Non-linear Response of CdSe/CdS Quantum Dots Driven by Intense Terahertz Pulses

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Abstract: We report on the observation of quantum confined stark effect (QCSE) in CdSe/CdS core/shell quantum dots (QDs) directly driven by an intense THz field, generated in the organic crystal DAST, which is pumped with multi-millijoule mid-IR pulses. © 2021 The Author(s)

The development of intense THz table-top sources in the past few decades paved the way for controlled manipulation over numerous reactions and processes. High energy THz pulses with an electric field strength exceeding the intrinsic field of atoms have a large potential for controlling matter by coherent lattice excitation, triggering phase transitions and for engineering new dynamic states of materials [1], such as THz enhanced superconductivity [2], polarization switching in ferroelectric materials [3], or ultrafast switching and control of magnetic domains [4]. Furthermore, rapidly developing modern optical communication systems demand small-scale electro-optic devices with large and fast changes in optical properties. Among others, such are semiconductor quantum dots (QDs) manipulated at THz frequencies. Recently, femtosecond all-optical switching of optical absorption in an InGaAs/GaAs QD-based saturable absorber mirror, induced by the electric field of an incident THz pulse was demonstrated [5]. A few years later, Pein and co-workers [6,7] reported on a THz-field induced QCSE in CdSe/CdS colloidal QDs. However, due to difficulties to generate THz radiation with the electric field in the MV/cm range, necessary to alter the QD band gap and to change the optical transmission, THz field enhancing structures have been used.

In this work, we demonstrate a direct all optical encoding of a free-space, ultrafast, high-bandwidth THz signal onto an optical signal probing the absorption of a film consisting of CdSe/CdS QDs. In contrast to previous works, the manipulation of the optical absorption in the sub-picosecond time scale is achieved without any field enhancing structure. Instead, the QDs are deposited onto a glass substrate by a simple drop-casting method (see a QD sample in Fig. 2 (a)).

![Diagram](image)

Fig 1. (a) Schematics of the experimental setup. A conventional EOS setup with a 1 mm thick ZnTe crystal is used in configuration (1) to sample the THz field. To measure the change in transmission, the ZnTe crystal is replaced with the QD sample and a reference beam (2) is used. BS - beam splitter, LPF – long pass filter, WP-Wollaston prism. (b) Normalized absorption spectrum of QDs (solid red line) and spectrum of the probe pulse centered at 621 nm (dashed green line).

Figure 1 (a) depicts the experimental setup, wherein a high energy optical parametric chirped pulse amplifier (OPCPA) [8] generating 100 fs pulses centered at 3.9 µm is used to pump the organic crystal DAST for efficient THz generation, providing a THz pulse energy of 13 µJ at the sample position, with a spectral bandwidth of 4 THz at
FWMH level. Long pass filters (LPF) are used to separate the driving mid-IR pulse from the THz radiation. The generated THz field in time domain is monitored by electro-optical sampling (EOS) in a 1 mm thick ZnTe crystal (see setup configuration (1) in Fig. 1 (a)). The probe pulse is provided by a wavelength tunable non-collinear optical parametric amplifier (NOPA) which is synchronized with the mid-IR driving pulse. In order to measure a change in transmission of the probe pulse with respect to the THz pump, the CdSe/CdS QD sample is placed at the position of the ZnTe crystal. As it is shown in Fig.1 (a), during the measurements, path (1) is blocked and an independent reference beam (2) is used. Figure 1 (b) shows the normalized absorption spectrum of the colloidal QDs containing a CdSe core of 4.1 nm in diameter and CdS shell with a thicknesses of 2.35 nm (see the TEM image in Fig. 2 (b)). The photoluminescence spectrum (not shown here) is centered at 633 nm. The NOPA is tuned to a central wavelength of 621 nm, at which an efficient modulation of the signal by THz pulses can be observed.

The shape of the sampled THz electric field is shown in Fig. 2 (c), and the square of the field amplitude is presented by the green area in Fig. 2 (d). As it can be seen from the figure, a change in transmission of the QDs, shown by the red curve, evidently follows the THz electric field. As it was discussed in [7], the behavior can be explained by QCSE, resulting in the shift of electron states to lower energies, while the hole states shift to higher energies when an external electric field is applied. As a result, the band gap is modulated, and the transmission spectrum is modified accordingly. Obtained results demonstrate the feasibility to manipulate the electronic structure of QDs by direct THz excitation without a need of field enhancement techniques, which is of great importance for the future developments in the areas of THz opto-electronics, wireless communications and THz driven non-linear optics. Currently, spectrally resolved studies of QCSE in CdSe/CdS QDs are in progress.

![Fig 2. (a) QD films deposited on a glass substrate with drop casting. (b) Transmission electron microscopy (TEM) image of colloidal QDs. (c) THz E-field measured with EOS. (d) THz Intensity (green area) and normalized change in absorption from QDs (red) with respect to the time delay of the THz pump and probe pulse. The change in absorption follows the shape of the THz field.](image)

References


