

Figure S1. (top) HRTEM images of a nanorod (adapted from [S4]. Copyright 2013 by the American Physical Society) and a nanodot (reprinted with permission from [S5]. Copyright 2010 IOP Publishing). Scale bar is 2 nm. (bottom) Fourier

Figure S2. (left) Schematics of the reference sample of ensemble of spherical NCs in nanowalls prepared by implantation and annealing with corresponding PL image ($\sim 15 \times 50 \mu\text{m}$

Absorption curve measurements on single nanoparticles. To obtain the excitation energy dependence of absorption, we performed photoluminescence excitation measurements. A Laser-driven Xe lamp (Energetic) with an attached wavelength-selecting monochromator (Princeton Instruments) was used for the excitation below the photoluminescence saturation regime. The spectral resolution of the excitation

Absorption cross-section measurements on single nanoparticles. To calibrate the obtained absorption curves we measured luminescence decay and rise times under modulated 405 nm laser diode excitation of varying power. Since the non-polarized light from the wavelength-selected xenon lamp is difficult to modulate with necessary parameters (<100 ns rise time and >10 kHz repetition rate) here we reli

Figure S4. *Calculated absorbed power for a Si sphere and ellipsoids of the same volume oriented parallel and perpendicular to the electric field (along y- and x-axes). The incident electric field is polarized along x- and travels along z-direction (405 nm wavelength in air). The absorption is slightly reduced in the nanorods perpendicular to the field and is strongly*

Atomistic calculation of the quantum mechanical electronic structure. The single particle eigenstates ($\psi_i; \psi_i(\mathbf{r})$) of differently shaped Si NCs were obtained from direct diagonalization, in a basis set of plane-wave functions, of the Schrödinger equation.⁶ The crystal potential of the NC plus its matrix are both described as a superposition of atomic screened (semi-empirical pseudopotential) potentials of atom type at each atomic site $\mathbf{R}_{i,n}$ within the lattice site n : $V(\mathbf{r}) = \sum_n V_{i,n}(\mathbf{r} - \mathbf{R}_{i,n})$. The semi-empirical pseudopotential method takes into account inter-band coupling, inter-valley coupling (coupling between different parts of the Brillouin zone), and spin orbit coupling.²⁹ For the modeling of the matrix a fictitious, lattice-matched barrier material having a wide bandgap was introduced. The matrix material reproducing the experimentally measured bandgap of Si QDs in SiO₂ in a wide energy range was used.⁶

This method was shown to be more accurate than continuum-based approaches, such as effective mass approximation, both for nanocrystals and nanowires.^{30, S7} The no-phonon optical absorption spectrum in single-particle basis is then calculated, given the dipole transition matrix $\overline{P}_{vc} = \langle \psi_v | \hat{p} | \psi_c \rangle$, according to Fermi's golden rule:

$$A(\omega) = \frac{2\pi}{\hbar} \sum_{v,c} |\overline{P}_{vc}|^2 \delta(E_c - E_v - \hbar\omega) \quad (\text{S3}).$$

Here $E_{vc} = E_c - E_v$ is the transition energy from hole state v to electron state c , m_0 is the free-electron mass, e is the free-electron charge, and γ represents the spectral line broadening. The value of the broadening in calculations of the absorption curve was set to 50 meV. It corresponds to the experimental conditions of the convoluted broadening from the 20-60 meV probe energy resolution and ~ 25 meV thermal broadening (all measurements were performed at room temperature). Examples of the obtained absorption curves for a spherical particle and nanorods of the same volume are shown in Figure S6.

