Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Photoluminescence of a Single Quantum Emitter in a Strongly Inhomogeneous Chemical Environment

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Synthesis of silica nanoparticles and size distribution analysis

SiO_2 nanoparticles were synthasized by a modified Stöber method in a biphasic system using an amino acid as base catalyst [1, 2]. In a typical preparation, L-arginine (0.24 mmol) was dissolved in 40 mL of deionized water under gentle mixing. Then 2.1 mL of cyclohexane was added and the mixture was heated to 65°C. Once reached this temperature, the reaction was started by the addition of 3.2 mL of TEOS. The solution was kept under constant stirring at 65°C for 24 h before cooling down at room temperature. The resulting SiO_2 colloidal sample was dried under vacuum and stored as powder.

A transmission electron microscope (Philips model 208, operating at 80 kV of beam acceleration) was used to morphologically characterize the SiO_2 samples. A drop of the SiO_2 aqueous suspension was deposited in a 400 mesh copper-coated with Formvar support grid and left overnight in a desiccator to allow the solvent to evaporate. Figure S1 shows two exemplary transmission electron microscopy images of SiO_2 nanoparticles.

We determined the nanoparticles size distribution from the TEM images (figure S2). By fitting the histogram with a Gaussian function, we obtained the average particle diameter of 11±1 nm.

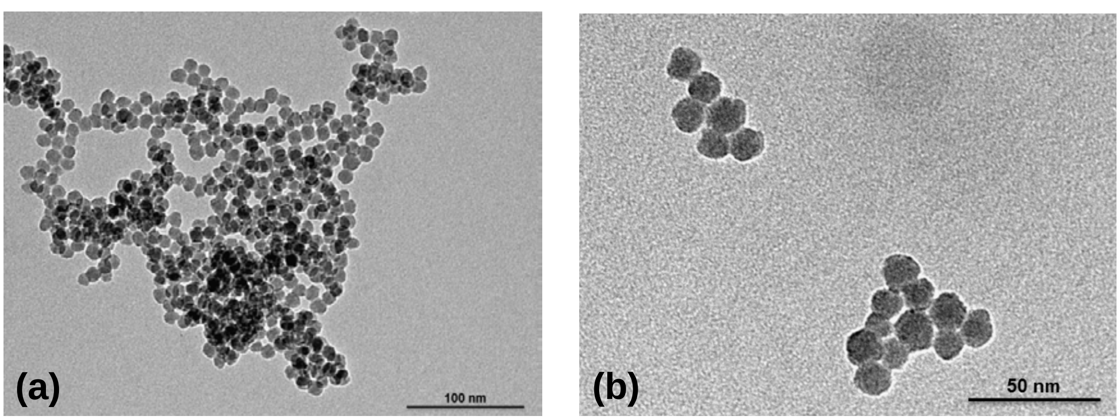

Figure S1. Transmission electron microscopy images of SiO_2 nanoparticles.

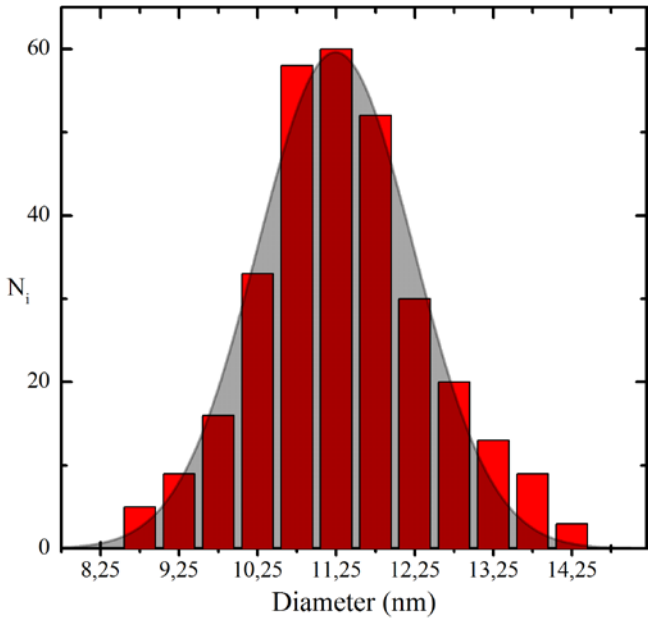

Figure S2. Histogram of the NP size from the analysis of TEM images. The size distribution was fitted with a Gaussian function. The fitted parameters are: Mean diameter = 11.2 nm; σ = 0.99 nm; FWHM = 2.34 nm.

Photoluminescence measurements

Photoluminescence measurements were performed with a home-built confocal microscope equipped with an objective lens of high numerical aperture (Apo N, 60×/1.49 NA oil immersion, Olympus). A pulsed white light laser system (Fianium SC400-4-20, pulse width ~50 ps, repetition rate 20 MHz) with a tunable filter (AOTFnC- 400.650-TN) served as the excitation source. The light was reflected by a non-polarizing beam splitter towards the high numerical aperture objective lens (Apo N, 60×/1.49 NA oil immersion, Olympus), and backscattered excitation light was blocked with a long pass filter (Semrock EdgeBasic BLP01-488R). Collected photoluminescence was focused onto the active area of an avalanche photo diode (PicoQuant τ-SPAD). Data acquisition was accomplished with a multichannel picosecond event timer (PicoQuant HydraHarp 400). PL spectra of single SiO_2 were recorded using a spectrograph (Andor SR 303i) and a CCD camera (Andor iXon DU897 BV).

For the direct measurements of the single SiO_2 NPs excitation spectra, we used the following optical filters. The PL was transmitted through the Semrock FF01-593/40 BrightLine. For transmitting the excitation laser light, the following filters were used: Chroma Z467/10X, Semrock FF01-474/23 BrightLine, Chroma X485/10X, Semrock FF01-504/12 BrightLine, Semrock FF01-525/45 BrightLine, Semrock FF01-536/40 BrightLine, Semrock - LL02-561 MaxLine.

For the single particle PL study, a 10 µl droplet of aqueous solution of SiO_2 NPs was spin coated on the surface of a clean glass cover slide at rotational speed 2000 rpm. Prior to the PL study, each glass cover slide was verified to be free of contamination using the same excitation conditions as were used for the single particle study. For the ensemble measurement, a 20 µl droplet of the same SiO_2 NP concentration was dried on the surface of a clean glass cover slide. This resulted in a dense monolayer of SiO_2 NPs on the substrate surface. From the total PL intensity of the ensemble PL spectrum, we estimated that near 100 SiO_2 NPs were located within the diffraction limited focal spot.

The excitation conditions were kept the same both for single particle and ensemble measurements.

Generation of an azimuthally polarized laser beam

An azimuthal polarization of the excitation light was generated by passing a linearly polarized laser beam through the polarization converter (Arcoptix). The mode converter is composed of a liquid crystal cell. Depending on the local alignment of the liquid crystal, which is controlled by the applied voltage, the polarization of the incident light is turned by a certain angle. The schematic is shown in figure S3 (a). A pinhole is used to remove higher spatial frequencies. A focused azimuthally polarized laser beam contains only the in-plane component of polarization, which is directed around the center of the focal spot (figure S3 (b)). The characteristic distribution of the excitation field within the focal spot allows for probing the orientation of the excitation transition moment of a single emitter within the horizontal plane. Figure S3 (c) shows a simulated excitation pattern of a single emitter, excited with an azimuthally polarized laser beam. The white arrow represents the projection of the transition dipole moment on the horizontal plane. Further details of the single molecule spectroscopy using an azimuthally polarized laser beam can be found elsewhere [3, 4].

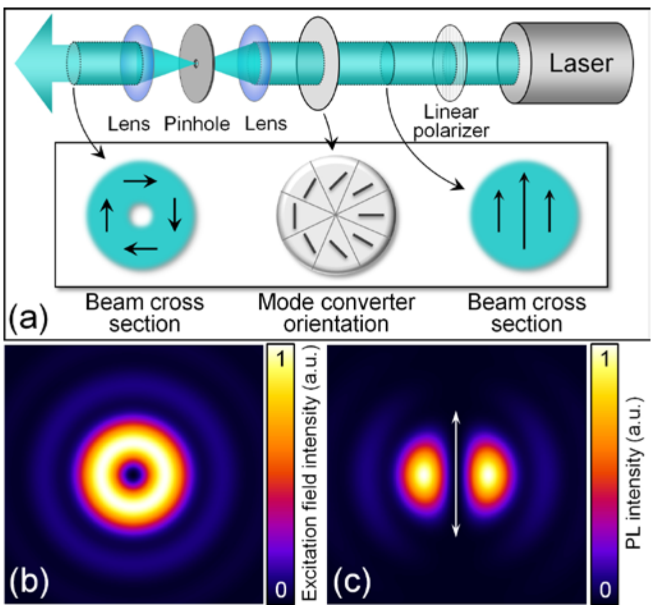

Figure S3. (a): Scheme of the polarization conversion optical line. (b): Excitation field in-plane and longitudinal components intensity distribution within the focal spot of the microscope objective in the case of the radially polarized laser beam. The distribution is calculated for the case of a 1.49 numerical aperture objective and an excitation wavelength of 488 nm. (c): simulated excitation pattern of a single dipole emitter in case of the excitation with an azimuthal mode. The arrow shows the projection of the excitation transition dipole of an emitter on the horizontal plane.

Photoluminescence lifetime imaging of single SiO_2 nanoparticles

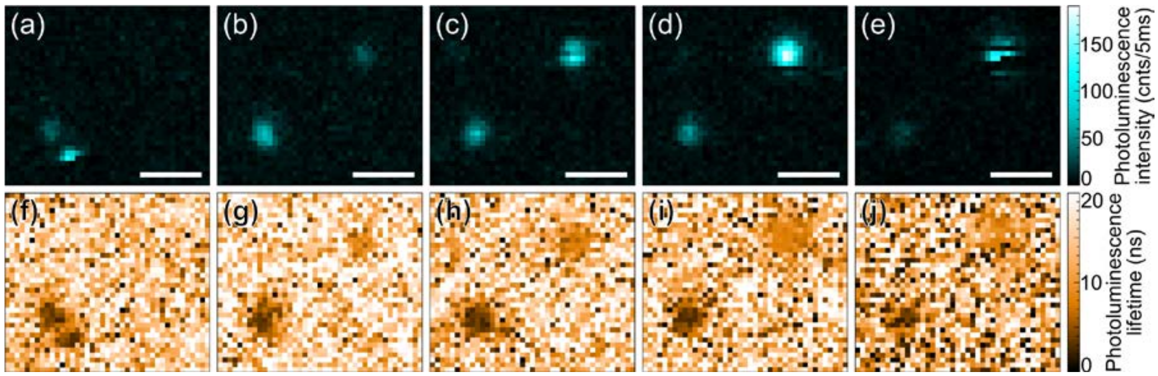

Figure S4. Photoluminescence intensity (a-e) and lifetime (f-j) images of the same sample area obtained using different excitation wavelengths. The images were recorded using 488, 500, 510, 520, and 530 nm excitation wavelengths (images (a), (b), (c), (d), and (e), respectively). The SiO_2 nanoparticle at the left-bottom corner has the photoluminescence lifetime of 3.6±0.2 ns; the lifetime of the particle at the right-upper corner is 7.4 ± 0.3 ns. Scale bars, 1 μm.

The full series of single SiO_2 NPs excitation spectra

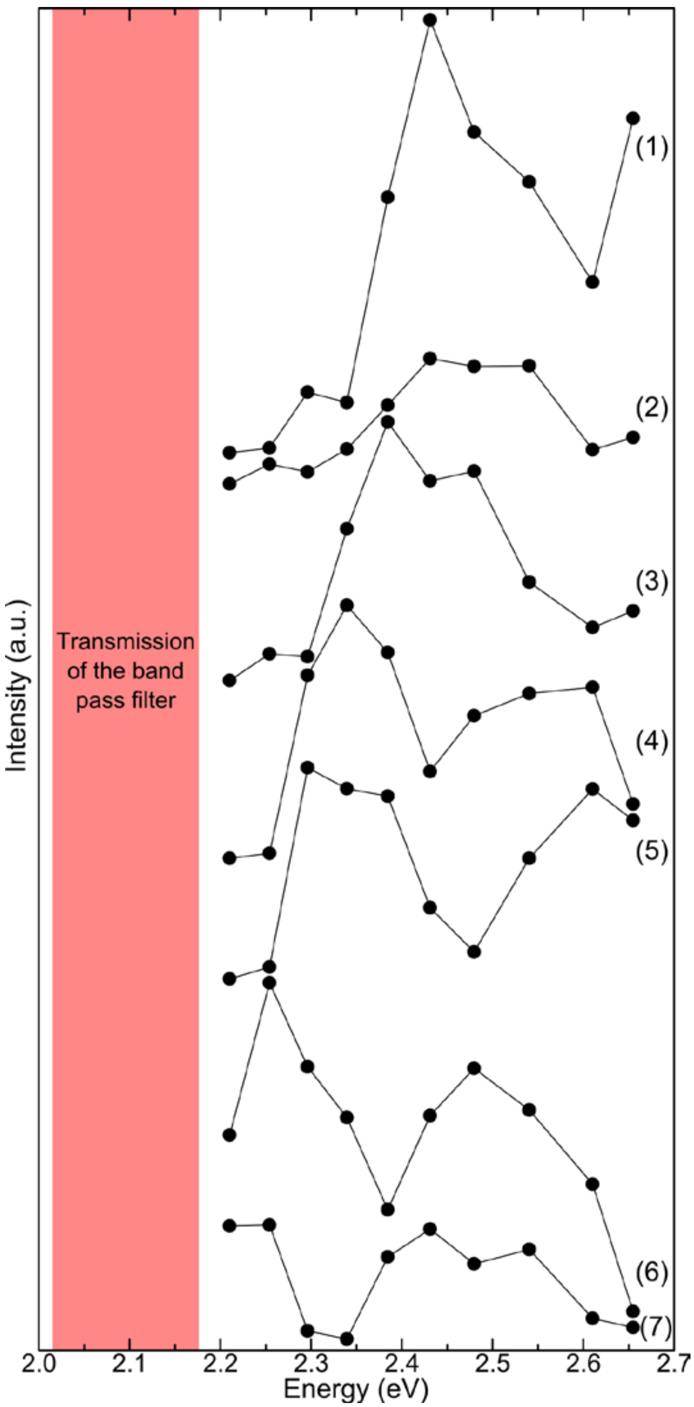

Figure S5. Excitation spectra of single SiO_2 nanoparticles dispersed on the surface of a glass cover slide. The red shaded area represents the transmission spectrum of the band pass filter, which was used for recording the excitation spectra.

Quantum yield of SiO_2 NPs

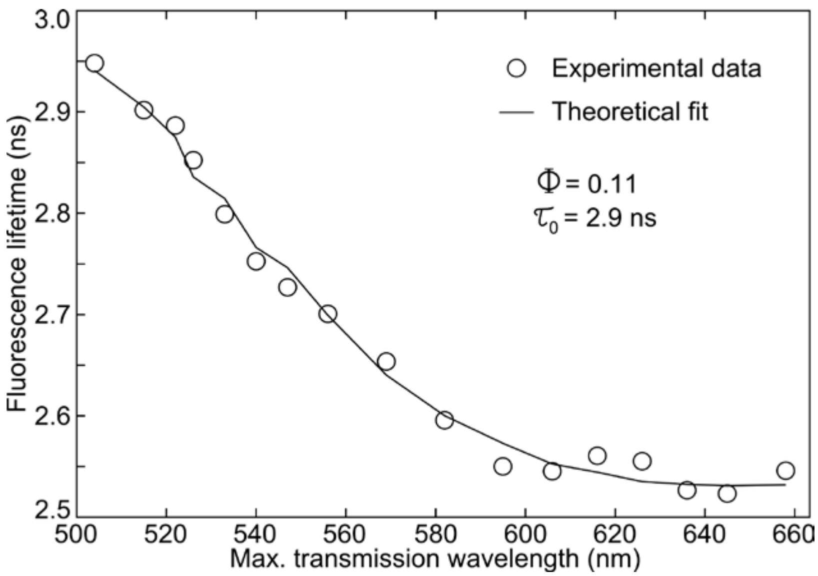

Figure S6. Cavity-modified PL lifetime of SiO_2 NPs in aqueous solution as a function of the maximum transmission wavelength of the cavity, which is linearly proportional to the cavity length. Open circles are experimental data, the solid curve is a model fit. Φ and τ_0 are the values of the quantum yield and free space PL lifetime, respectively.

Photoluminescence decay curves of individual SiO_2 nanoparticles

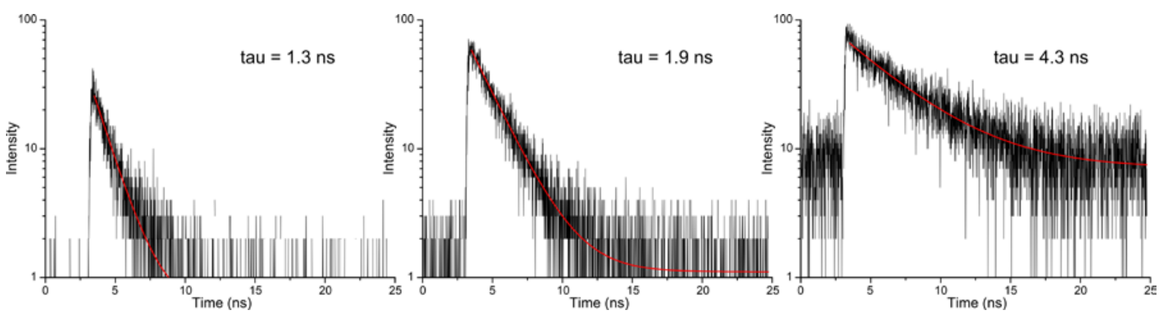

Figure S7. The photoluminescence decay curves measured from three different SiO_2 nanoparticles. The red curves show the fits to the measured data with a mono-exponential decay function.

The histograms of the single particle lifetime and emission energy distributions

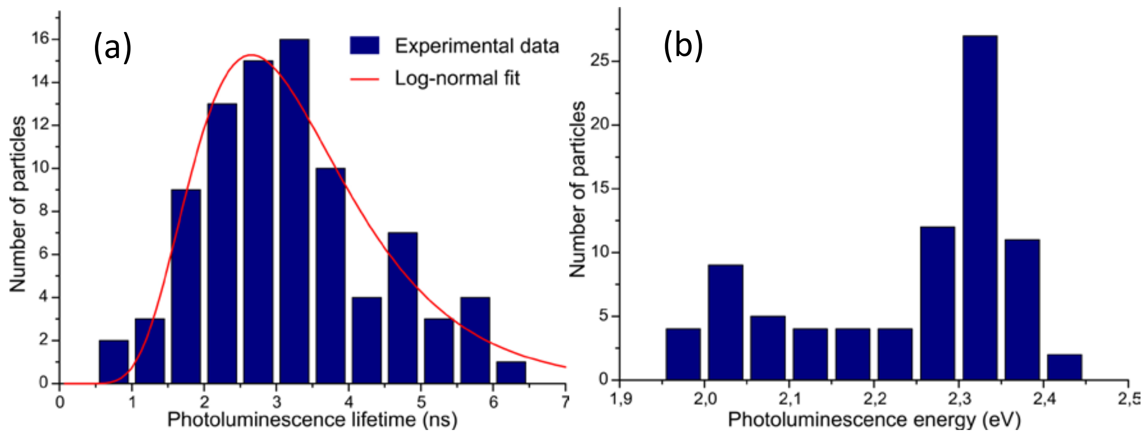

Figure S8. (a): Histogram of the photoluminescence lifetimes of single SiO_2 nanoparticles. Red curve shows the fit with a log-normal function. (b) Histogram of the emission energy maxima of single SiO_2 nanoparticles.

Ensemble excitation spectrum of SiO_2 nanoparticles

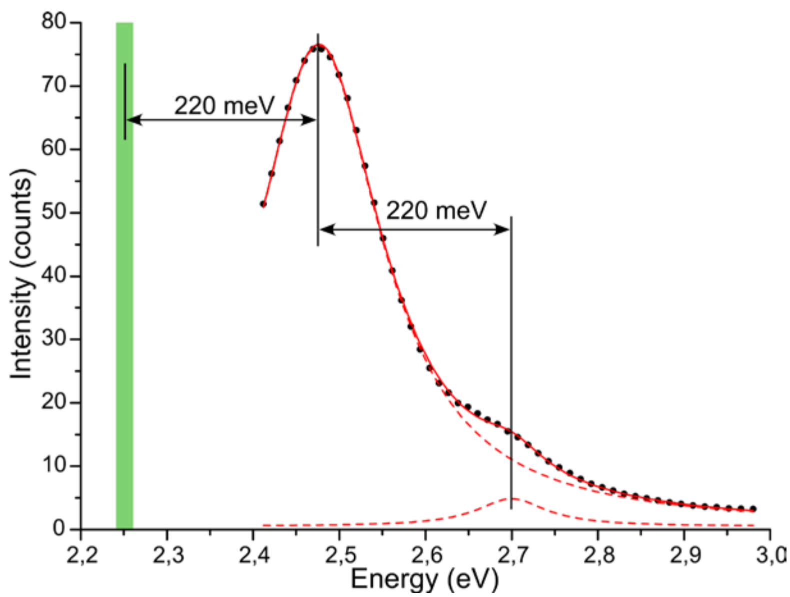

Figure S9. Solid circles: excitation spectrum obtained from low concentrated aqueous solution of SiO_2 nanoparticles. The photoluminescence was collected from the narrow spectral window (0.02 eV) at 2.25 eV, where the maximum emission intensity was observed. The solid red curve shows a fit of two Lorentzian functions to the data. The dashed red curves show the two individual Lorentzian peaks.

1. Yokoi, T. et al. Periodic Arrangement of Silica Nanospheres Assisted by Amino Acids. *Journal of the American Chemical Society* **128**, 13664-13665 (2006).
2. Hartlen, K.D., Athanasopoulos, A.P.T. & Kitaev, V. Facile Preparation of Highly Monodisperse Small Silica Spheres (15 to >200 nm) Suitable for Colloidal Templating and Formation of Ordered Arrays. *Langmuir* **24**, 1714-1720 (2008).
3. Chizhik, A.I., Chizhik, A.M., Khoptyar, D., Bär, S. & Meixner, A.J. Excitation Isotropy of Single CdSe/ZnS Nanocrystals. *Nano Letters* **11**, 1131-1135 (2011).
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