Supporting Information:

Title: Free Electron-Driven Photophysics in n-Type Doped Silicon Nanocrystals Authors: R. Limpens $^{1\#}$ & N.R. Neale 1

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Verfication of the XRD-to-size correlation

Without a direct structural characterization technique, the size determination of (crystalline) nanoparticles often relies on correlation with reports were similar systems have been characterized both structurally and optically. Here we apply an additional verification of our X-ray diffraction (XRD) derived nanocrystal (NC) sizes by making use of such a correlation. For this purpose we produced three intrinsic NC ensembles, a system of which the photoluminescence (PL) properties are extensively related to the dimensions of the nanoparticles, as was shown by Wheeler et al.¹ and which follows the following dependence:

1) $PL_{peak} = E_{bulkSi} + 3.73 D_{NC}^{-1.69}$.

With PL_{peak} the peak position of the PL spectrum (in eV), E_{bulkSi} representing the bandgap of bulk Si (1.12 eV) and D_{NC} the diameter of the respective NC. In Fig S1 we show the PL spectra (a), the XRD patterns (b) and the derived NC sizes for both techniques for our intrinsic Si NC samples (c). We derived the sizes from the PL spectra by making use of Eq. 1. From the comparison of Fig. S1c it is clear that the two different approaches are in excellent agreement, with the sizes from the XRD-approach exhibiting slightly lower values. It is expected that the XRD-approach would result in a slightly lower estimate of the average size, since broadening of the crystalline (111) peak is not solely assigned to the Scherrer-effect². We do indeed observe a small underestimation of the XRD-sizes due to this effect.



Figure S1. Average NC size derivation by making use of two independent methods, for intrinsic Si NC ensembles of three different sizes. a) PL spectra with their linked NC size from Eq. 1. b) XRD patterns and the belonging Voight fits. In the legends we depict the estimated NC sizes by making use of the Sherrer equation. c) comparison of techniques. The black dashed line is a modeled one-on-one correlation of both techniques.

Determination of the free carrier concentration

The free carrier concentration n_{FC} ³ in the main text is calculated by making use of Eq.2:

2)
$$f_{plasmon} = \frac{1}{2\pi} \sqrt{n_{FC} e^2 / (m^* \cdot \varepsilon_0 (\varepsilon + 2\varepsilon_{matrix}))}$$

with $f_{plasmon}$ the localized surface plasmon resonance (LSPR) mode in [s⁻¹], n_{FC} in [m⁻³], m^{*} the effective mass of the carriers where we took the mass of a free electron (m^{*}/m₀=1)⁴, ε the complex dielectric constant of the plasmonic material (i.e., Si=11.7), ε_0 the permittivity of free space and e_{charge} the elemental charge. ε_{matrix} represents the dielectric constant of the surrounding argon ambient (ε =1). Eq.2 ignores potential perturbation effects such as interparticle plasmon coupling⁵ or interface scattering processes³, and hence might provide a lower limit of the n_{FC} . The calculated n_{FC} values are close to the solubility limit of P in bulk Si ⁶.

Time-dependent FTIR-measurements on P:Si-R



Figure S2. Main panel) FTIR spectra of P:Si-R, at several oxidation times. Inset) Intensity of the LSPR-mode, taken as the FTIR absorbance at 1600 cm⁻¹, as a function of the oxidation time. The red-dashed line is a fit following a power function and serves to guide the eye.

The main panel of Figure S2 presents FTIR measurements of P:Si-R at various oxidation times. The experiment was conducted by measuring P:Si-R on a gold coated Si substrate, in air. The broad LSPR-mode clearly disappears with increasing oxidation times, explained by the Cabrera-Mott theory in the main text. Signal intensity of the SiH_x-groups (\sim 2100 cm⁻¹) FTIR absorbance remains identical and serves as a benchmark. The inset shows the LSPR intensity (taken as the FTIR absorbance at 1600 cm⁻¹) as a function of the oxidation time.

EPR measurements on Si-R and P:Si-R

Figure S3 depicts EPR measurements on functionalized (-R) Si NCs, upon oxidation. All signals in Figure S3a (Si-R) reflect the surface radical at a g-factor of 2.006, which increases in magnitude with oxidation time. Note that the EPR signal of the un-oxidized Si-H sample in Figure 1d is free from such a surface radical signal. Hence, upon functionalization some surface radicals are created, as expected from the observed trace oxidation in Figure 1e in the main text, and with further oxidation this radical signal is intensified. For the P:Si-R in panel b, all signals reflect the free-electron feature at a g-factor of 1.998, decreasing in

amplitude with oxidation. No sign of the surface radical is observed before oxidation, although we know that the functionalization process should induce some surface radicals (panel a). As such, we argue that some free electrons neutralize these minor amount of surface radicals. Upon further oxidation the free carrier signal decreases and this is accompanied by an upcoming surface radical signal, in line with the main text. Note that the oxidation rates are significantly slower than the ones reported in Figure S2. This is because oxygen in the EPR measurement is achieved by letting air in through the small opening of the EPR tube (\sim mm in diameter), as opposed to the large surface area for the FTIR-oxidation experiment.



Figure S3. a) EPR measurements on functionalized Si NCs (Si-R), upon oxidation (from dark to light blue, reflecting fresh, 1 day oxidized and 2-day oxidized NCs). b) EPR measurements on P:Si-R, upon oxidation (from dark to light red, reflecting fresh, 0.5 day oxidized, 1 day oxidized and 2-day oxidized NCs). The blue dashed line is the Si-R (fresh) sample from panel (a) and serves to indicate the surface radical signal.

XRD comparison between P:Si-H and P:Si-R



Figure S4. XRD measurements for P:Si-H (yellow) and P:Si-R (red). The dashed lines represent Voight fitting functions indicating no size change upon functionalization (the constructed NC sizes are 7.8 ± 0.2 nm and 7.9 ± 0.4 nm for P:Si-H and P:Si-R, respectively, following the Scherrer equation, as explained in the main text).

NC size upon oxidation (by XRD)

Figure S5 illustrates the independence of the NC size upon the surface oxidation effect that is extensively discussed in the main text. We use this result to explain the size deviation between the XRD measurements (~7.5 m, Figure 1) and the PL measurements (~5.3 nm, Figure 2) in the main text. As we show in Fig. S5, the actual NC size remains unaltered upon surface oxidation, illustrating that the apparent 5.3 nm diameter (from PL) results from selective emission by smaller Si NCs. In the main text we consider a statistical doping argument to account for the observed behavior.



Figure S5. a) XRD pattern of octadecene P-doped Si NCs, fresh out of the glovebox (red), and after being one month in solution (orange). The text indicates the average NC sizes derived through the Scherrer approach. The black dashed line displayes the Voight fitting function. b) The PL spectra of the one-month old (slowly oxidized) P-doped Si NCs, combined with a Gaussian fit (red dashed line).

Exclusion of the hot-carrier trapping effect in the sub-15ps time-regime



Figure S6. IA traces of the medium doped P:Si-R for t<15 ps, at several pump wavelengths (400, 500 and 600). A probe wavelength of 1200 nm is used for all these traces.

In the main text we make the argument the \sim 6 ps decay component (that we observe for all of our samples) cannot be explained by hot carrier relaxation. We make this claim based on Fig. S6. If hot carrier trapping would be playing a significant role, variations in the pump energy (as shown in Figure S6) would significantly alter the decay on the ultrafast time-scale. Here we show this is not the case. We do note that the 600 pump shows a slight increase in the first time-bin after photo-excitation, which is ascribed to the solvent-response (toluene).

Multiexciton fits for the intrinsic Si NCs

Figure S7 shows the derivation of the biexciton lifetime according to the method of Klimov et al.⁷, for four differently sized intrinsic Si NC ensembles. These values have been used in Figure 4 (main text) to reference the biexciton lifetimes of the P-doped Si NCs.



Figure S7. Derivation of the biexciton lifetime for four sizes of intrinsic Si NCs. The traces have been scaled according to the method of Klimov et al.⁷, by subtracting traces taken in the linear excitation regime from ones in the nonlinear regime. The red dotted lines present biexponential fits with the longer component representing the biexciton lifetime.

Inability of applying symmetric stochastic model approach to multi-exciton interactions in P-doped NCs

In recent work⁸, we have shown that the multiexciton interactions in both intrinsic Si NCs and small (D_{NC} <6 nm) P-B codoped Si NCs can be modelled by a symmetric three-charge interaction model. As we show in Fig. S8, this is not the case for the P-doped Si NCs in this work, and this is explained by the electronic interaction between the free carriers and the photo-excited e-h pairs. We tried to model the multiexciton interactions by making use of an exciton and three-charge interaction fit, with the exciton interaction model given by:

3)
$$\Gamma_n = \frac{1}{2}n(n-1)\Gamma_2$$
,

and the three-charge interaction model by:

4)
$$\Gamma_n = \left(\frac{1}{2}n\right)^2 (n-1)\Gamma_2.$$

In which Γ_n is the decay rate from *n* to (*n*-1) excitons per NC, and Γ_2 the biexciton recombination rate. The forthcoming fits in Fig. S8 indicate that both interaction model cannot satisfactorily explain the observed multiexciton interactions. This indicates that a more complicated (assymetrical) interaction model is needed, in which the interaction of the free carriers is included.



Figure S8. The average number of excitons per NC as a function of time, according to the method of Schaller et al.⁹, for the medium P-doped Si NCs. The red and orange dotted lines

representing interaction models based on an exciton interaction and a three-charge interaction, respectively.

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