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Deformation-induced blueshift in emission spectrum of CdTe quantum dot composites

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ABSTRACT

Polymer or glass films impregnated with quantum dots (QDs) have potential applications for mesoscale stress/strain sensing in the interior of materials under mechanical loading. One requirement in the development of such nanocomposite sensor materials is the establishment of calibrated relations between shifts in the emission spectrum of QD systems and the input stress/strain on the composites. Here, we use a multiscale computational framework to quantify the strain-dependent blueshift in the emission spectrum of CdTe QDs uniformly distributed in a matrix material under loading of a range of strain triaxiality. The framework, which combines the finite element method, molecular dynamics simulations and the empirical tight-binding method, captures the QD/matrix interactions, possible deformation-induced phase transformations and strain-dependent band structures of the QDs. Calculations reveal that the response of the QDs is strongly dependent on state of input strain. Under hydrostatic compression, the blueshift increases monotonically with strain. Under compression with lateral/axial strain ratios between 0.0 and 0.5, the blueshift initially increases, reaches a peak at an intermediate strain, and subsequently decreases with strain. This trend reflects a competition between increases in the energy levels associated with the conduction and valence bands of the QDs. The deformation-induced blueshift is also found to be dependent on QD orientations. The averaged blueshift over all orientations for the composite under uniaxial strain condition explains the blueshift variation trend observed in laser-driven shock compression experiments. Based on the simulation result, guidelines for developing QD composites as stress/strain sensing materials are discussed.

1. Introduction

Laser-driven shock compression (LSC) is a commonly used experimental technique to examine materials under loadings at extremely high strain rates (e.g., up to 10^8 s^{-1}) [1–5]. The LSC of microstructurally heterogeneous materials (materials composed of dissimilar constituents or materials containing geometric discontinuities such as voids, microcracks, interfaces or grain boundaries) usually results in highly inhomogeneous dynamic responses dominated by mesoscale processes in the interior of the materials which manifest on times scales of tens or hundreds of nanoseconds. Particle-level stress/strain measurement in the interior of materials under such extreme conditions requires special stress/strain sensing materials (SSM) that are small in size and fast in response. Specifically, the SSM should possess stress-dependent physical properties (e.g., optical properties) whose signal(s) can be captured and recorded in real time to achieve temporal resolutions of nanoseconds. Additionally, calibrated relations between the input stress/strain and the output optical responses of the SSM should be well established theoretically, computationally, and/or experimentally. Recently, a pressure-sensitive paint consisting of rhodamine 6G dye in poly-methylacryate (PMMA) polymer was found to be able to function as a recorder of the density profile under shock conditions with nanosecond resolutions [6,7]. However, due to the complex configuration of polymer, it is difficult to improve sensing accuracy via molecular design [7].

Quantum dots (QDs), with diameters of several nm, exhibit unique optical properties due to the quantum confinement effect

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[8]. They have been widely used as nanoscale electronic [9], photoluminescence [10,11], electrochemical [12] and temperature sensors [13]. QDs can also be used as pressure sensors and is potential candidates for stress/strain sensing. In particular, pressure- and strain-dependent optical properties have been reported for several types of QDs [14–16]. Compared polymer-based shock sensors (e.g., rhodamine 6G dye [7] and polyvinylidene fluoride polymer [17]) which are relatively large, QDs can be well controlled in experiments in terms of both size and shape. Since, QDs can be embedded in materials and optical emissions are used for measurement, techniques based on QDs are non-intrusive. Moreover, the optical responses of QDs under different loading conditions can be more precisely determined through theoretical analysis or numerical calculations [18].

Recently, LSC experiments on nanocomposite films on CdTe QDs dispersed in a soft polyvinyl alcohol (PVA) polymer matrix and in a hard inorganic sodium silicate glass matrix were carried out to study their suitability as internal SSM for LSC experiments [19,20]. Particle-level stress sensing with a temporal resolution of 0.5 ns was obtained in the experiments. The result points out that the wavelength blueshift history of QDs is deformation-dependent and can be used as an indicator and measure for internal stress during shock loading. It is found that the blueshift observed from LSC experiments first increases with pressure to a maximum and subsequently decreases with pressure. The trend is different from the monotonic increase of blueshift with pressure observed under conditions of quasistatic hydrostatic compression. Additionally, the blueshift in the LSC experiments is smaller than that in hydrostatic experiments at the same pressure levels. The difference highlights the need to delineate and understand the mechanism underlying the loading condition-dependent blueshift. The mulitscale nature of the structure of the QD composites and the coupling between the mechanical and optical properties necessitate a systematic analysis. Specifically, proper understanding and quantification of relations for the CdTe nanocomposite system should consider the deformation of the QDs in the matrix materials, the different stress/strain states in the constituents of the composite, the possibility of stress-induced phase transformations and the deformation-dependent nature of the band structures of the QDs. In the present work, a multiscale computational framework combining the empirical tight binding (ETB) method, molecular dynamics (MD) simulations and the finite element method (FEM) is employed to address this challenge.

CdTe is a direct band gap semiconductor and the emission wavelengths of CdTe QDs are determined by their band structures. To calculate the band structure of a specific CdTe QD under a specific strain state, a quantum theory-based method is required. Several methods, such as the empirical pseudo-potential method [21,22], ETB [23–25] and density functional theory [26] have been applied to calculate the strain-dependent band structures of QDs. The ETB method is used here due to its high efficiency and reliability [27]. Since phase transition was reported in bulk CdTe under high pressures [28–30], MD simulations are performed here to investigate the possibility of structure transformations of QDs under the conditions of interest. Our approach entails the use of top-down multiscale simulations. First, FEM simulations with explicit account of the QDs/matrix nanocomposite structure are carried out to quantify the stress/strain states of the QDs in the overall nanocomposite. The stress states so obtained are used as input boundary conditions for subsequent MD simulations. Finally, ETB calculations are used to calculate the band structures of the QDs which are in turn used to evaluate the emission spectrum and blueshift under given loading on the overall nanocomposite.

In experiments like those reported in Ref. [19] the effects of many factors, including stress-induced bandgap change, temperature, viscosity of the matrix materials, and charge of ligands at the QD/matrix interfaces, are at work. These effects cannot be experimentally isolated. Computational analyses can be used to isolate and analyze these effects. Such a task is carried out in this paper. Specifically, we focus on the effect of stress on the blueshift. Therefore, the band gap and blueshift of the QDs under loading of a range of strain triaxiality for the nanocomposite are considered. Since the QDs are distributed randomly in the matrix and the response of the QDs are orientation-dependent, the blueshift-strain relations for QDs in all possible spatial directions are used to evaluate the response of the QD ensemble as a whole under the conditions of different load triaxialities (or different stress states) of the overall nanocomposite. The results allow the differences in the trends of blueshift observed from the LSC and hydrostatic compression experiments to be explained. We conclude with considerations and guidelines for the development of CdTe QD nanocomposites as SSM in experiments.

2. Computational framework

The composite film consisting of matrix material and uniformly distributed CdTe QDs is illustrated in Fig. 1(a). An illustration of a unit cell of the nanocomposite film is given in Fig. 1(b). The FEM model with element discretization for the unit cell used in the computations is shown in Fig. 1(c). Compression under conditions of uniaxial strain due to impact loading is in the vertical direction in Fig. 1(b–c). External pressure (P_z) is applied on the top surface of the unit cell, with fixed constrains on the bottom surface. The lateral surfaces of the unit cell are constrained in the horizontal direction to effect the overall uniaxial state of strain under normal impact loading [20]. The silica glass [31] as used in experiments is the matrix material. To simplify the analysis, both CdTe and the glass matrix are assumed to be linear elastic. The specific material parameters are Young's modulus (E), Poisson's ratio (ν) and mass density (ρ), as listed in Table 1. In the experiments [20,32], the concentration x_{QD} of QDs in the matrix is approximately 0.15% by weight. For $x_{QD} << 1$, the separation between QDs or the dimension of the unit cell (L) can be estimated as

$$L \approx \left(\frac{\pi \rho_{CdTe}}{6 \rho_m x_{QD}} \right)^{1/3} d, \tag{1}$$

where ρ_m and ρ_{CdTe} are densities of the matrix and CdTe, respectively, and d is the QD diameter. For QDs with diameters of 4.5 and 6.5 nm, the estimated L is about 43.9 and 63.4 nm (or 9.8d), respectively.

The materials are represented by nodes and elements in FEM and by atoms in MD. In order to pass strain and deformation state information from FEM to MD, the MD simulations in the CdTe QD region of the unit cell uses a displacement boundary condition extracted from the FEM model. The implementation uses spatial interpolation of the displacement field at each atomic site, as illustrated in Fig. 2(c). After the application of the boundary displacement field, the deformed atomic configuration of the entire QD is relaxed with the surface atoms constrained via an equilibration MD calculation in order to ascertain if the applied deformation would lead to phase transformation in the QD. No phase transition is observed. A Stillinger-Weber (SW) type potential is used to describe the interatomic interactions in the CdTe atomic system [33]. The SW potential is known to provide reasonable tracking of different phases of CdTe [34]. Recently, a new analytical bond-order potential (BOP) was proposed for CdTe which gives some structural and properties trends close to those observed in experiments and quantum-mechanical calculations [34]. However,