

Reply to “Comment on ‘Ultrafast Photoluminescence in Quantum-Confinement Silicon Nanocrystals Arises from an Amorphous Surface Layer’”

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We respond here to the Comment of Kůsová, Ondič, and Pelant that offers a critique of our recent report.¹ In our paper, which primarily considers the ultrafast photoluminescence (PL) decay of high-energy (2–3 eV) photons from several sizes and crystallinities of plasma-synthesized, alkyl-passivated silicon nanoparticles (Si NPs), we report a ~30 ps decay lifetime for above-gap blue emission that appears consistently for the multiple samples studied regardless of the particle size range probed, and particle crystallinity (as followed by X-ray diffraction and Raman). Our work did not examine the variable of surface termination. We conjecture that the observed 30 ps decay feature is too slow to be associated with any process that competes with intraband carrier thermalization (where thermalization times, we suggest, are indicated by the ultrafast <3 ps formation time of the lower energy, highly fluorescent “band-edge” red emission) and further suggest that the absence of a prominent feature in the ground state optical spectrum of the Si NPs also makes radiative recombination an unlikely source of the decay time constant. Based on TEM and Raman characterization of the Si NPs, we propose hole trapping in a persistent layer of disordered surface Si as the source of the observed dynamics, the presence of which is supported by agreement with the results of lattice dynamics calculations performed on mixed-phase amorphous/crystalline Si NPs. By comparing the PL spectra of Si NPs having identical size and surface termination but varied degrees of crystallinity, we also suggest that high-energy PL is related to the presence of this amorphous material. It is important to note that no arguments in the commentary by Kůsová et al. refute the central points outlined above; rather, the commentary focuses on the applicability of these claims to oxide-terminated and tensile-strained Si NPs, which we have not studied. Below, we address each of the points outlined in the comment.

Comment 1: (All quotations copied from the Comment) “This finding is generalized and their conclusion are applied also to previous reports on blue PL in SiNPs In summary, we believe that similar features in the PL of SiNPs can be of different origin in samples prepared by different methods. The alternative viewpoints thus deserve fair discussion, especially in works claiming to have found the ultimate interpretation.”

Response to Comment 1: In the beginning of our report, we clearly state that we examine plasma-synthesized, alkane-terminated Si NPs and include synthetic details. We do appreciate the complexity of Si NPs and certainly do not aim to suggest that we have determined an “ultimate” interpretation irrespective of synthetic method, surface termination, strain, etc. Indeed, given that we attribute our findings to an interface-related feature of the system, we would expect manipulations of the interface with oxide, strain, reconstructions, etc. to alter the described processes. We do make statements regarding the generality of our measurements to all samples in the obvious context of the materials studied in the manuscript (different sizes and crystallinities).

Our experiments were inspired by results from the Si NP field more broadly and may indeed inform observations in other particles than those that we specifically studied. While we acknowledge the potential impact of surface chemistry on the optical properties presented by Si NPs, our work was motivated by the observation of similar dynamics arising from Si NPs passivated by an oxide-layer, a qualitatively different surface than the alkyl-passivated Si NPs studied in our work. In a recent paper by de Boer and co-workers,² SiO₂-embedded Si NPs were characterized using time-resolved PL spectroscopy. Under low-fluence, pulsed excitation conditions, the results obtained with a longer time window and inherently lower time resolution (owing to the longer streak camera window) are very similar to those presented in our work.² Figure 4a from ref 2 displays the time-resolved PL spectrum being described. While the time scales are slightly longer in the spectra noted in ref 2, the results otherwise resemble those presented in our work; both samples exhibit a high-energy, rapidly decaying PL band with no apparent time-dependent redshift and a low-energy, long-lived PL band presenting a roughly identical rise time to the high-energy band. In light of the similar results obtained for Si NPs having a rather different surface chemistry than those studied in our work, we feel it is reasonable to suggest that our model may be a valid explanation of ultrafast, visible-PL dynamics in a variety of Si NP types. We stress that this is merely a

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hypothesis; certainly further investigation of samples similar to those used in ref 2 using, for example, Raman spectroscopy would be warranted to ascertain the extent to which amorphous Si might be present. Rather than claiming to have unified existing literature on this complex topic, we are suggesting that disorder in the surface layer should be taken into account alongside other factors (such as the presence of oxide, defects, and strain) when unraveling PL mechanisms of Si NPs.

Comment 2: “Moreover, again in contrast to the report by Hannah et al.,¹ the spectral position of our emission shifts with progressing measurement time, compare Figure 1b and c. Clearly, the (ultra)fast PL component in SiNPs and consequently also its origin can differ from sample to sample and no ultimate conclusion can be drawn based just on a study of a single type of sample.”

Response to Comment 2: As Kůsová and co-workers point out in their commentary, we see little-to-no spectral shift in our time-resolved PL spectra for a similar, nanosecond time window. As described above, our findings are similar to the results for oxide-embedded Si NPs presented by de Boer et al.,² who observe a constant PL maximum on nanosecond time scales for the high energy band (see Figure 1a in ref 2). Again, we clearly state in our manuscript that our results are obtained for plasma-synthesized, alkyl-passivated Si NPs and note that our hypothesis may also be consistent with a variety of prior published results. While the central purpose of our manuscript is to examine the fast, picosecond decay dynamics presented by the Si NPs (for a shorter time window), we do also note a nanosecond decay in our manuscript (see Figure 1a in ref 1). The primary difference between the nanosecond decay we observe and the one described by Ondič et al.³ is the presence of a red spectral shift in ref 3. Ondič et al.³ suggest that their observed redshift may be associated with an ensemble effect related to size-dependent decay rates and their suggestion of slowly thermalizing hot holes. We note that the Si NP ensembles probed in our work exhibit a size dispersion of roughly 20%,⁴ similar to the 19% size dispersion noted in ref 2. This stands in contrast to the broader ensemble characterized in ref 3, which notes a size dispersion of ~58%. Thus, differences in monodispersity, rather than surface chemistry, may help to explain the presence or absence of a redshift in the high-energy PL band. Ref 3 implicates also a role of strain, which different surfaces can impose upon the core.

Comment 3: “Apart from the recent study of oxide-covered Si NPs,³ also other reports on the ultrafast PL of SiNPs were published prior to the supposedly first study by Hannah et al.¹ Both oxide-^{5,6} and alkyl-passivated^{6,7} SiNPs were investigated with the highest temporal resolution reaching^{5,6} 280 fs.”

Response to Comment 3: In our manuscript, we aimed to convey that our work was the first example of simultaneous spectral and single-picosecond temporal resolution of the high-energy PL band, which we continue to understand to be correct. We do not dispute that prior studies of Si NPs with similar or higher time resolution than presented in our manuscript exist; indeed a subset of authors have contributed to the work cited in the Comment. While the first of the reports noted here as ref 5 utilizes an upconversion method capable of resolving a 400 fs decay component, PL dynamics in that work were monitored only at 630 nm.⁵ As seen in Figure 1 of ref 5, 630 nm corresponds roughly to the maximum intensity of the low-energy PL feature, which is substantially separated from the maximum intensity of high-energy shoulder evident at 450 nm. The second study referenced⁶ does examine ultrafast PL at a

variety of wavelengths for both alkyl- and oxide-passivated Si NPs; however, the aim of this study was to investigate the effect of *k*-space broadening and interfacial trapping on the band which dominates the steady-state PL spectrum. This feature is likely analogous to the red PL band in our study. While a range of wavelengths are examined in ref 6, this range primarily spans the line width of the steady-state PL spectrum; no distinct high-energy band is observed or temporally resolved (see Figures 1 and 2 of ref 6). Finally, we are aware of the third study⁷ referenced in Comment 4 and cite it in our original manuscript. In the work of Sykora et al.,⁷ an emission spectrum for a sample at 2 ps is shown in Figure 1a. However, all other spectral dynamics shown in the report utilize ~100 ps time resolution from time-correlated single photon counting. Dynamics using high time resolution are examined at the peak of the blue and red spectral features for a 10 ps window in ref 7, but simultaneous spectral and dynamical resolution such as that presented in our work (ref 1) are not presented.

Comment 4: “Thus, the argumentation used by Hannah et al.¹ does not apply to our case of direct-bandgap SiNPs and similarly, it might not apply also to the SiNPs reported on by Dohnalova et al.⁸”

Response to Comment 4: The tensile-strained Si NPs recently studied by the Comment's authors exhibit interesting behavior and shift differently than amorphous Si NPs under pressure, suggesting a different origin for the observed PL.⁹ The Si NPs that exhibit a red-shift were prepared via chemical treatments of electrochemically etched, oxide-terminated Si NPs to yield organically passivated particles. In our study, we examine plasma-synthesized particles functionalized initially by hydrogen, then by a layer of covalently bonded dodecane following reaction with the surface. As both our synthetic method and final surface structures are different from the particles studied by Kůsová et al., the origin of the observed PL dynamics can certainly differ. Despite experimental evidence of its existence,^{1,10,11} a persistent amorphous Si layer had not been considered in the PL dynamics of Si NPs prior to our manuscript. Therefore, we point to examples where our hypothesis may also be consistent with presented results. For example, in the work by Dohnalova et al.,⁸ a lack of picosecond-scale characterization of dynamics or time-resolved collection of PL spectra makes it difficult to directly compare these results with the work presented in our manuscript and ref 3. Furthermore, ref 11 does not present any characterization which would distinguish changes in surface chemistry from changes in crystallinity (such as XPS studies demonstrating oxidation or Raman spectroscopy demonstrating crystallinity). Distinguishing our proposed mechanism from the capping-induced *k*-space broadening mechanism advanced in ref 11 would require further characterization of the Si NPs utilized in that work.

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Notes

The authors declare no competing financial interest.

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