Size-controlled quantum dots reveal the impact of intraband transitions on high-order harmonic generation in solids

Kotaro Nakagawa\textsuperscript{1}, Hideki Hirori\textsuperscript{1,2,3,4}, Shunsuke A. Sato\textsuperscript{2,3}, Hirokazu Tahara\textsuperscript{1}, Fumiya Sekiguchi\textsuperscript{1}, Go Yamoto\textsuperscript{1}, Masaki Saruyama\textsuperscript{1}, Ryota Sato\textsuperscript{1}, Toshiharu Teranishi\textsuperscript{1} and Yoshihiko Kanemitsu\textsuperscript{1,2}

Since the discovery of high-order harmonic generation (HHG) in solids\textsuperscript{5–9}, much effort has been devoted to understanding its generation mechanism and how different inter- and intraband transitions are known to be essential\textsuperscript{10–12}. However, intraband transitions are affected by the electronic structure of a solid, and how they contribute to nonlinear carrier generation and HHG remains an open question. Here we study HHG in CdSe and CdS quantum dots, where quantum confinement can be used to control the intraband transitions. We find that both HHG intensity and generated carrier density increase when the average quantum dot size is increased from about 2 to 3 nm. We show that the reduction in sub-bandgap energy in larger quantum dots enhances intraband transitions, and this—in turn—increases the rate of photocarrier injection by coupling with interband transitions, resulting in enhanced HHG.

Transitions between the valence band (VB) and conduction band (CB) are responsible for photon absorption in a semiconductor\textsuperscript{11}. However, a strong nonlinear optical response is not necessarily governed only by such interband transitions, and thus, we need to understand the interplay between inter- and intraband transitions. In the case that the electric field \(E(t)\) of a laser accelerates an electron, the temporal change in the electron wavenumber \(k(t)\) can be described by \(\hbar \frac{d}{dt} k = e E(t)\), where \(e\) is the electron charge and \(\hbar\) is the reduced Planck constant. Depending on the degree of change in \(k\), two regimes can be considered: conventional and extreme nonlinear optical phenomena. In the conventional regime (that is, under resonant or near-resonant conditions), the optical field induces only small changes in the wavenumber, leading to a dominant contribution of the interband transitions\textsuperscript{12–14}. In the extreme nonlinear regime where the excitation photon energy \(\omega_o\) is much smaller than bandgap energy \(E_g\), efficient carrier acceleration is possible without damaging the sample by excessive carrier generation. Thus, it is possible to use strong long-wavelength laser fields that induce large changes in the wavenumber. In this case, intraband transitions play a major role in the extreme nonlinear dynamics of the system.

Recently, a rather unexpected role of intraband transitions was found: carrier injection into the CB of GaAs is enhanced by coupling of inter- and intraband transitions\textsuperscript{15}. Also, it has been shown that nonlinear-carrier-generation processes in the extreme nonlinear regime play an important role in the modification of optical and electric properties of solids in the ultrafast timescales\textsuperscript{16–18}. These phenomena are related to high-order harmonic generation (HHG) in solids because in addition to interband transition, nonlinear intraband transition is considered to be responsible for the elementary excitation process behind this phenomenon. However, the relation between nonlinear carrier generation and HHG has not yet been experimentally studied, and thus, it has remained elusive how intraband transitions correlate with the electronic structure of a solid and eventually with nonlinear carrier generation and HHG. To clarify the impact of intraband transitions on extreme nonlinear optical phenomena, it is necessary to study it from materials in which the electronic band structure and thus intraband transition can be freely controlled. Because the nature of the electronic bands of quantum dots (QDs) can be continuously tuned from atom-like discrete states to a solid-state band continuum simply by changing their size, without changing the constituting elements\textsuperscript{19–21}, they are ideal materials to examine the role of intraband transitions in carrier generation and its relation to HHG.

Here we studied HHG in CdSe and CdS QD films. Figure 1a (dashed lines, left) illustrates a schematic of the energy levels of a QD; \(E_g\) is the QD bandgap energy and \(\Delta_{ab}\) is the first sub-bandgap energy. Both parameters depend on the QD diameter. Figure 1a (middle) shows the absorption spectra of CdSe QDs with different diameters (Supplementary Section 1). Owing to the strong quantum confinement in these small QDs, \(E_g\) is larger than in the bulk by up to several hundred millielectronvolts (the bandgap energies of bulk CdSe and CdS are 1.75 and 2.58 eV, respectively), and the electronic states become discrete\textsuperscript{22–27}. Figure 1a (right) shows the excitation and detection geometry used to measure the HHG emission spectra of the CdSe QD film (Methods) and the typical transmission electron microscopy (TEM) images. Figure 1b shows the high-order harmonic (HH) intensities per excited volume as a function of photon energy \(\omega_o\), namely, \(I_{HHG}(\omega_o)\), for CdSe and CdS QD films under excitation with linearly polarized mid-infrared (MIR) light. The spectra extend from the visible to the ultraviolet region and the peaks correspond to the 7th–13th orders. We find that \(I_{HHG}(\omega_o)\) tends to increase as the average QD diameter \(d\) increases, and it increases abruptly in the range from 2 to 3 nm.

Figure 2 provides data on CdSe (red circles) and CdS (blue squares): it shows the integrated HH peak intensity of each order \(I_{\omega_o}\) where \(\omega_o\) is the harmonic order) as a function of \(d\) to clarify the QD size dependence of the HH intensity. For CdSe QDs, \(I_{\omega_o}\) significantly increases with \(d\) in the range of \(d \approx 1.8–3.8\) nm. For example, \(I_{\omega_o}\) increases by a factor of about 100 from \(d = 2.1\) to 3.8 nm. Note that the \(E_g\) value of CdSe QDs with \(d\) in the range of 2.1–3.8 nm changes from 2.6 to 2.1 eV, but the absorption spectra (Fig. 1a)
indicate that the required number of photons in the multiphoton absorption process for the VB–CB transition remains almost the same (that is, the band edge lies in the region near $k=7$ or 2.48 eV).

Although the bandgap energy for $d=2.4 \text{ nm}$ lies closer to the 7th resonant multiphoton absorption than for 2.8 nm, the HH intensities of the smaller QDs are much smaller. Also, an almost constant behaviour in the range $d \approx 3.8-14.0 \text{ nm}$ (Fig. 2a, inset) is observed despite the difference in the order of multiphoton absorption. In addition, the excitation intensity dependence shows that the HHG mechanism in CdSe QDs under these excitation conditions is non-perturbative (Supplementary Sections II and III). These results show that the size dependence of $I_\text{HHG}$ cannot be simply explained by the difference in the multiphoton absorption process considering only interband transitions.

To obtain the relation between the actual carrier density generated by the MIR pump pulse and HHG, we measured the transient absorption (TA) change in the CdSe QD films in experiments with an MIR pump and a white-light probe. The schematic of the setup including TEM images of CdSe QD films (right). The ODs are normalized by the lowest-energy exciton peaks. The TEM images of CdSe QD film (3.8 and 14.0 nm) are shown.

The carrier density was determined by dividing the absorbance at the band edge of the QD film by the absorption cross section per unit volume. The four graphs shown in Fig. 3b show the TA dynamics integrated over the energy region $\Delta$OD divided by optical density OD. The four graphs shown in Fig. 3b show the TA dynamics integrated over the energy region $\Delta$OD divided by optical density OD. The four graphs shown in Fig. 3b show the TA dynamics integrated over the energy region $\Delta$OD divided by optical density OD. The four graphs shown in Fig. 3b show the TA dynamics integrated over the energy region $\Delta$OD divided by optical density OD. The four graphs shown in Fig. 3b show the TA dynamics integrated over the energy region $\Delta$OD divided by optical density OD.
components in the Hamiltonian are set to zero (Fig. 4b, blue curve, and Supplementary Section VI), the intensities are substantially reduced. This result indicates that the observed nonlinear responses are determined by the size dependence of the intraband transitions. Note that $E_p$ increases as $d$ becomes smaller ($\propto 1/d^2$) and energy gap $\Delta_{ab}$ between the quantum states with quantum numbers $n=1$ and $n=2$ is roughly proportional to $n^2/m^*d^2$ (Extended Data Fig. 1a), where $m^*$ is the reduced mass. To see which parameter governs the size dependence, we also evaluated the size dependence of $I_x$ under the assumption of a size-independent $E_p$. The obtained size dependence (Extended Data Fig. 1b) resembles the red solid curve shown in Fig. 4b, and this indicates that the actual increase in $E_p$ for smaller QDs does not govern the observed size dependence. To understand the effect of discretization of QDs on the HH intensity, we studied the influence of $m^*$ on the size dependence: Fig. 4c shows that $I_x$ of QDs with small diameters ($d \approx 1$ nm) becomes smaller as the mass becomes smaller. This result is consistent with the experimental results shown in Fig. 2, since the $m^*$ value of CdSe (0.1 $m_H$) is smaller than that of CdS (0.2 $m_H$) (ref. 23). Moreover, the dependence of $I_x$ on $\Delta_{ab}$ which can be changed by varying $m^*$, is shown in Extended Data Fig. 1c. The obtained curves of $I_x$ as a function of $\Delta_{ab}$ are similar regardless of the value of $m^*$. This result shows that the discrete electronic states due to confinement in small QDs suppress intraband transitions.

The good agreement between the experimental QD size dependence and our calculations shows that intraband transitions cause efficient nonlinear carrier generation and HHG in larger QDs. Nonlinear carrier generation is a coherent optical process and thus involves a superposition of multiple transitions from various VB–CB excitation paths (Supplementary Section VI). It is due to nonlinear coupling between inter- and intraband transitions: in addition to the contribution from pure interband-transition terms, the contribution from the coupling terms increases when the intraband transitions are enhanced (Fig. 4d, schematic, and Extended Data Fig. 2). In the case of coherent excitation of small QDs, carrier acceleration (intraband transition) is drastically suppressed by discrete electronic states. Meanwhile, larger QDs (bulk form) provide more efficient carrier acceleration and thus cause an additional coupling between inter- and intraband transitions, which results in efficient carrier generation and consequently stronger HHG.

Note that although our calculations can explain the overall behaviour of the experimental results (Figs. 2 and 3), there is a slight quantitative discrepancy between the observed trends (Figs. 2 and 3). To clarify this, we considered the yield ratio, which is the HH intensity per ionization event, namely, $I_x/n_0$. In Extended Data Fig. 3, we can confirm an increase in the yield ratio of the 7th harmonic as the QD diameter decreases from about 7 to 3 nm. Therefore, with respect to the number of electrons in the CB, the 7th harmonic is generated more efficiently in smaller QDs. In smaller QDs, which are tightly confined systems, the number of excited carriers is reduced by the amount by which intraband transitions are quenched as the sub-bandgap energy is increased. On the other hand, the overlap of excited electrons and holes increases in smaller QDs, and thus, the probability of recombination increases $^{21,24}$. Therefore, the yield ratio of smaller QDs can be larger.

By using size-controlled QDs, we show that quantum confinement can indeed be used to control intraband transitions and therefore influence the carrier density and HHG. This means that the size of a structure constitutes a parameter that can be used to control extreme nonlinear optical phenomena. Our findings on the control of nonlinear optical phenomena by nanosizing can be used in designing sophisticated petahertz optoelectronic devices that will be implemented at the nanoscale $^{25,26}$. The impact of intraband transitions on carrier excitation shown in our work has
Fig. 3 | TA measurements. a, Schematic of the experiment and typical TA spectrum of CdSe QDs obtained using an MIR pump pulse (3 μm, 0.36 TW cm⁻²). b, Time evolution of ΔOD/OD near the bandgap energy for d = 2.4, 2.8, 3.8 and 6.4 nm. Here ΔOD/OD was obtained by measuring the sample transmissivities with and without pump pulse excitation. c, Average number of carriers per excited volume, n_d, estimated from the exciton amplitudes in TA signals. The vertical and horizontal error bars represent the standard deviation calculated from the exciton amplitude as well as the diameter. The solid curve is a guide to the eye. Since the TA signal of the sample with d = 2.4 nm was smaller than the background level, the point at d = 2.4 nm plots the upper limit of n_d estimated from the background level.

Fig. 4 | Calculation results. a, HH spectra per excited volume for different QD diameters (chain lengths). For this calculation, we assumed ℏω₀ = 0.35 eV and E = 11 MV cm⁻¹, which resembles the experimental conditions. b, Diameter dependence of I_7 and n_d obtained by using the full model (red circles and squares) and diameter dependence of I_7 obtained by using a model excluding the intraband-transition term (blue triangles). c, Dependence of I_7 on the diameter for different reduced masses. d, Schematic describing nonlinear carrier generation via an additional path including excitation processes due to the coupling of inter- and intraband transitions.
important implications for light-driven control of material properties and also for micromachining\textsuperscript{1,2}, which can be realized, for example, by using two light sources with different wavelengths and a tunable phase offset or different polarization states to manipulate intraband transitions\textsuperscript{3}.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41567-022-01639-3.

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Methods

QD synthesis. The CdSe and CdS QDs were prepared in our laboratory by wet chemical synthesis, which provides precise control over the QD size (Supplementary Section I).

HHG spectrum measurements. For the measurement of the HH spectra, QD thin films were excited by linearly polarized MIR pulses with $h\omega_0 = 0.35$ eV ($\lambda_0 = 3.5 \mu m$). The MIR pulses were generated using a multistage optical parametric amplifier system (OPerA with the NDFG1 option, Coherent) driven by a Ti:sapphire laser with a repetition rate of 1 kHz. The QD thin-film samples were prepared by the spin coating of colloidal QDs dispersed in hexane on a sapphire substrate with a thickness of 0.5 mm. For all the QD samples, hexane was evaporated after spin coating on the substrate, and it was confirmed that the substrate and surface-protecting ligands for QD do not contribute to the HH spectra. The experiments were conducted with excitation intensities below the damage threshold of the QDs; the excitation peak intensities were 0.45 TW cm$^{-2}$ for CdSe QDs and 0.75 TW cm$^{-2}$ for CdS QDs (the pulse width was 80 fs and spot diameter was ~300 µm). We verified that linear absorption at the excitation spot did not change during the MIR pulse irradiation and that the observed change in $I_{HH}$ for smaller QDs was not due to sample damage (Supplementary Fig. 3). All the experiments were performed at room temperature. The HHs were detected using a charge-coupled-device (CCD) camera (PIXIS, Teledyne Princeton Instruments) attached to a spectrometer (SpectraPro, Teledyne Princeton Instruments).

TA spectroscopy. In the MIR-pump–visible-probe TA measurements, we used an MIR excitation pulse with $h\omega_0 = 0.41$ eV ($\lambda_0 = 3 \mu m$ and the temporal pulse width was 100 fs), which was generated from a home-made optical parametric amplifier system based on an Yb:KGW femtosecond laser system (PHAROS, Light Conversion) with a centre wavelength of 1.033 nm, pulse width of 180 fs and 2 mJ per pulse at a repetition frequency of 1 kHz. To avoid the additional small thermal-decay contribution in the TA signal due to the ligands of QDs, it was necessary to use an MIR excitation wavelength (3 µm) that is shorter than the one used in the HH spectrum measurements (Fig. 1). We verified that the different MIR excitation wavelengths did not cause a notable change in the size dependence of $I_{HH}$ (Supplementary Fig. 4). For the probe pulses, white light was generated by focusing a small fraction of the output beam of the Yb:KGW laser into a 10-mm-thick quartz cell containing water (Supplementary Section V). This method provided a better signal-to-noise ratio compared with a Ti:sapphire laser owing to better laser stability. The generated continuum spectrum ranged from the visible to near infrared regime. The MIR pump and visible probe beams were focused onto the sample and the beam spot diameters were about 250 and 150 µm, respectively. For the TA measurements with visible pump pulses ($h\omega_0 = 2.40$ eV ($\lambda_0 = 517$ nm) and temporal pulse width of 180 fs), we used frequency doubling of the fundamental pulses in a beta barium borate crystal. Here we used QDs with $d = 2.4, 2.8, 3.1, 3.8, 4.3$ and 6.4 nm because the band-edge exciton energies were 2.40, 2.31, 2.24, 2.19 and 1.91 eV, respectively, allowing a band-to-band excitation by the second harmonic of the fundamental pulse ($h\omega_{nm} = 2.40$ eV). The probe light transmitted through the sample was spectrally resolved by a spectrometer and detected using a CCD camera. To obtain a high signal-to-noise ratio, we synchronously chopped the pump beam at 500 Hz, thereby blocking every second pump pulse. A computer collected the signals to obtain the TA signal, which was calculated from the probe transmission with and without the influence of the pump light.

Data availability

Source data are provided with this paper. All other data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions

K.N. and H.H. carried out the experiments. K.N., H.H., S.A.S., H.T., F.S., G.Y. and Y.K. analysed the data; S.A.S. performed the simulations. M.S., R.S. and T.T. synthesized the QDs. H.H. and Y.K. conceived and supervised the project. All the authors discussed the results and contributed to the writing of the paper.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Hideki Hirori or Yoshihiko Kanemitsu.

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Extended Data Fig. 1 | Additional calculation results. **a**, Bandgap energy $E_g$ (blue squares) and subband gap, $\Delta_{\text{sub}}$ (red circles), as a function of the QD diameter (chain length). **b**, Diameter dependence of $I_7$ obtained by assuming a size-independent $E_g$ (green squares) and that obtained by the full model with a size-dependent $E_g$ (red circles). **c**, Dependence of $I_7$ on $\Delta_{\text{sub}}$ for different reduced masses.
Extended Data Fig. 2 | Schematics of multiple excitation paths. In addition to the contribution of the pure interband transition terms (left), the efficient intraband transition in larger QDs (or bulk) opens multiple excitation paths due to the nonlinear coupling between the intra- and interband transitions (right). These additional excitation channels due to the coupling promote nonlinear carrier injection and enhance HHG in larger QDs.
Extended Data Fig. 3 | Yield ratio. Diameter dependence of the yield ratio of the 7th order for CdSe, $I_7/n_d$. The data is normalized to the value at $d = 6.4$ nm. Vertical and horizontal error bars represent the standard deviation of yield ratio and that of diameter. The solid curve is a guide to the eye.