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Comment

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Comment on "Ultrafast Photoluminescence in Quantum-Confined Silicon Nanocrystals Arises from an Amorphous Surface Layer"

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The authors of a recent article[1] claim that because they "for the first time, temporally resolve photoluminescence (PL) from the (silicon nano-)particles with up to single-picosecond time resolution," they can finally "resolve long-standing controversies regarding the fast PL band in quantum confined Si and conclusively attribute observed dynamics to a non-radiative decay process which (they) suggest is hole trapping in a persistent surface layer of amorphous Si." Their argumentation is based mostly on the similarity of the fast emission observed in their mixed-phase (crystalline/amorphous) silicon nanoparticles (Si NP) with that of their purely amorphous Si NPs. This finding is generalized and their conclusions are applied also to previous reports on blue PL in Si NPs.[2−6]

Here, we want to provide a counterargument against the generality of the claim that (ultra)fast PL in *all* Si NP samples originates in a surface amorphous layer. Recently, our group has reported[7] on the ultrafast PL of oxide-covered Si NPs with temporal resolution comparable to that in the report by Hannah et al.[1] In addition to ultrafast temporal resolution, in our report, we studied a broad temperature range from room temperature down to 4 K. Our explanation of the observed decay was based on the core-related quasi-direct radiative recombination governed by slowly thermalizing photoholes, which as a process has been theoretically predicted.[8]

The comparison of our ultrafast measurements[7] of oxide-covered Si NPs with that of organically capped ones by Hannah et al.[1] is shown in Figure 1a. Whereas, in our case, the temporal resolution is slightly lower (by about a factor of 4), measurements in shorter temporal windows were not performed because, unlike in the report by Hannah et al., no ultrafast component (of the order of 30 ps) was observed. 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 Si NPs 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 (as we point out in our report[7]).

Apart from the recent study of oxide-covered Si NPs,[7] also other reports on the ultrafast PL of Si NPs were published prior to the supposedly first study by Hannah et al.[1] Both oxide-[9,10] and alkyl-passivated[10,11] Si NPs were investigated, with the highest temporal resolution reaching[9,10] 280 fs.

Another example that the authors use to support their scenario is the report by Dohnalova et al.,[4] who studied chemically synthesized Si NPs possessing only a fast (∼10 ns) PL component and who attributed it to direct-bandgap-like transitions induced by the carbon-linked surface capping. An independent confirmation of the possibility of direct-bandgap transitions in Si NPs is our report on SiNPs prepared by a different method but also exhibiting only a fast (∼ns) PL component,[12] which, as we have recently proven using both theoretical and experimental evidence,[13] actually are a direct-bandgap material. Unlike in the study by Dohnalova et al.,[4] we connect the direct-bandgap character with tensile strain induced by surface capping.[13] A part of the experimental

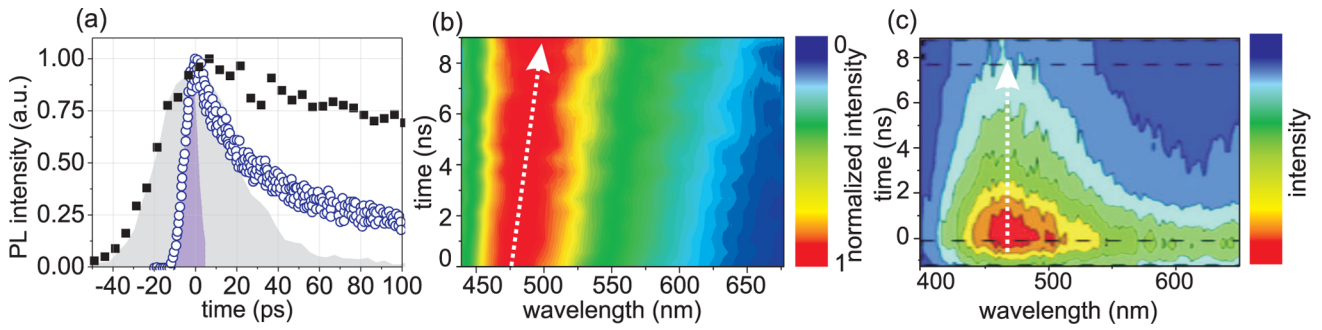

Figure 1. (a) Comparison of ultrafast PL measurements of Si NPs by Hannah et al.[1] (blue data) and Ondič et al.[7] (black data). The data points are measured PL decays at room temperature, the shaded curves represent the instrument response functions. (b, c) Comparison of spectrally and temporally resolved PL decays by Ondič et al.[7] in (b) and Hannah et al.[1] in (c). Please note that in (b) the individual PL spectra are normalized, while in (c) they are not. The white arrows indicate (b) the existence and (c) the nonexistence of spectral shift with progressing measurement time.

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evidence for the direct-bandgap behavior of our strain-engineered SiNPs lies in the study of the direct-bandgap PL under pressure. Among other things, this experiment proves that the PL observed from our direct-bandgap Si NPs does not come from the amorphous phase since completely different trends of PL under pressure were observed in amorphous SiNPs.[14] 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.[4]

In summary, we believe that similar features in the PL of Si NPs can be of different origins in samples prepared by different methods. The alternative viewpoints thus deserve fair discussion, especially in works claiming to have found the ultimate interpretation.

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Notes

The authors declare no competing financial interest.

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ACS Photonics 2015, 2, 454−455