Spectral jitter of single CdSe/ZnS nanoparticles: Where is the charge?

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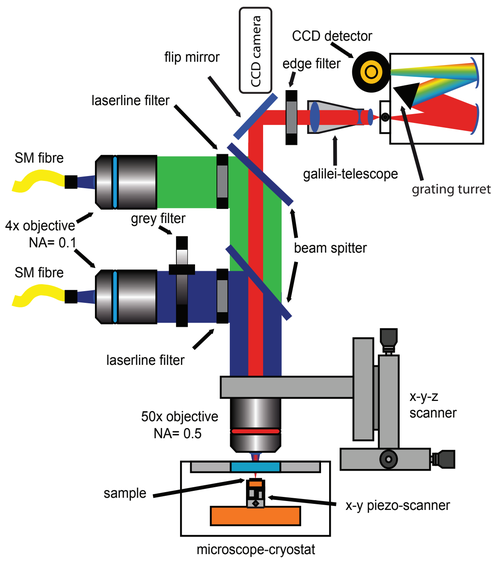
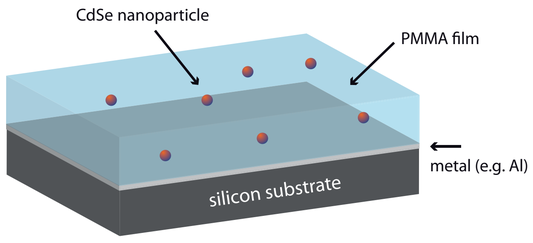
Measurement setup



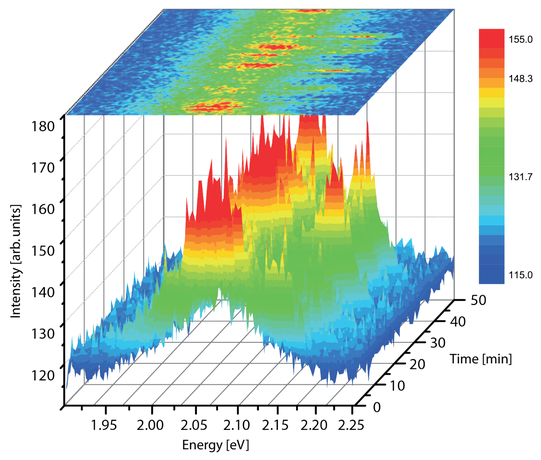
- Single quantum dot and nanoparticle photoluminescence (PL) from 8 to 300 K
- µ-PL and Raman measurements
- 405 nm and 532 nm laser with power ranging from µW to W

Sample design



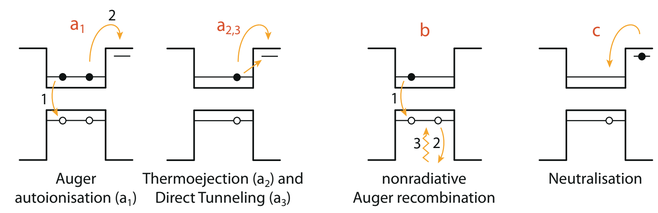
- CdSe/ZnS (core/shell) nanoparticles (NP) are dispersed in toluene (C_7H_8) and 1% PMMA
- An extremely dilute nanoparticle dispersion is necessary (about 1pmol/ml), which results in less than 1 NP per µm²
- Some substrates are covered with a thin metal layer
- CdSe nanoparticles are embedded in a PMMA matrix

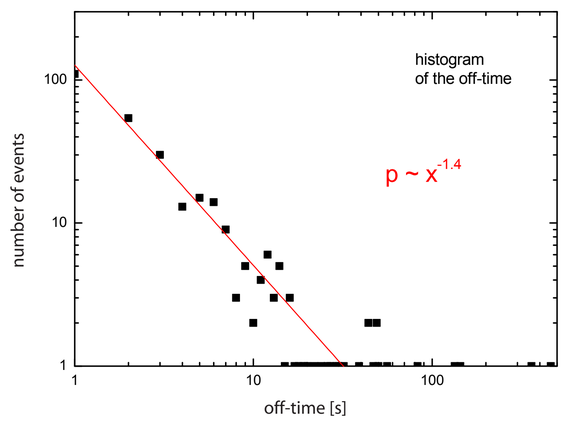
PL: Blinking and statistics



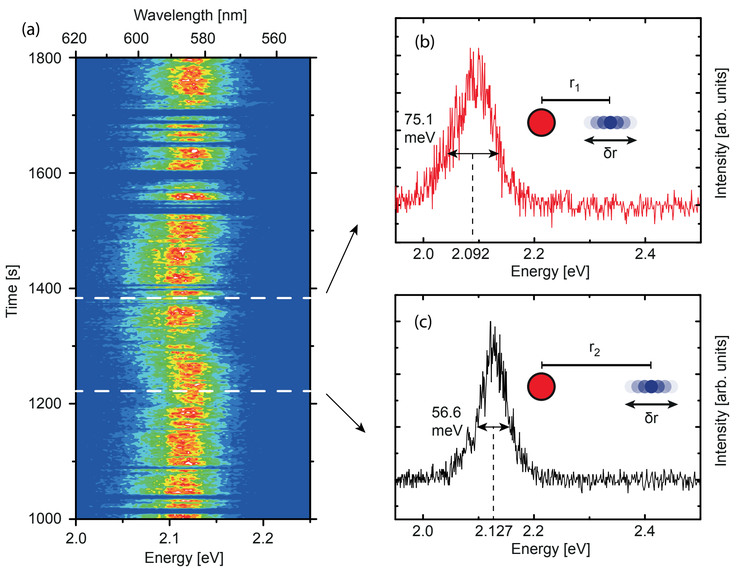
- Continuously illuminated single CdSe/ZnS nanoparticles randomly switch on and off (blinking)
- An additional charge inside the quantum dot leads to non-radiative Auger recombination (Efros-Rosen Model) [1]
- Evaluation of on/off-statistics exhibits a power-law time dependence

Efros-Rosen model





Spectral time evolution

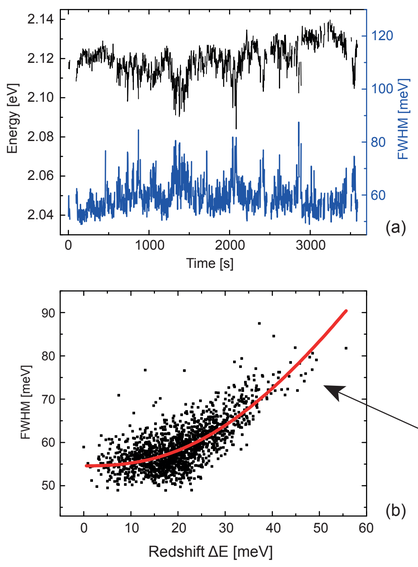


$$\Delta E = \alpha \mathcal{E}^2$$

- A single CdSe nanoparticle exhibits spectral diffusion, i.e. reversible fluctuations of the emission energy
- An anticorrelation exists between emission energy and FWHM

Conclusion:
- The electric field of outside charge carriers leads to a quantum confined Stark shift (QCSE) [2], alterating both energy and linewidth of the naoparticle's emission line

Energy-FWHM-anticorrelation: Single charge assumption



- PL emission energy (black) and its corresponding FWHM (blue)
- An anticorrelation is clearly observable
- The electric field of a single electron ouside a dielectric sphere, screened by the surrounding permittivity [3]:

$$\mathcal{E} = \frac{e}{4\pi\epsilon_r^e r^2} \cdot \frac{3}{2+\epsilon_r^{\mathrm{core}}/\epsilon_r^e}$$

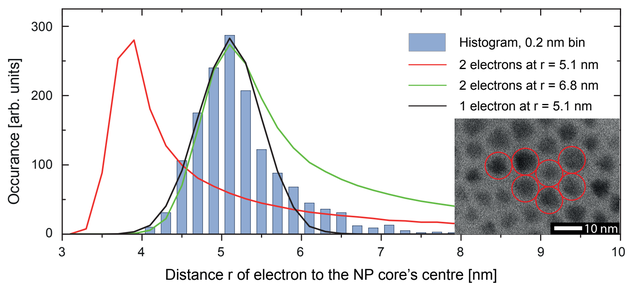
- Calculation of the FWHM by using the QCSE results in

$$FWHM = \delta F = \sqrt{(\delta F_T)^2 + k^2(\Delta E)^{5/2}(\delta r)^2}$$

- Due to the quadratic nature of the Stark shift, PL energies, which are strongly redshifted by the electric field, will be more susceptible to small field variations than PL energies, which are near the energy maximum, the apex of the QCSE parabola
- The assumption of a constant charge carrier fluctuation within the exp. integration time leads to a superlinear linewidth-redshift dependence [4]

Conclusion:
- A fit with the equation above results in an optical-phonon-scattering-limited linewidth of δF_T = 54 meV and a mean charge carrier fluctuation of δr = 1.2 nm

Calculation of the electron's distance



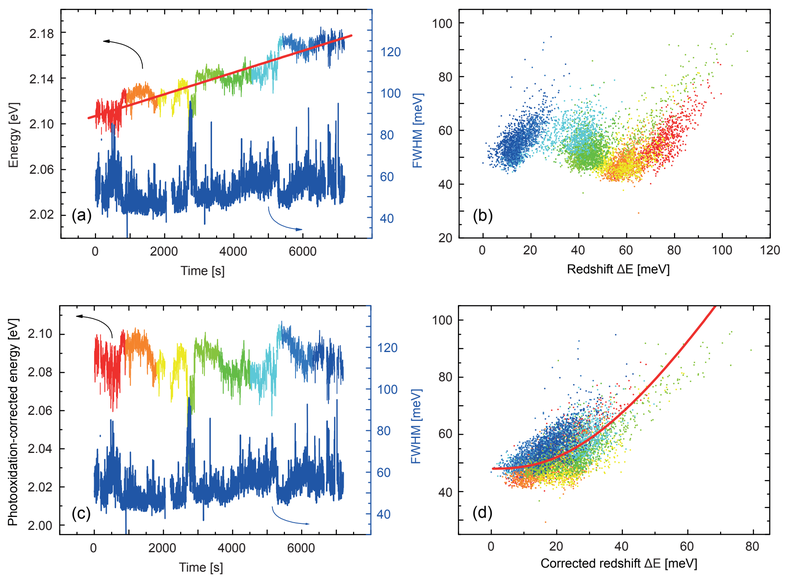
With Stark's equation and the Coulomb field of a single charge we can calculate the average distance of the electron to the nanoparticle's centre

$$r = \sqrt[4]{\frac{\alpha e^2}{(4\pi\varepsilon_r^e\varepsilon_0)^2\Delta E}\left(\frac{3}{2+\varepsilon_r^{\mathrm{core}}/\varepsilon_r^e}\right)^2}$$

- Strongly peaked Gaussian-shaped distance distribution with an its maximum at 5 nm (±1nm)
- The nanoparticles exhibit an overall radius of 5 nm (see TEM inset), consisting of 2 nm core, 1 nm shell and 2 nm ligands
- The assumption of a second electron at the same distance would lead to a strongly asymmetric distribution and unphysical distances

Conclusion:
- The fluctuating electron is situated in the ligands or on the outer boundary
- The observed asymmetry might be caused by additional fluctuating charges at least 10 nm away

Blueing



(a) Spectral diffusion and linewidth dependence of a single CdSe/ZnS nanoparticle influenced by photooxidation (PO) [5], which shifts the emission line towards higher energies ("blueing") up to 150 meV

(b) Plotting FWHM versus the redshift results in a blur of points

(c) When the blueing is eliminated by a linear correction (red line), the energy-FWHM-anticorrelation is again visible, even though the emission energy has changed continuously

(d) The dependence between FWHM and redshift can again be fitted with the equation above and leads to the same results

Conclusion:
- Photooxidation and FWHM-energy-anticorrelation are two distinct effects
- Since blueing influences core and shell and can be well separated from the anticorrelation, it supports the conclusion that the charge is located in the ligands

References

[1] A. L. Efros, Nature Materials **7**, 612 (2008).
[2] J. Müller et al., Physical Review B **72**, 205339 (2005).
[3] J. D. Jackson, Classical Electrodynamics, 3rd ed. (Wiley, 1999).
[4] D. Braam et al., arXiv:1303.5625
[5] W.G.J.H.M. van Sark et al., Chemphyschem **3**, 871 (2002)

Conclusion

We find that our data can be well described using a model of a single migrating charge in the vicinity of the particle. Our data allows us to deduce the typical distance of the external charge as a function of the PL energy shift.
The deduced values show that the fluctuating charge is located within the ligands layer, or on its boundary surface.
This conclusion is supported by an evaluation of PL data from particles which also show blueing, caused by photooxidation. The data furthermore allows us to estimate the mean spatial fluctuation of δr = 1.2 nm in the time interval of t = 2 s.

Outlook

Our findings show that both the shell thickness and the choice of ligands for CdSe nanoparticles may be crucial steps to reduce spectral jitter and inhomogeneous line broadening, two effects, which are commonly found in nanoparticle devices, particularly when working at technically relevant temperatures. Therefore, more attention should be given to the ligand layer when trying to improve the optical properties of nanoparticle-based devices.