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PAPER

Exciton radiative lifetime in a monoatomic carbon chain

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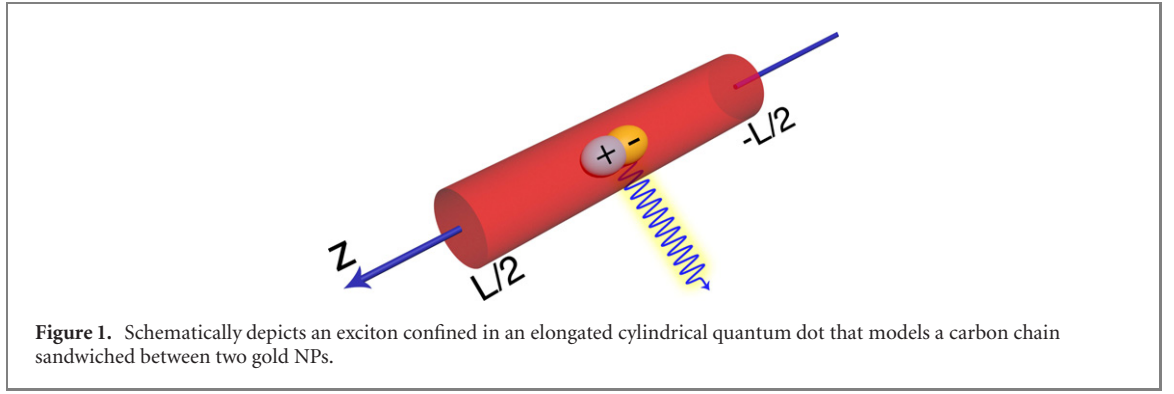
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Abstract

Linear carbon-based materials such as polyene and cumulene oligomers provide a versatile platform for nano-physics and engineering. Direct gap quasi-1D polyene structures are promising for the observation of strong and unusual excitonic effects arising due to the two-dimensional quantum confinement. Recently, we reported on the observation of sharp exciton peaks in low temperature photoluminescence spectra of polyene chains (Kutrovskaya *S et al* 2020 *Nano Lett.* **20** 6502–9). Here, we analyze the time-resolved optical response of this system. We extend the non-local dielectric response theory to predict the exciton radiative lifetime dependence on the band-gap value and on the length of the chain. A good agreement between the experiment and the theory is achieved.

1. Introduction

The hybridization of *s*- and *p*-orbitals of carbon atoms gives rise to the formation of a rich variety of allotropic forms of carbon crystals including sp^1 (carbyne), sp^2 (graphite), $sp^{2+\epsilon}$ (fullerenes), sp^3 (diamond) etc. For a long time, only diamond, graphite and coal were widely known. Fullerenes have been discovered in 1985 [2, 3], then carbon nanotubes [4] and graphene [5] entered into play. Despite of the rapid progress in the methods of synthesis of low-dimensional carbon based structures, the controllable synthesis of linear sp^1 -hybridized carbon materials is still quite challenging. The interest in sp^1 -carbon is flaring up since 1969, when chaoite in shock-fused graphite gneiss from the Ries crater in Bavaria was discovered [6]. Long linear carbon chains (LLCC) exist in two allotropic forms, namely, polyene characterized by alternating single and triple electronic bonds between atoms and cumulene characterised by double bonds. It has been shown in multiple publications that polyene represents a direct band gap semiconductor, while infinite cumulene chains are expected to be metallic [7, 8]. Due to its direct gap belonging to the optical frequency range, polyene attracted much interest from the point of view of optical effects and applications. In particular, a possibility to tune the band gap of polyene across nearly the full visible range by changing the length of the chain offers an opportunity to use LLCCs as nanoscale light sources [9, 10]. In order to achieve a further in-site into quantum and optical properties of polyene-based nanostructures, we studied recently the excitonic spectra that dominate the photoluminescence of polyene chains at low temperatures [1]. The recent observation of excitons and trions in LLCCs has a fundamental importance as it presents the first experimental evidence of bright exciton states in monoatomic chains. It crowns an effort of many groups who provided the excitonic gaps calculation in one-dimensional carbon chains [11, 12] and predicted the



excitonic features in carbon chains [13]. This study has revealed the radiative lifetime of an exciton of the order of 1 ns [1]. In addition, it was found that the increase of the band gap width with the decrease of the LLCC length is accompanied by a significant shortening of the exciton radiative lifetime. The present work is aimed at the interpretation of this result and modeling of radiative properties of exciton states in linear carbon chains of finite lengths. We have extended the non-local dielectric response theory formulated for excitons in semiconductor quantum wells, wires and dots in 1990s [14] in order to account for the specific features of excitons in finite-size monoatomic chains. Comparison of the predictions of the model with the data allowed to extract a precious information on the main excitonic characteristics such as the oscillator strength, Bohr radius and binding energy.

2. The model

We shall theoretically describe the radiative decay of excitons in kinked monoatomic carbon chains confined between gold nanoparticles (NPs). First, we neglect the kink effect and assume that an exciton as a whole particle is confined between two gold NPs. Since the distance between NPs is comparable with the wavelength of light, each chain may be conveniently modeled as a large and strongly anisotropic quantum dot (QD) (figure 1). Following the non-local dielectric response model developed in reference [14], the exciton radiative lifetime in an individual QD can be found as:

$$\tau_{\text{QD}} = \frac{1}{2\Gamma_0^{\text{QD}}}, \quad (1)$$

where

$$\Gamma_0^{\text{QD}} = \frac{1}{6} \omega_{\text{LT}} k_0^3 a_{\text{B}}^3 \left[\int \cos(\vec{k}\vec{r}) \Phi(\vec{r}) d\vec{r} \right]^2. \quad (2)$$

Here ω_{LT} is the exciton longitudinal–transverse splitting in a bulk crystal, $k^2 = \epsilon_{\text{b}} k_0^2$, $k_0 = \omega_0/c$, ϵ_{b} is the background dielectric constant, ω_0 is the exciton resonance frequency, a_{B} is the three-dimensional exciton Bohr-radius, $\Phi(\vec{r}) = \Psi(\vec{r}_{\text{e}}, \vec{r}_{\text{h}})$ is the full exciton wave function taken with equal electron and hole coordinates. The QD is strongly elongated, and the exciton center of mass wavefunction is a one-dimensional function quantized due to the exciton confinement between the ends of the chain. We shall use the trial wave-function of electron–hole relative motion along the axis of the chain introduced in reference [15] and assume that the center of mass wave-function may be represented in a form:

$$\Psi(\vec{r}_{\text{e}}, \vec{r}_{\text{h}}) = U_{\text{h}}(\vec{\rho}_{\text{h}}) U_{\text{e}}(\vec{\rho}_{\text{e}}) f(z) F(Z) = \frac{\sqrt{a}}{\pi R_{\text{h}} R_{\text{e}}} \sqrt{\frac{2}{L}} \exp\left(-\frac{\rho_{\text{h}}^2}{2R_{\text{h}}^2}\right) \exp\left(-\frac{\rho_{\text{e}}^2}{2R_{\text{e}}^2}\right) \exp(-a|z|) \cos\left(\frac{\pi}{L}Z\right), \quad (3)$$

where $z = z_{\text{e}} - z_{\text{h}}$, $Z = (z_{\text{e}} m_{\text{e}} + z_{\text{h}} m_{\text{h}})/(m_{\text{e}} + m_{\text{h}})$ is the center of mass coordinate, $R_{\text{h}} = 0.1$ nm, $R_{\text{e}} = 0.25$ nm, $a = 0.351$ nm⁻¹.

The exciton longitudinal–transverse splitting can be expressed as [16]:

$$w_{\text{LT}} = \frac{4e^2 |p_{\text{cv}}|^2}{\hbar \omega_0^2 m_0^2 \epsilon_{\text{b}} a_{\text{B}}^3}, \quad (4)$$

where m_0 is the free electron mass, $|p_{\text{cv}}|^2$ is the interband dipole matrix element. Combining equations (2)–(4) we obtain:

$$\Gamma_0^{\text{QD}} = \frac{2}{3} \frac{e^2 |p_{cv}|^2 \omega_0}{\hbar m_0^2 c^3 \epsilon_B} \frac{2a}{L} \left[\int_0^\infty 2\pi \rho U_e(\rho) U_h(\rho) d\rho \right]^2 \left[\int_{-L/2}^{L/2} \cos(kZ) \cos\left(\frac{\pi}{L}Z\right) dZ \right]^2. \quad (5)$$

Using the $\mathbf{k} \cdot \mathbf{p}$ -method of band-structure calculations we estimate the interband matrix element as [17]:

$$|p_{cv}|^2 = \left(\frac{m_0^2}{m_c} - m_0 \right) \frac{E_g}{2}, \quad (6)$$

where $m_c = 0.078m_0$ is the electron effective mass in the conduction band [1]. Thus, the exciton radiative lifetime can be found as:

$$\tau_{\text{QD}} = \frac{3\hbar^2 c^3 \epsilon_B}{2e^2 (1/m_c - 1/m_0) E_g^2} \frac{L}{2a} I_{eh}^{-2} [J(L)]^{-2}, \quad (7)$$

where

$$I_{eh} = \int_0^\infty 2\pi \rho U_e(\rho) U_h(\rho) d\rho, \quad (8)$$

and

$$J(L) = \frac{\frac{2\pi}{L} \cos\left(\frac{kL}{2}\right)}{\frac{\pi^2}{L^2} - k^2}. \quad (9)$$

3. Results and discussion

Figure 2 shows the experimental low temperature time-resolved photoluminescence spectra (TRPL) of linear carbon chains adapted from reference [1]. TRPL curves of different color correspond to different spectral bands, as shown in the inset. Each specific spectral band is attributed to a fixed number of atoms contained in a straight part of the chain. We note that virtually all the studied chains contain kinks dividing them into straight parts containing even numbers of carbon atoms. The band gap width in polyyne depends on a number of atoms in the straight part of the chain confined between the neighboring kinks or between the first (last) kink and the gold NP. In our experiments, the gap width varies from 2.2 to 2.8 eV for the straight parts of chains ranging in length from 10 to 20 atoms. In order to analyze this set of data, first, we shall fix the average value of the band gap for whole chain taking $E_g = \hbar\omega_0 = 2.5$ eV and study the dependence of the exciton radiative lifetime on the chain length. Our calculation shows that excitons in the polyyne chains of 20–100 nm lengths are characterized by the radiative lifetimes of the order of 1 ns, that nicely agrees with the experiment data. Having obtained, within the framework of the developed model, the correct order of magnitude for the radiative lifetime for the experimentally observed lengths, our next step is to study the dependence of the radiative lifetime on the band gap width. To do this, we will fix the chain length and plot the calculated exciton lifetime as a function of the band gap value, which depends on the number of atoms in the linear parts of polyyne chain between kinks in our experiments. Figure 3 presents a dependence of the exciton radiative lifetime on the band gap for the straight parts of the chains of different lengths. The results of this calculation are compared to the experimental data extracted from figure 2 and shown by stars in figure 3.

It is important to note that the experimentally studied chains are of an average total length (the spacing between two gold NPs) of about 50 nm. On the other hand, the length of the straight parts of the chains separated by kinks is in the range of 1–3 nm. This estimate is obtained having in mind that we usually have 10–20 atoms between the neighboring kinks [1] and the interatomic distances in polyyne are known to be 0.133 nm (C–C) and 0.123 nm (C≡C), respectively. The length of the straight parts (number of atoms) determines the transition frequency [1]. Clearly, each individual chain may be composed of straight parts of different lengths characterised by different energy gaps. We assume that the exciton as a whole may resonantly transfer between identical straight parts of different chains in a bundle. This is a reasonable assumption as the band-gap energies in the straight parts of the chains of the same length match, and the exciton transfer between them would not cost any energy. Based on this assumption, we consider the distance between two gold NPs as a characteristic size of the nano-object that confines excitons contributing to the radiative decay signal figure 4. This assumption is confirmed by two experimental observations. Reference [1] demonstrated the thermal dissociation of an exciton as a result of hopping of one of the carriers, which indicates that hops between parallel chains are, in principle, possible, and nothing prevents the exciton as a whole from hopping onto one of the neighboring chains provided that it finds a section characterised by the same energy as one where it departs from. The second argument is that if the exciton would be strictly confined to every individual straight part of a chain between two neighboring kinks, then both the dependence of the lifetime on the band gap and the absolute value of the lifetime would be

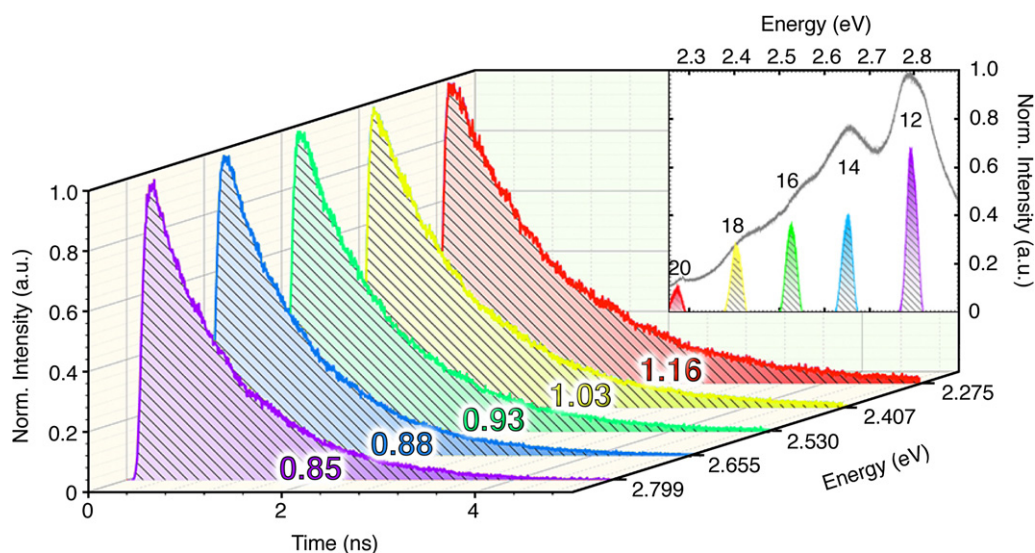


Figure 2. The experimentally measured time resolved photoluminescence (TRPL) spectra of gold-stabilized linear carbon chains acquired at 4 K. The inset shows the spectral bands corresponding to each TRPL measurement. The selected bands correspond to the excitonic transitions in straight chains of a different within the 5 nm accuracy (the number of atoms in the chain is indicated on the top of the corresponding spectral resonance). The extracted exciton radiative life-time (in nanoseconds) is indicated for each band.

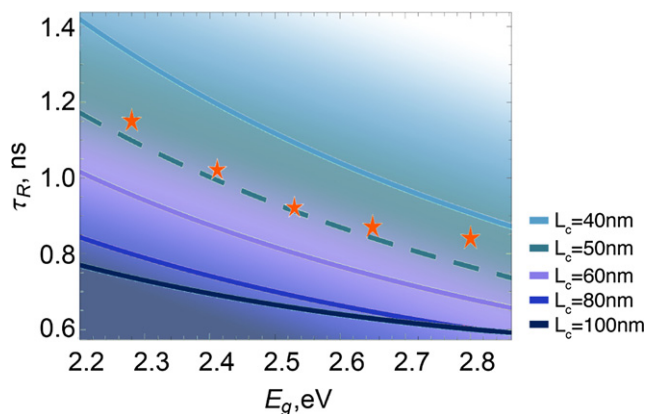


Figure 3. The radiative decay time of excitons versus the band gap energy for different fixed distances between NPs $L_c = 40$ nm, 60 nm, 80 nm, 100 nm respectively. Stars display the experimental data taken from Figure 2. The best fit is achieved at $L_c = 50$ nm (shown by the dotted line).

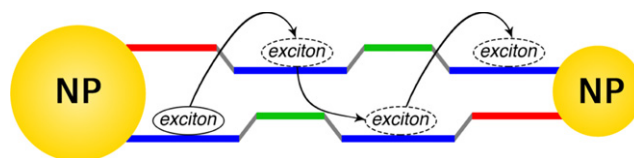


Figure 4. A schematic that illustrates the confinement of an exciton in a bundle of polyyne chains sandwiched between two gold NPs and separated into straight parts by the kinks. As all excitons belonging to the straight parts of the same length emit at the same energy, in a bundle that contains a sufficiently large number of chains, the volume occupied by excitons that contribute to the radiative recombination at a given energy is limited by the distance between the gold NPs.

strongly different. It was shown in [18, 19] that the lifetime of an exciton critically depends on the relationship between the size of the exciton, the size of the QD, and the wavelength at the exciton resonance. Clearly, in the case where the size of the quantum dot is significantly smaller than the wavelength of light, the retardation effects can be neglected, but in the case where the size of the quantum dot approaches the wavelength of light, they begin to play an essential role and cause a strong increase of the radiative lifetime.

In conclusion, we calculated the exciton radiative lifetime in bundles of monoatomic linear carbon chains sandwiched between gold NPs in the framework of the non-local dielectric response theory. We have

found a good agreement between the results of the present model and the data of low temperature time-resolved photoluminescence measurements. The time-resolved optical response of excitons in carbon chains is found to be dependent on the band-gap of the chain and the lengths of straight parts of the chains that provides a control tool for fine tuning of the radiative properties of carbon chains for applications in carbon lasers and light-emitting diodes.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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