau_{Xnr}$), i.e.

$$\frac{1}{\tau_X} = \frac{1}{\tau_{Xr}} + \frac{1}{\tau_{Xnr}}. \quad (7)$$

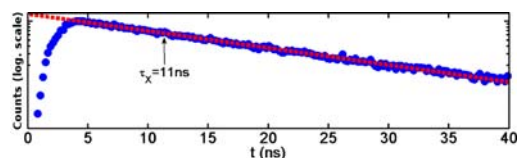


Figure 3 Decay curve measured on an isolated DR (blue dots) and its exponential fit (red dashed line).

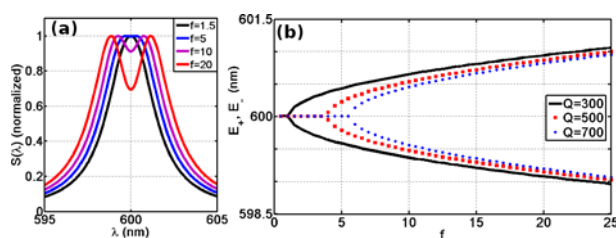


Figure 4 (a) Luminescence spectra for several values of the oscillator strength and $Q=300$. (b) Spectral position of the eigenmodes for several values of Q and as a function of f .

However it has been demonstrated that for colloidal NCs and DRs the internal quantum efficiency approaches 100% [14, 24]. As a consequence, the non radiative rate can be considered negligible and the estimated τ_X assigned to purely radiative processes, i.e. $\tau_X = \tau_{Xr}$. By considering $\tau_X \sim 11$ ns the oscillator strength obtained via Eq. (6) can be assessed to be 1.5. Lifetime measurements as a function of the intensity power were also performed. Consistently with the results reported in ref. [15], the lifetime of the excited state is almost constant at values of ~ 11 ns.

On the basis of the discussion in Section 2, we can infer that, for a cavity with $V \sim 0.48(\lambda/n)^3$, a Q -factor between 150 and 400 is needed to reach the strong coupling regime with a DR characterized by an oscillator strength of $f=1.5$. However these parameters lead to the condition of Fig. 2(b), in which the strong coupling is theoretically achieved but not experimentally observable. Moreover, it has been demonstrated that colloidal nanorods presents a lifetime at cryogenic temperatures of $\tau_r < 1$ ns [18] leading to a higher oscillator strength. For example $f \sim 20$ for $\tau_r = 800$ ps can be obtained via Eq. (6). Figures 4(a) and (b) display that for these values f the doublet is clearly visible in the PL spectrum and that the two eigenmode are not degenerated, making us to envision the possibility to observe the strong coupling between a colloidal dot-in-rod and a photonic crystals cavity at cryogenic temperatures.

5 Conclusions In summary, we discussed the possibility to reach the strong coupling regime with colloidal dots-in-rods. The oscillator strength of DRs has been measured by time resolved spectroscopy, assessing a value of $f \sim 1.5$ at room temperature. Moreover, photonic crystals nanocavities have been suggested as appealing nanostructures to achieve this result because of their extremely low modal volume and the possibility to tune the quality factor of the resonant mode. Taking into account the obtained oscillator strength, analytical computations showed the possibility to achieve a strong coupling which nevertheless does not lead to a visible doublet in the PL spectrum. However, taking into account a decreasing of the DRs lifetime at cryogenic temperatures, the possibility to experimentally observe the vacuum Rabi splitting in the investigated system can be envisioned.

Acknowledgements The help of Benedetta Antonazzo in the synthesis of high quality dot-in-rods is acknowledge. This

work was supported by the Agence Nationale de la Recherche (reference number ANR-08-BLAN-0070-01).

References

- [1] C. Weisbuch, M. Nishioka, A. Ishikawa, and Y. Arakawa, *Phys. Rev. Lett.* **69**, 3314 (1992).
- [2] A. Quattieri, G. Morello, P. Spinicelli, M. T. Todaro, T. Stomeo, L. Martiradonna, M. De Giorgi, X. Quélin, S. Buil, A. Bramati, J. P. Hermier, R. Cingolani, and M. De Vittorio, *New J. Phys.* **11**, 033025 (2009).
- [3] L. C. Andreani, G. Panzarini, and J.-M. Gérard, *Phys. Rev. B* **60**, 13276 (1999).
- [4] E. M. Purcell, *Phys. Rev.* **69**, 681 (1946).
- [5] J. P. Reithmaier, G. Sek, A. Löffler, C. Hofmann, S. Kuhn, S. Reitzenstein, L. V. Keldysh, V. D. Kulakovskii, T. L. Reinecke, and A. Forchel, *Nature* **432**, 197 (2004).
- [6] T. Yoshie, A. Scherer, J. Hendrickson, G. Khitrova, H. M. Gibbs, G. Rupper, C. Ell, O. B. Shchekin, and D. G. Depp, *Nature* **432**, 200 (2004).
- [7] K. Hennessy, A. Badolato, M. Winger, D. Gerace, M. Atatüre, S. Gulde, S. Fält, E. L. Hu, and A. Imamolu, *Nature* **445**, 896 (2007).
- [8] E. Peter, P. Senellart, D. Martrou, A. Lemaître, J. Hours, J. M. Gérard, and J. Bloch, *Phys. Rev. Lett.* **95**, 067401 (2005).
- [9] W. J. Parak, D. Gerion, T. Pellegrino, D. Zanchet, C. Micheel, S. C. Williams, R. Boudreau, M. A. Le Gros, C. A. Larabell, and A. P. Alivisatos, *Nanotechnology* **14**, R15 (2003).
- [10] X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, and A. P. Alivisatos, *Nature* **404**, 59 (2000).
- [11] X. Brokmann, L. Coolen, M. Dahan, and J. P. Hermier, *Phys. Rev. Lett.* **93**, 107403 (2004).
- [12] B. Mahler, P. Spinicelli, S. Buil, X. Quélin, J. P. Hermier, and B. Dubertret, *Nature Mater.* **7**, 659 (2008).
- [13] X. Wang, X. Ren, K. Kahen, M. A. Hahn, M. Rajeswaran, S. Maccagnano-Zacher, J. Silcox, G. E. Cragg, A. L. Efros, and T. D. Krauss, *Nature* **459**, 686 (2009).
- [14] L. Carbone et al., *Nano Lett.* **7**, 2942-2950 (2008).
- [15] G. Morello, F. Della Sala, L. Carbone, L. Manna, G. Maruccio, R. Cingolani, and M. De Giorgi, *Phys. Rev. B* **78**, 195313 (2008).
- [16] M. D. Leistikow, J. Johansen, A. J. Kettelarij, P. Lodahl, and W. L. Vos, *Phys. Rev. B* **79**, 045301 (2009).
- [17] J. T. Hu, L. S. Li, W. Yang, L. Manna, L. W. Wang, and A. P. Alivisatos, *Science* **292**, 2060 (2001).
- [18] N. Le Thomas, U. Woggon, and O. Schöps, *Nano Lett.* **6**, 557 (2006).
- [19] F. P. Laussy, E. del Valle, and C. Tejedor, *Phys. Rev. B* **79**, 235325 (2009).
- [20] O. Painter, R. K. Lee, A. Scherer, A. Yariv, J. D. O'Brien, P. D. Dapkus, and I. Kim, *Science* **284**, 1819 (1999).
- [21] L. Martiradonna, L. Carbone, A. Tandraechanurat, M. Kitamura, S. Iwamoto, L. Manna, M. De Vittorio, R. Cingolani, and Y. Arakawa, *Nano Lett.* **8**, 260 (2008).
- [22] F. Pisanello, M. De Vittorio, and R. Cingolani, *Superlattice Microstruct.*; doi:10.1016/j.spmi.2009.06.003.
- [23] F. Pisanello et al., *Superlattices Microstruct.* doi:10.1016/j.spmi.2009.06.009 (2009).
- [24] S. Deka et al., *J. Am. Chem. Soc.* **131**, 2948 (2009).