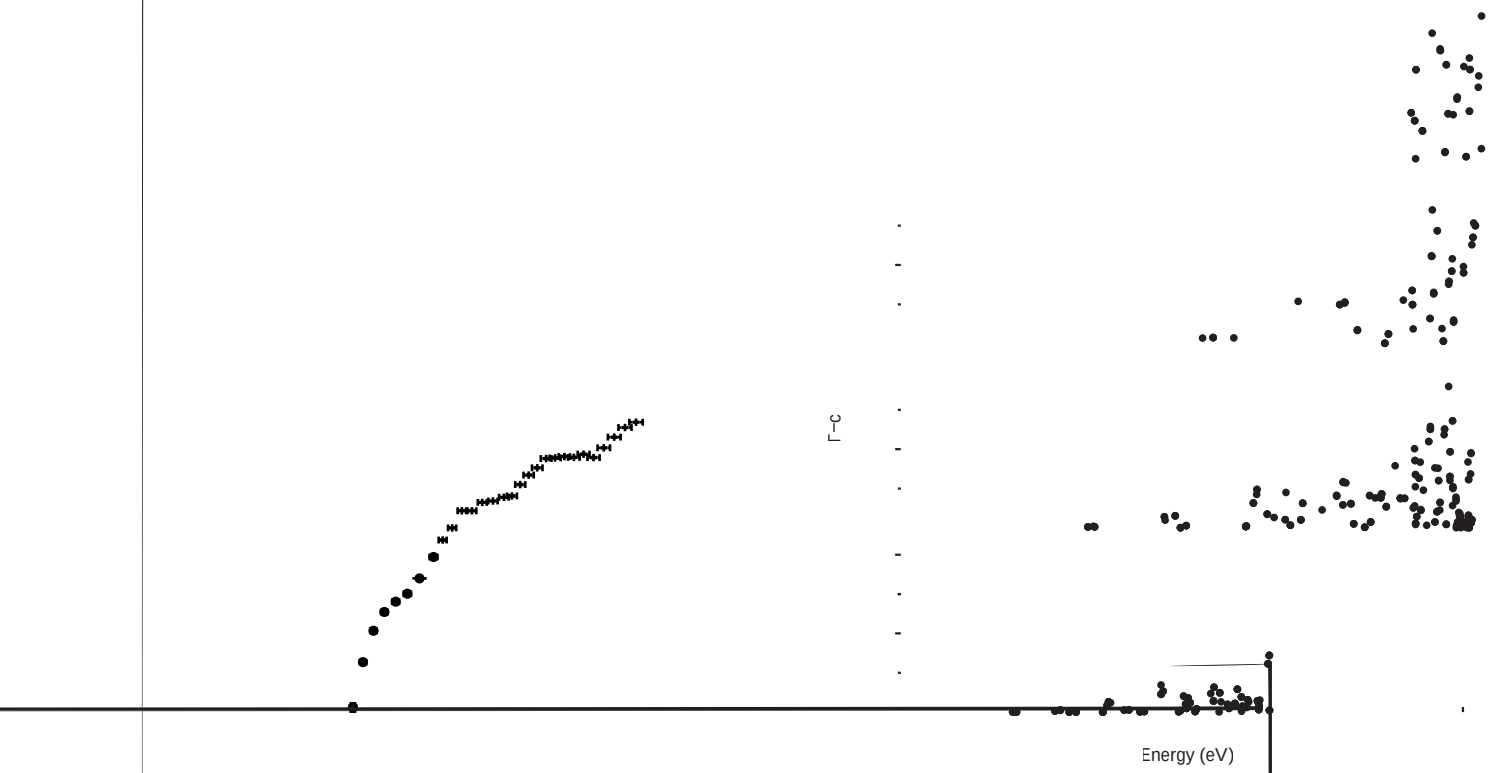
— Silicon is an indirect-bandgap semiconductor and thus an ine cient light emitter, a fact that has posed a serious impediment to the long-standing dream of integrating Si electronics with Si photonics into a combined dual-functional monolithic platform[1,2]. An encouraging experiment that held promise of creating a breakthrough for large-scale integrated complementary metal-oxide–semiconductor-based optoelectronics was published in this journal by de Boer *e al.*[3], who observed, in an ensemble of Si nanocrystals, a high-energy direct transition that rapidly lowered its energy (redshi ed) with decreasing nanocrystal size, projected to lead at su ciently small sizes to a Si nanocrystal with a truly direct gap. e authors observed a hot photoluminescence band and wrote, "…we assign this band to no-phonon hot carrier radiative recombination at levelr(.3 00(su2kq2m1n5DC BT9.3 0 0 9.3 36 525.8622 Tm(An encr8.8622 Tm(its(en4-[ng (en-GB)MC



an ensemble experiment in which they observed many di erent sizes[3]. Also, the theoretical calculations had to be done at the time by deducing the nanocrystal energy levels from the simpli ed e ective mass approach[5] rather than by the more accurate (but demanding) method of considering a nite nanocrystal as a giant molecule in its own right[6,7]. We have recently overcome both di culties and were able to combine our well-tested[6,8–10] atomistic pseudopotential theory of single passivated Si nanocrystals[7,11], including excitonic e ects, with our newly developed single-dot absorption spectroscopy to reveal the origin of the redshi ed transition in Si nanocrystals. ese advanced theoretical and experimental methods enabled us to question the main points of the original paper[3], as we found no signi cant redshi ed direct-bandgap transitions in Si nanocrystals that could be attributed to the e ects of decreasing size at the nanoscale.

Bulk crystalline Si is characterized by an indirect Γ–X bandgap of 1.1 eV with the valence-band maximum (VBM) located at the centre of the Brillouin zone, whereas the conduction-band minimum (CBM) occurs near the X-point (X-valley). e conduction band at the Γ-point (Γ-valley) is high-lying and marks the direct Γ–Γ bandgap of 3.32 eV (Fig. 1a). e breaking of translational symmetry in the nite nanocrystal and the existence of interfacial discontinuities at the nanocrystal surface[11–13] promote inter-valley coupling. e electron states of Si nanocrystals therefore represent a superposition of 3D bulk X-like and Γ-like (and other) Bloch states, rather than being modi ed single-valley states as depicted in simpli ed perturbation approaches[5]. In the modern theory of nanostructures[6,8–10], we solve the atomistic Schrödinger equation explicitly for thousand-atom to multimillion-atom nanocrystals, treated as a giant molecule without reference to the bulk states, with atoms located at speci c positions, each carrying its own (screened) pseudopotential[6,7,14]. e ensuing nanocrystal wavefunctions are then projected onto bulk Bloch states[7,8] (see Supplementary Eq. (2) for details), as shown in Fig. 1c. We see an appreciable Γ-component in the nanocrystal electron states below 3.3 eV. But despite this enhancement of the Γ-component in the low-energy nanocrystal electron states, the lowest-energy nanocrystal state with signi cant Γ-component (about 50%) lies as high as 3.1 eV relative to the bulk Si VBM, well above the proposed[3] direct bandgap of about 2.2 eV (see Fig. 1c) and much higher than the X-valley-dominated nanocrystal CBM at 1.6 eV for a Si nanocrystal of 3-nm diameter. Reducing the nanocrystal size from 3 nm down to 1 nm, we nd no signi cant redshi of the Γ-dominated nanocrystal electron states, unlike the previous interpretation[3] (blue band in Fig. 1c) and calculations using the e ective mass approximation[5]. Instead, we observe a slight blueshi of the Γ-dominated nanocrystal electron states with reducing nanocrystal size (red band in Fig. 1c).

We have compared the calculated absorption spectrum with the measured single-dot absorption curve in a wide spectral range (Fig. 1b) for a Si nanocrystal of 3-nm diameter embedded in a silica matrix (see Supplementary Information for experimental details).

e measured peak position of the excitonic photoluminescence spectrum, corresponding to the fundamental bandgap for the nanocrystal, ts our calculation for a dot of 3-nm diameter. Figure 1b shows good agreement between experimental and theoretical results over nearly three orders of magnitude in absorption intensity, where a growing curve with several

12. Zhang, L., D'Avezac, M., Luo, J.-W. & Zunger, A. *Na Le* . **1** , 984–991 (2012).
14. Wang, L.-W. & Zunger, A. *J. Chem. Ph* . **100,** 2394–2397 (1994).
15. Green, M. A. *S l. E e g. Ma . S l. Cell* , 1305–1310 (2008).
16. Mustafeez, W., Majumdar, A., Vučković, J. & Salleo, A. *J. A l. Ph* . **11** , 103515 (2014).
17. Sykora, M. *e al. Ph . Re . Le* . **100,** 067401 (2008).

Acknowledgements

J.-W.L. was supported by the National Young 1000 Talents Plan and the National Science Foundation of China (NSFC grant 61474116). A.Z. was supported by the US Department of Energy grant DE-FG02-13ER46959 to the University of Colorado, Boulder. I.S., F.P. and J.L. acknowledge support from the Swedish Research Council (VR) through an individual contract and through a Linné grant (ADOPT), and from the Göran Gustafssons Foundation.

Additional information

Supplementary information is available in the online version of the paper.

Jun-Wei Luo[1,2]*, Shu-Shen Li[1,2], Ilya Sychugov[3], Federico Pevere[3], Jan Linnros[3] and Alex Zunger[4]*
[1] K L
M , I
C A , B 12, B 1000 3, C . [2] I C , I , C A 23002 , C . [3] M D , K H , K , , 1 440, . [4] E I , C , B , C 030 , A.
* -