Multi-chromatic silicon nanocrystals
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Overview of Silica defects

Various defects with efficient absorption and emission, usually referred to as a color centers, have been reported in nanostructured or bulk silica that has been strained, damaged, or irradiated by high energy electrons or photons and/or non-stoichiometric (both crystalline and amorphous) (e.g. Refs. 1-28). In the visible range, characteristic bright red, green and blue emission bands were observed:

The red ~650 nm (~1.9 eV) emission is most often ascribed to non-bridging oxygen hole centers (NBOHC) =Si-O•, where one of the O-Si bonds is broken 1,2,11-13 (see Figure 1a in the main article). This interpretation is based usually on the correlation between absorption, luminescence and ESR signals or site-selective experiments that evidence the vibration of dangling oxygen (see for instance Ref. 21 and references therein). NBOHC is found both in the bulk and at the surface of silica. Alternatively, this red emission has been ascribed to interstitial oxygen or ozone gas molecules captured inside oxygen-rich silica.1 The former origin (respectively its surface variant) is more likely, when a characteristic double-peak feature is observed, as in our case. We observe a double peak with splitting of 0.07 eV, which is consistent with the energy difference between the 2px or 2py orbitals, due to the Jahn-Teller effect.11-13 Alternatively, the two peaks were also assigned to the two possible conformations of the NBOHC in the presence of the Si-OH bond.14 In the final PL spectra, this band is expected to be less intense due to the reduced excitation cross-section at 3 eV.15

The green ~550 nm (2.25 eV) emission band is of relatively unclear origin in damaged bulk Si-rich silica.1,2 In nanostructured silica, the interpretation involves an unstable silanone Si=O bond.20 Possible are also not very stable hydride =Si-H species, especially when vibrational spectral features are present.10 Another interpretation involves water-related species (2≡Si-H) + =Si-O• → ≡Si-O–(H-Si≡)2,10 dioxsilyrane =Si(O2),6 presence of water 23 or alternatively even deposited organic material.24-28

In the blue region, at least 2 components are recognized in literature, both related to silanol groups ≡Si-OH16,17 or their derivative silylene =Si••,7,11 also known as oxygen-deficiency center ODC in bulk silica.1,2 Such ODC can be present as relaxed ≡Si-Si≡ or unrelaxed =Si••Si≡ oxygen vacancies and their emission includes energy transfer from and to =Si•• (for details see Ref. 1). Singlet-singlet transition in the ODC site can lead to a fast decaying band (~ns) at 280 nm (4.4 eV) and triple-singlet to a slow decaying band (~ms) at ~460 nm (2.7 eV). Concerning the origin of the ODC center, it is known that two neighboring silanol Si–OH bonds can connect and release molecular hydrogen (plus heat), leading to the formation of an oxygen deficiency center following the reaction scheme (=Si-O-H+H-O-Si≡
Interestingly, the Si-OH groups are abundant on the surface of our por-SiNC sample due to a specific post-etch procedure in hydrogen peroxide,\textsuperscript{29} which might stay behind the bright blue emission band present already in the original PL before irradiation by e-beam and also support the idea of common origin of the blue band in PL and CL. Often observed is also fast decaying (~ns) blue band at around 2.8 eV, associated with a defect pair consisting of a dioxa-silyl, $\text{=Si(O}_2\text{)}$, and a silylene $\text{=Si} \bullet \bullet$ \textsuperscript{22} that can occur through reaction ($\text{=Si(}\text{OH})_2\text{)+(HO)}_2\text{Si=} \leftrightarrow \text{=Si} \bullet \bullet + \text{=Si(O}_2\text{)} + 2\text{H}_2\text{O}$).\textsuperscript{1,3} Older literature suggests self-trapped excitons (STE) as origin.\textsuperscript{8} The STE origin can be, however, excluded, since this emission has been shown to be removed (and not steadily grow, as we observe) by exposure to 15 keV e-beam irradiation.\textsuperscript{30-33} Our observations indicate also that the blue PL in our samples does not originate from excitonic recombination from ultrasmall Si clusters, as has been suggested for oxide capped SiNCs previously in literature,\textsuperscript{34,35} since the sizes of our samples are definitely larger than 2 nm. Furthermore, the blue band appears in the Plasma-SiNCs next to the NIR intrinsic PL band, whose emission energy did not change after e-beam exposure, i.e. the core size remained the same. Another possible origin of the blue band has been suggested to be from O$_2$ molecules, if vibrational spectral features are observed.\textsuperscript{9}

Together, these color sites give rise to a broad emission spectrum in bulk silica that can be excited typically by high-energy photons or e-beam due to wide bandgap of the silica host.

**Sample characterization**

In this section we provide detailed characterization of the samples by SEM and PL microscopy. Images taken by optical reflection, PL and scanning electron microscopy of the e-beam exposed areas of the samples are shown in Figure S1. These give an idea of the sample features and the measured areas. The patterns helped us to recognize and measure precisely the same area in the optical and electron microscopes. Sample features are as follows:

- **Plasma-SiNCs** (Figures S1a-S1c) were prepared by plasma synthesis as described in Ref. 36, and consists of large (~4 nm) oxide-capped SiNCs that are free-standing (powder-like). In this case, the partially gold-coated substrate allowed for conduction without disturbance of the PL and CL signal (Figures S1a-S1c): The aggregated SiNCs can be seen in Figure S1a as dark spots, in Figure S1b as light emitting (lighter) spots and in Figure S1c as lighter aggregates.

- **Por-SiNCs sample** was prepared via electrochemical etching described in Ref. 29 and consists of freestanding aggregates of smaller (2-3 nm) oxide-capped SiNCs. Optical reflection (left) and PL images (right) of the Por-SiNC samples (Figures S1d and S1e) show the patterned Si substrate with drop-cast por-SiNCs agglomerates: in reflection, SiNCs appear as darker spots, while in PL image as lighter ones (emitting light). The circles delineate the agglomerates exposed to the electron beam. The sample before irradiation is shown in Figure S1d, and after irradiation in Figure S1e.
Litho-SiNCs was prepared by electron-beam lithography as described in Ref. 37, and consists of ordered arrays of silica walls and pillars containing larger (~4 nm) SiNCs, see Figures S1g and S1f. These SiNCs are very far from each other, allowing for single-dot measurement, as maximally one SiNC is present within the diffraction limited detection area (~200 nm²). Cross sections of a nanowall milled with a focused ion beam and a top-view of nanowalls are shown in Figures S1h and S1i. The arrow in S1h indicates the position of the luminescent nanostructures, which are too small to be resolved by SEM. Circles in Figure S1i demarcate the positions investigated in the CL experiment. A PL image of the exposed area (the same area as in S1f and g) is shown in Figure S1j. The strong PL likely originates from an increased number of oxide centers. The arrow in the inset (magnification of the dashed rectangle area) indicates the position of the exposed nanowall, which is situated inside the black dot surrounded by the light circle.

Figure S1 – Characterization of samples. Plasma-SiNC sample on a partially gold-coated glass surface: (a) Optical reflection image, (b) PL image and (c) SEM image. The inset in (c) shows a magnified image of a NCs agglomerate. Por-SiNC sample on patterned Si substrate: (d) optical reflection image (left) and PL image (right), where the circles indicate the
agglomerates to be exposed to the electron beam. (e) As in (d), but after exposure to e-beam irradiation. Litho-SiNC sample – (f) optical reflection image of the pillar area, (g) PL image of the same region as in (f). (h) SEM image of cross section of a nanowall, milled with FIB. (i) Top view of a nanowall. (j) PL image of the same structure as in (g) after exposure to e-beam irradiation.

Possible organic contamination in CL measurements

Organic contamination is always a concern in the electron microscope measurements, which is why we have studied the cathodoluminescence (CL), emission from the irradiated area in the very well defined sample Litho-SiNCs in more detail (Figure S2). A PL image of the sample area after long-term e-beam irradiation (Figure S2 right) reveals the center of exposure as small black spots, while regions irradiated with a lower dose by indirect electrons appear as brighter surrounding areas. The dimmer areas have not been irradiated (i.e., irradiation is very localized and irradiated places easily traced from their bright emission). The left-panel shows PL spectra taken from single Litho-SiNCs as indicated in the PL on the right in Figures S2a, S2b – dark irradiated area (green line and arrow), light irradiated area (red line and arrow) and non-irradiated area (blue line and arrow). It is apparent that PL emission is enhanced in the less directly irradiated area, while it is attenuated in the directly irradiated place (dark spot in the center). This indicates that lower dosage or lower electron beam energy is most suitable for effective material treatment. It is important to note that the area that has not been irradiated by e-beam appears much darker (lower PL signal) and the PL from that area (blue curve in Figure S2a) show the original infrared PL peak (only foot of the peak visible in Figure S2a). The intensity of PL from irradiated areas is in both cases higher and shows spectrally broad PL spectrum (Figure S2a, red and green curves).

![Figure S2 – Litho-SiNC under prolonged e-beam irradiation. (Left) PL spectra of 3 different places in Litho-SiNC sample after prolonger e-beam irradiation as shown in PL image on the (right): PL spectra are taken for the areas picked from the first column of SiNCs with dark spot (pixels 372-384, green arrow at the top left corner of the image), lighter ring]
To check for possible organic deposition, we studied the exposed area by AFM. Topography (a) and phase (b) images recorded by Atomic Force Microscopy (AFM) in tapping mode are shown in Figure S3 together with the PL image (c) of the measured area (red square) next to the nanowall. In the topography, no step or increase in height is observed in the areas that appear lighter and darker in PL. Similarly, no change is observed in the phase AFM image of these areas. This shows that the lighter area in PL is not due to extra deposited material, such as a possible organic material layer, suggested previously.24-28

Figure S3 – Test for organic contamination in Litho-SiNC. (a,b) AFM measurements (tapping mode) of the irradiated area in Litho-SiNC sample (x is the fast scale, y the slow one) - (a) AFM topography (circle denotes separation of the exposed area that would appear as dark spot in PL image and the lighter outer-ring area), (b) phase contrast of the AFM signal of the same area. (c) PL image of the irradiated area where the AFM measured area is depicted by red square.

Energy dependence and time-CL scan - Por-SiNCs and C-SiNCs

To optimize the electron energy in the CL measurements for the highest (optimum) signal, we studied the CL intensity as function of electron energy for C-SiNCs and Por-SiNC (Figures S4a, S4b). Higher energies lead to deeper penetration of the e-beam into the Si substrate, decreasing the efficiency of excitation of the SiNC structures. Indeed, the intensity changes significantly upon varying the electron energy, while the spectral shape remains rather constant. For C-SiNCs (Figure S4a), the intensity is the strongest at 7-9 keV (Figure S4c, inset), while for Por-SiNCs, the optimal energy is 15 keV (Figure S4b). This energy was chosen for all oxide-capped SiNC samples. The difference in electron energy can originate from the different thickness of the SiNC layers: the C-SiNCs are expected to form only a very thin layer of non-agglomerated SiNCs, while the Por-SiNCs as well as the Plasma-SiNCs combine into larger agglomerates, sometimes about 1 micrometer thick. The Litho-SiNCs are expected to have similar properties.
We finally investigate the carbon-capped nanocrystals (C-SiNCs). We argue in the main manuscript that for those nanocrystals, no spectral changes occur upon irradiation, neither upon short nor upon long irradiation. To show this, in Figure S4c, we compare the original PL and CL for short and long e-beam exposure for these carbon-capped samples. No change in the spectral features is observed, only a minor decrease in emission intensity.

**Figure S4 – Excitation spectra for Por-SiNCs and C-SiNCs.** CL signal as a function of electron energy for (a) C-SiNC and (b) Por-SiNC sample (insets show integrated CL intensity as a function of the electron energy). (c) CL spectra from C-SiNC for short (black curve) and long (red curve) e-beam exposure. For comparison we also show the original normalized PL spectrum (blue curve). Inset shows the CL intensity dependence on electron energy.

**Emission efficiency estimate – Plasma-SiNCs and Por-SiNCs**

To evaluate possible enhancement of emission intensity, we need to evaluate micro-PL and CL intensity for the different stages of the irradiation of the sample – before/after irradiation and for short/long term CL irradiation. Figure S5 shows CL emission signal from dark counts, substrate and Plasma-SiNCs, all measured under comparable conditions. While we correct the intensity of the Plasma-SiNCs CL emission for the dark counts (Figure S5a)
and substrate signal (Figure S5b), we can clearly see that compared to Plasma-SiNC signal (Figure S5c, S5d), these are negligible. CL from Plasma-SiNCs for short (0.2 min) and long (117 min) exposure (“before”/“after”) to e-beam of energy 15 keV is shown in Figure S5c. While the spectral shape changes drastically, the overall integral intensity of CL remains very similar (Figure S5c). In time-scan (Figure S5d), the spectral changes are shown as a gradual decrease of the original PL peak and gradual rise of the blue and red defect bands.

**Figure S5 – References samples and time-evolution of CL in Plasma-SiNC.** (a) Dark counts in CL measurements. (b) Signal from Si substrate from two different spots. (c) CL from Plasma-SiNC for short exposure (“before”, 0.2 min) and prolonged exposure (“after”, 117 min) to e-beam from two different spots. (d) Time-scan of the CL signal from Plasma-SiNCs up to 117 minutes of e-beam exposure. For all measurements was used e-beam of energy 15 keV and integration time for each spectrum of 1s.
Figure S6 – Time evolution of CL spectra in Por-SiNC sample. Each spectrum was integrated 5 s and taken under 15 keV e-beam exposure. The time between measurements is of the order of a minute, but longer before the last two measurements due to manual operation. Inset: Evolution with e-beam exposures of the total intensity (green), and the intensity de-convoluted into three peaks – a PL peak (black), red peak at ~1.9 eV (red) and blue peak at ~2.7 eV (blue). Their integrated intensity, as a function of exposure time, is plotted in the inset, together with the integrated intensity of the whole CL spectrum (green).

In Figure S6 we show the evolution of the spectral features in CL upon irradiation in Por-SiNC. A continuous rise of red and blue bands is observed. Upon prolonged exposure, both bands intensify due to the increasing amount of generated defect centers. Total integral enhancement of the CL signal in this case is about factor of 3. From Figure S6, we obtained the fitting parameters for the blue and red bands. Here, they show up the best and are clearly distinguishable from the time-resolved measurements. The red CL emission band clearly shows double peak structure indicating NBOHC origin (see discussion in the first section of the Supplementary materials). The alternative explanation in terms of self-trapped excitons can be excluded here, since (as discussed above), this emission has been shown to be removed (and not steadily grow, as we observe in Figure S6) by exposure to 15 keV e-beam irradiation.30-33

Micro-PL, measured before and after irradiation by e-beam, is shown in Figure S7. While both spectral profiles for Plasma-SiNCs (Figure S7a) and Por-SiNC (Figure S7b) changed dramatically after irradiation, integral intensity of the PL appears to be same for the Plasma-SiNC (Figure S7a) and about twice higher after irradiation for the Por-SiNCs (Figure S7b). This is consistent with the integral intensity increase observed in the CL measurement, where Plasma-SiNC remained similar integral intensity and Por-SiNCs had about 3 times enhanced integral intensity after prolonged irradiation, both despite drastic spectral changes (see Figures S5 and S6).
Figure S7 – Micro-PL emission before and after irradiation for (a) Plasma-SiNCs and (b) Por-SiNCs sample. Both spectra for each sample are measured under comparable conditions, i.e. the PL intensities are comparable for before and after, but not between the two types of materials. In green line are fits to “before”-curve and in blue are the “after”-curve fits.

PL stability over time

After about one year of storage under ambient conditions, we have re-measured the Plasma-SiNCs sample’s micro-PL spectra (Figure S8) on e-beam irradiated places and non-irradiated places. Interestingly, for both, irradiated and non-irradiated places, a strong blue component at around 2.5-2.8 eV developed. In the measurement, this blue band is spectrally cut due to excitation filter used for the micro-spectroscopy measurements with excitation at 3.1 eV. This occurrence of the blue band is very interesting and is probably result of slow oxidation upon exposure to air for the one year period. Nevertheless, since the PL peak in NIR range has stable position at 1.7 eV, we deduce that the core size of the SiNC did not change. This means that sample has not developed thicker oxide on the account of the shrinking core, but rather has increased amount of stable blue-emitting defects in the thin silica shell. Comparing the e-beam irradiated and non-irradiated places, we also see clear spectral difference – the irradiated places do not show original PL NIR band, and only broad blue-green band is present. The red band at 1.9 eV nearly disappeared. This suggests that full exposure to air for such a long time is not beneficial to the defect PL bands and maintaining the red and green part of the spectrum. Additionally, we can see that integral intensity of irradiated and non-irradiated places is comparable, as before seen for the Plasma-SiNCs, despite the spectral differences.
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