Millimeter wave absorption by confined acoustic modes in CdSe/CdTe core-shell quantum dots

2007 J. Phys.: Conf. Ser. 92 012039

(http://iopscience.iop.org/1742-6596/92/1/012039)

Journal of Physics: Conference Series **92** (2007) 012039 doi:10.1088/1742-6596/92/1/012039

Millimeter wave absorption by confined acoustic modes in CdSe/CdTe core-shell quantum dots

Tzu-Ming Liu[1], Ja-Yu Lu[1], Chung-Chiu Kuo[1], Yu-Chieh Wen[1], Chih-Wei Lai[2], Meng-Ju Yang[2], Pi-Tai Chou[2], Daniel B. Murray[3], Lucien Saviot[4] and Chi-Kuang Sun[1,5]

[1]Graduate Institute of Photonics and Optoelectronics, National Taiwan University, Taipei 10617, Taiwan R.O.C.
[2]Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan R.O.C.
[3]Mathematics, Statistics and Physics Unit, University of British Columbia Okanagan, Kelowna, British Columbia, Canada V1V 1V7
[4]Institut Carnot de Bourgogne, UMR 5209 CNRS-Université de Bourgogne, 9 Av. A. Savary, BP 47 870, F-21078 DIJON Cedex, FRANCE
[5] Department of Electrical Engineering and Graduate Institute of Photonics and Optoelectronics, National Taiwan University, Taipei 10617, Taiwan R.O.C.

E-mail: f88941002@ntu.edu.tw

Abstract. Taking advantage of the specific core-shell charge separation structure in the CdSe/CdTe core-shell Type-II quantum dots (QDs), we experimentally observed the resonant-enhanced dipolar interaction between millimeter-wave (MMW) photons and their corresponding (l=1) confined acoustic phonons. With proper choice of size, the absorption band can be tuned to desired frequency of MMW imaging. Exploiting this characteristic absorption, in a fiber-scanned MMW imaging system, we demonstrated the feasibility of CdSe/CdTe QDs as the contrast agents of MMW imaging.

1. Introduction

With spatial confinement, a low dimension system such as quantum dot or nano-wire exhibits not only electronic but also acoustic energy quantization. When mechanical vibration of the quantized acoustic modes modifies local dipole-moments, electromagnetic waves should be able to be resonantly coupled to the confined acoustic phonons, allowing the conversion of a low-frequency photon into a phonon of the same frequency. According to elastic continuum theory [1], for homogeneous nanospheres, the frequency of fundamental dipolar modes (l=1) falls in the millimeter wave (MMW) range (30~300 GHz). It is thus highly desirable to use the MMW to identify or even image different nanospheres through resonant coupling with the quantized acoustic vibration in low-dimensional systems, which has never been demonstrated up to date. Here we synthesized CdSe/CdTe (core-shell) type-II quantum dots (QDs) with size around 10 nm. The core-shell spatial charge separation induced obvious MMW absorption around the frequency of fundamental (l=1) acoustic confined modes. With proper choice of size, we demonstrated the contrast of probes in the MMW imaging of a bio-sample. Our method provides a substantial advance in the development of bio-probes in MMW bio-imaging.

2. Principles

The spheroidal (SPH) vibrations in a free homogeneous isotropic continuum sphere can modify its optical properties [2] and induce either inelastic light scattering [3] or MMW absorption [4]. The former processes are related to the SPH modes with quantum number l=0 or 2, which have been widely investigated through low-frequency Raman scattering (LFR) [3] and pump-probe pulsed laser (PPPL) experiments [5]. In contrast, the latter process is only related to scarcely studied l=1 modes [4]. The distribution of the displacement vector of the (SPH, l=1) dipolar modes in a nanosphere have relative displacement between the center (core) and the outer (shell) regions [4]. Therefore, a core-shell charge separation is required to match the motional pattern, to induce the change of dipole moment, and to activate the resonant absorption of (SPH, l=1) dipolar modes. Except for core-shell charge separation, the challenges to observe the spectrally-resolved resonant electromagnetic absorption related to (SPH, l=1) modes in nanoparticles also include: (1) uniform size distribution, (2) high quality factor for the confinement of acoustic waves in the sphere, and (3) long term charge distribution for the dipolar coupling. Challenges (1) and (2) are related to inhomogeneous and homogeneous broadening of acoustic modes, respectively. Chemically prepared nanopowders could have reasonable size uniformity and provide high-enough confinement of acoustic waves [4]. However, it's hard for inorganic clusters to create specific and long term charge separation. Besides, the amount of charge should be large enough to induce detectable excess absorption over the background dielectric absorption [6]. That could be the main reason why the report is rare for MMW absorption related to (SPH, l=1) modes. Following these properties and requirements, we prepared CdSe/CdTe (core/shell) type-II QDs by chemical synthesis [7]. Due to large surface to volume ratio, the surface lone-pairs on the Tellurium dangling bonds [8] could be thermally or optically excited to the conduction band of CdTe and then falls into the CdSe core with lower electric potential. This process can result in negatively charged core and a positively charged ion shell on the CdTe surface (see figure 1A). This specific core-shell charge separation should enable the studies of the dipolar interaction between MMW photons and confined acoustic modes in NCs.

3. Experiments and Conclusion

To allow the dipolar resonance frequency to fall into the MMW range, we chose CdSe/CdTe (core/shell) type-II QDs with 13 nm (5.3 nm core) and 10.4 nm (4.3 nm core) diameters. We synthesized 3.6×10^{15} and 1.4×10^{16} particles of 13 nm and 10 nm CdSe/CdTe QDs, respectively. From transmission electron microscope (TEM) images, it was determined that the variation of their sizes was ~20%. Both CdSe and CdTe show cubic zinc-blende structures from the X-ray diffraction measurements [7]. Calculated using elastic continuum theory for the core-shell structure [9], the frequencies of corresponding (SPH, l=1, n=0) dipolar modes are 141±11 GHz and 177±17 GHz, respectively. The frequency of (SPH, l=1, n=1) modes are expected to be twice that of (SPH, l=1, n=0) modes, with also two times the frequency uncertainty due to the size nonuniformity. To measure the MMW absorption of QDs, we employed an edge-coupled membrane photonic transmitter to generate quasi-continuous MMW pulses with a tunable central frequency [10]. The MMW power was recorded by a bolometer through lock-in detection. The type-II QD powders were separately sealed with a 30 μm poly-ethylene (PE) film with an area of 3×10 mm. Sample thicknesses are 640 μm and 540 μm for the 10.4 nm and 13 nm nanoparticles, respectively. Figure 1B (solid curve) shows the measured emission spectrum of the photonic transmitter after the PE film without CdSe/CdTe QDs. The spectral power reached a maximum of 150 nW at 100 GHz and extended to 500 GHz with a substantial signal to noise ratio. With the PE film containing 13nm CdSe/CdTe QDs the measured millimeter wave power spectrum shows obvious attenuation (dotted curve in figure 1C). Dividing these two data sets, we can calculate the extinction cross section by $\sigma_{ex} = \ln(T)A/N$, where T is the transmission, A is the excitation area, and N is the number of QDs in the excitation area. The spectrum of the extinction cross section σ_{ex} shows a 125-205 GHz peak accompanied by a shoulder (figure 1D). The absorption feature was smeared, not only due to the non-uniform particle size, but possibly also due to other physical mechanisms such as interparticle interactions and the large resolution bandwidth of our

microwave source (~50 GHz). At the frequency of peak absorption, the transmitted microwave power decayed to 0.65 of the original, corresponding to ~5.7×10^{-21} m^2 extinction cross sections for each QD. For the smaller 10.4 nm QDs, the extinction peaks blue shifted to 160-280 GHz and shows an harmonics around 290-430 GHz (see figure 1C). Considering the resolution of our source and the uncertainties in the size distribution, these extinction peaks are close to theoretical predictions, matching the frequencies of (SPH, l=1) dipolar modes.

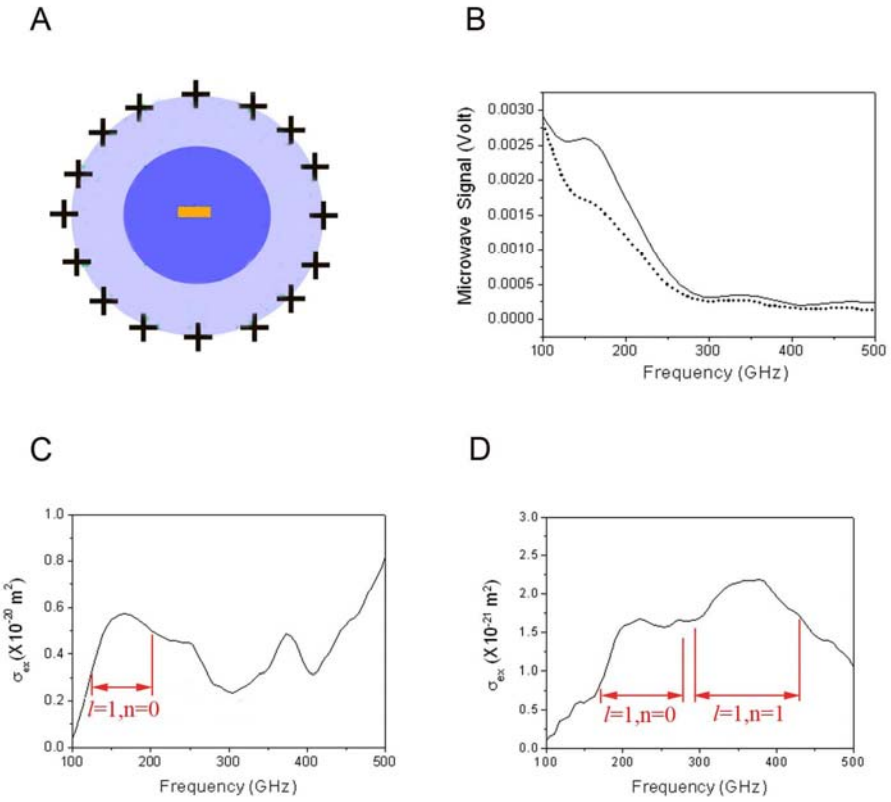

Figure 1. (A) Charge distribution of CdSe/CdTe (core/shell) type-II QDs. **(B)** Power spectra after PE film with (dotted line) and without (solid line) 13 nm CdSe/CdTe QDs. The spectrum of the extinction cross section σ_{ex} of **(C)** 13 nm and **(D)** 10.4 nm CdSe/CdTe QDs.

Exploiting this dipolar resonant absorption feature, type-II QDs can thus serve as contrast agents for microwave millimeter wave imaging. The required absorption contrast at a specific microwave imaging frequency can be designed by tailoring the size of the QDs. To demonstrate this idea, we employed a sub-wavelength fiber scanned MMW imaging system (see figure 2A) [11]. The imaging frequency was 320 GHz, which was determined by the sub-wavelength fiber [11]. As a comparison, we first took the transmission MMW images of three different QDs, which were 4.4 nm CdSe, 8 nm CdSe/CdTe, and 10.4 nm CdSe/CdTe (see figure 2B). Characterized by their size-dependent dipolar coupling characteristics, only 10.4 nm CdSe/CdTe QDs can resonantly absorb 320 GHz microwaves, which results in the transmission contrast for the fiber scanned image (dark region of figure 2C). We then selected the 10.4 nm QD as a contrast agent and applied them to a bio-sample, a dry sea horse. Before using these contrast agents, the MMW transmission image (see figure 2D) could clearly distinguish the detailed structure inside the body of the dry seahorse including the spine, the brain cavity, the abdominal cavity, and somite. After depositing 10.4 nm CdSe/CdTe QDs into the brain cavity, we could observe obvious contrast from the corresponding MMW image (figure 2E, indicated by a red arrow). This result demonstrates the feasibility that type-II QDs can be used as contrast agents for MMW resonant molecular imaging.

In conclusion, with specific charge separation in CdSe/CdTe type-II NCs, we successfully induced MMW resonant absorption related to l=1 confined acoustic modes. Exploiting this characteristic absorption, by tailoring the size of NCs, type-II QD can serve as contrast agents for MMW imaging.

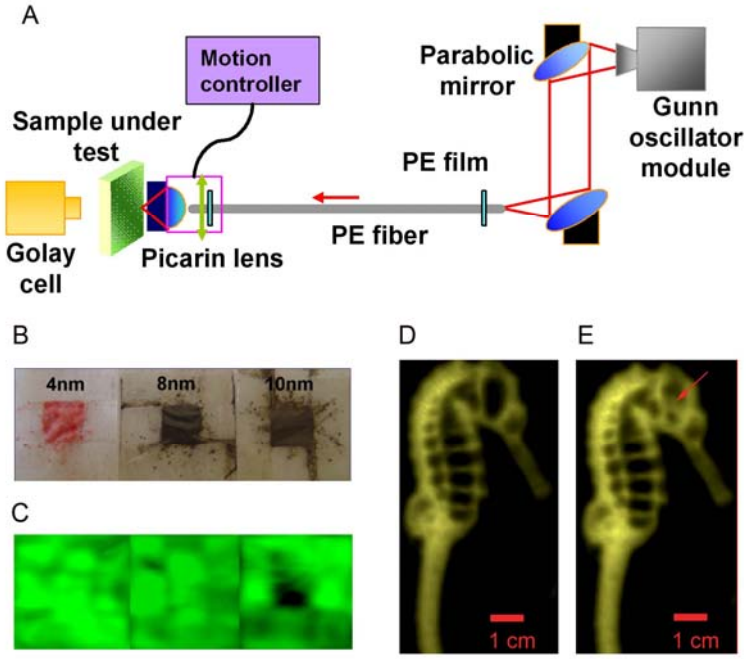

Figure 2. (A) (color online) Schematic diagram of subwavelength fiber-scanned MMW imaging system. **(B)** Camera pictures of three different QDs. From left to right, they are powders of 4.4 nm CdSe, 8 nm CdSe/CdTe, and 10.4 nm CdSe/CdTe. **(C)** MMW transmission images of the corresponding QDs listed above. The color green represents high transmission **(D)** MMW transmission images of a bio-sample, a dry sea horse, without contrast agents. The color yellow represents the position where the material has MMW absorption. **(E)** MMW transmission images of a dry sea horse with QDs, mimicking contrast agents.

References

[1] Lamb H 1882 *Proc. London Math. Soc.***13** 189.
[2] Duval E 1992 *Phys. Rev.* B **46** 5795.
[3] Duval E, Boukenter A and Champagnon B 1986 *Phys. Rev. Lett.* **56** 2052.
[4] Murray D B, Netting C H, Saviot L, Pighini C, Millot N, Aymes D and Liu H-L 2006 *J. Nanoelectron. Optoelectron.* **1** 92.
[5] Krauss T D and Wise F W 1997 *Phys. Rev. Lett.* **79** 5102.
[6] Lee S-I, Noh T W, Cummings K and Gaines J R 1985 *Phys. Rev. Lett.* **55** 1626.
[7] Chen C-Y, Cheng C-T, Lai C-W, Hu Y-H, Chou P-T, Chou Y-H and Chiu H-T 2005 *Small* **1** 1215.
[8] Poznyak S K, Osipovich N P, Shavel A, Talapin D V, Gao M, Eychmüller A and Gaponik N 2005 *J. Phys. Chem.* B **109** 1094.
[9] Portalès H, Saviot L, Ducal E, Gaudry M, Cottancin E, Pellarin M, Lermé J and Broyer M 2002, *Phys. Rev.* B **65** 165422.
[10] Lu J-Y, Chen L-J, Kao T-F, Chang H-H, Chen H-W, Liu A-S, Chen Y-C, Wu R-B, Liu W-S, Chyi J-I and Sun C-K, *IEEE Photon. Technol. Lett.* 2006 **18** 2254.
[11] Chen L-J, Chen H-W, Kao T-F, Lu J-Y and Sun C-K 2006 *Opt. Lett.* **31** 308.