Size-dependent critical transition in the origin of light emission from core–shell Si–SiO_2 nanoparticles

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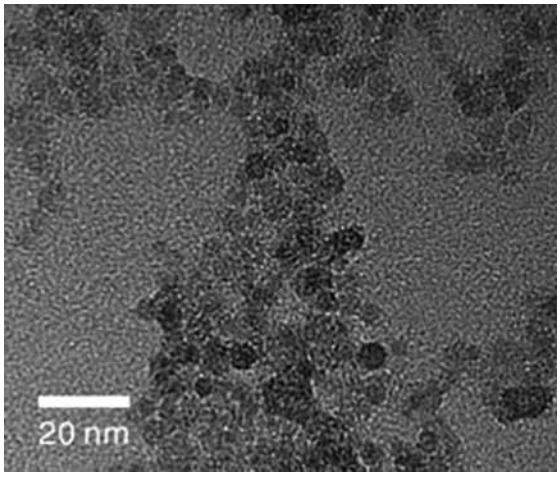
Nanosilicon is a promising environmentally friendly nanomaterial for future electronic, optoelectronic and biomedical applications. An important feature of nanosilicon is its ability to emit light under different external excitations, e.g. illumination or electric fields, which is useful for various nanotechnologies such as energy-efficient light emitting devices or medical imaging. The origin of light emission from nanosilicon systems, such as crystalline silicon nanoparticles (Si-NPs), has been an intensively debated issue, with seemingly contradicting studies pointing to different mechanisms. In this work, we established the origin of the photoluminescence (PL) from application-grade Si–SiO_2 core–shell NPs with different sizes and synthesized with an industrially scalable high-yield nonthermal plasma method. Through a comprehensive study of PL spectra measured for a well-characterized set of Si-NP samples, we unveiled a strong dependence of the origin of the luminescence on NP size. We found that the commonly observed PL from Si-NPs originates, in general, from two processes: (i) recombination of charges (photo-excited electrons and holes) within the Si core of the NPs and (ii) recombination involving the oxide shell. The photon energies of both emissions increase with decreasing NP size. Importantly, a NP size dependence of the relative contribution of the two processes (i) and (ii) to the overall PL was established. For large (small) Si-NPs, the luminescence is dominated by the core (oxide-shell) emission. Interestingly, the transition between these two regime limits occurs within an extremely narrow NP size range of only ~0.5 nm. This critical transition, in combination with the close photon energies of the emissions (i) and (ii), is responsible for the common observation of only a single unstructured PL band for Si-NPs and for the seemingly conflicting assignments of the origin of this luminescence found in the literature for apparently similar Si-NPs.



FIGURES 1
Transmission electron microscopy image of our Si-NPs (Si–SiO_2 core–shell NPs).

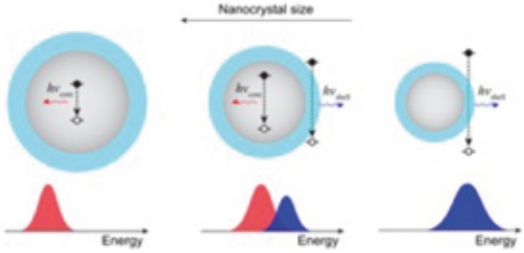


FIGURE 2
Scheme depicting the origin of light emission from the Si-NPs and the qualitative evolution of the relative contributions of the core- and shell-related emission components and corresponding energies on NP size.