On the origin of the step-like quantum yield of Si-nanocrystals: MEG or efficient exciton generation via critical points in *c*-Si?

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Multiple exciton generation (MEG) in nano-scale quantum dots (QD's) represents one of the most important candidate solutions to the fundamental problem of solar energy conversion efficiency in photovoltaic devices. The implication that the efficiency of a single junction cell can, in principle, be extended beyond the Shockley-Queisser limit has resulted in a dramatic acceleration of the global research effort in this field, exemplified by the recent report of a 'Step-like enhancement in the luminescence quantum yield (QY) of silicon nanocrystals' [1]. However, based on our measurements of photoluminescence excitation (PLE), which yield remarkably similar data, we propose an alternative model of efficient (but not necessarily multiple) exciton generation which occurs via the *c*-Si E_1 and E_2 (bulk-like) critical points (CP's) within the silicon nanocrystals.
The spatial confinement of carriers to the nano-scale provides an increase in the probability for carrier-carrier interactions, whilst the quantized energy spectra results in a suppression of the carrier-phonon interaction. The former increases the probability for the generation of multiple free carriers from a single absorbed photon whilst the latter minimizes the loss that occurs when carriers relax after absorbing high energy photons. Whilst there were a number of reports of MEG in a wide variety of nanostructure materials, including silicon [2], the measurement is notoriously fraught with difficulties and the matter remains the subject of intense debate [3, 4].
Evidence for MEG is usually derived from the observation of a fast transient in the absorption, or luminescence, dynamics during high energy ($h\nu > 2E_g$) photo-excitation at relatively low intensity, such that the average photo-generated exciton per QD, $\langle N \rangle \ll 1$ [3]. This fast transient, on the ps timescale, corresponds to the bi- (or indeed multi-) exciton lifetime, as measured during high intensity excitation ($\langle N \rangle \gg 1$). This fast transient is usually correlated with a sudden increase in the QY when $h\nu$ exceeds the threshold for MEG ($\geq 2E_g$) with the anticipation of a 'step-like' increase in the QY **and** an increase in the contribution of the fast component to the total absorption (or luminescence decay) transient for $h\nu = nE_g$ ($n = 2, 3, 4\ldots$).
However, in spite of the observed 'step-like' increase in the QY reported in [1], correlated changes in the fast absorption transient with excitation energy are conspicuous by their absence [1, 5]. Furthermore, the overlapping position of these 'steps' in the QY with peaks in the PLE data we have taken, shown in **Figure 1**, supported by an increasing number of similar reports [6-8], leads us to conclude that the physical origin of the observed effect may be fundamentally different from that suggested in [1].

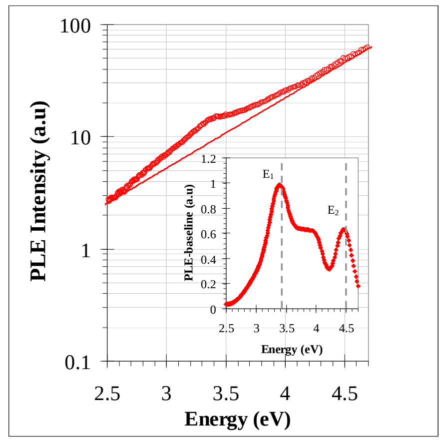

Figure 1 Semi-log scale of the Si-nanocrystal PLE spectrum (red circles) detected ~1.4eV with exponential baseline fit (dashed red line). Inset: linear scale of the PLE – baseline difference spectrum. The dashed vertical lines indicate the position of the bulk *c*-Si E_1 and E_2 critical points

Figure 1 shows a typical PLE spectrum from a silicon nanocrystal film (with an emission peak ~885nm). The peaks in the spectrum, which are more easily distinguished after removal of the exponential baseline (inset), are assigned to strong optical absorption and efficient exciton generation when $h\nu$ overlaps the silicon nanocrystal E_1 and E_2 CP's (indicated by the dashed vertical lines in the inset) where there is a high joint density of states [9]. We will show that the position of these peaks (and consequently the phonon dispersion around the CP energies) is relatively insensitive to changes in the silicon nanocrystal size, despite evident changes in the principal emission energy (band-gap). We therefore propose an alternative model, to that of MEG here, where enhanced absorption combined with efficient exciton generation occurs when the exciting photon energy, $h\nu$ matches one of the direct gap transitions in the Si-nanocrystals. We will discuss how defect-like levels, deep within the host SiO_2 band-gap, can mediate such excitations and propose simple experiments to elucidate our model. We will also discuss the implications of similar peaks observed in the PLE detected at different emission energies, including for the 1.5μm emission in erbium co-doped films.

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