Unraveling the Excitonic Transition and Associated Dynamics in Confined Long Linear Carbon Chains with Time-Resolved Resonance Raman Scattering

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Long linear carbon chains are attracting intense interest arising from their remarkable properties, such as the tunable direct energy gap, the high mechanical hardness, and the high Raman response cross section, which would play a great role in their potential applications in future nanotechnology. Here the excitonic transitions and the associated relaxation dynamics of nanotube confined long linear carbon chains are comprehensively interrogated by using steady state and time-resolved Raman spectroscopies. The exciton relaxation dynamics of the confined carbon chains occurs on a hundred of picoseconds timescale, in strong contrast to the host dynamics that occurs on a few picoseconds' timescale. A prominent time-resolved Raman response is observed over a broad energy range extending from 1.2 to 2.8 eV, which includes the strong Raman resonance region around 2.2 eV. Strong coupling between the chain and the nanotube host is found from the dynamics at high excitation energies which provide clear evidence for an efficient energy transfer from the host carbon nanotube to the chain. The experimental study presents the first unique characterization of the long linear carbon chain exciton dynamics, providing indispensable knowledge for the understanding of the interactions between different carbon allotropes.

1. Introduction

Long linear carbon chain (LLCC), with its infinite long form termed as carbyne,[1] is a 1D sp1-hybridized carbon allotrope unique from sp2-hybridized graphene and sp3-hybridized diamond. The backbone of carbyne is constructed by either (─C≡C─) or (═C═) as a repeating base element, and the unique sp-hybridization endows it a truly straight 1D crystalline material. The unique structure of LLCCs endows them with superior mechanical, optical, thermal, and electronic transport properties compared to other carbon allotropes. For example, the hardness of LLCCs has been predicted to be much higher than those of graphene, carbon nanotubes, and diamond.[2] The calculated thermal conductivity of LLCCs (4.4 × 10³ W m⁻¹ K⁻¹) is comparable to that of monolayer graphene (5 × 10³ W m⁻¹ K⁻¹).[3] Experiments using hydrostatic pressure have shown that mechanical properties of LLCCs, such as the Young’s modulus, the strain and the Grüneisen parameter, are widely tunable, making LLCCs potentially useful in nanometrology and nanodevices.[4] In addition, recent studies indicated that LLCCs have a resonant Raman scattering cross section per atom exceeding that of any other known materials by two orders of magnitude,[5] a property that can be applied to nanoscale...
temperature monitoring and biological imaging based on Raman scattering.[6]

Although carbyne has been proposed to exist long time ago,[7] experimental synthesis and identification of LLCCs was only realized in recent years. Due to the high reactivity of the sp2-hybridized bonds, synthesis of long and stable chains is still challenging. Without special protection and isolation, carbyne easily decays by forming either sp3 or sp3-carbon allotropes through crosslinking between adjacent chains or through cycloaddition reactions.[8] Different strategies have been adopted to stabilize LLCCs, the main ones being applying end-capping groups[9] or confining in host nanotubes.[10] Recently, LLCCs incorporating more than 6000 carbon atoms[11] have been synthesized in the double-walled carbon nanotube (DWCNT) hosts. For these confined chains, it has been shown that their properties depend strongly on the interaction with their hosts and only weakly on the length of the chain.[12]

Despite the progress in synthesis, the experimental characterization of LLCCs is still limited. This is in particular true for optically excited nonequilibrium states. The presence of other carbon allotropes[13] makes identifying the LLCC properties a challenging task. To date, the most successful techniques to address the properties are transmission electron microscopy and Raman scattering spectroscopy.[11,14] In particular Raman spectroscopy has proven to be a convenient tool to study the vibrational properties of LLCCs.[15] Taking it one step further, time-resolved Raman spectroscopy (TRRS) has demonstrated to be a powerful method to investigate both the vibrational relaxation and the electronic population dynamics for carbon based nanomaterials.[16] Especially, performing TRRS under strong resonance conditions allows addressing the electronic excitation dynamics directly from the differential Stokes signals.[16a] Here, we report on the temperature and wavelength dependent optical excitation relaxation dynamics in the carbon nanotube confined LLCCs and the excited state interactions by monitoring the optical phonons using TRRS under resonant conditions. The unique capability of TRRS allows us to separately detect the congested electronic relaxation dynamics of each component by real-time monitoring the impact of electron population on the phonon Raman scattering. On the basis of this methodology, we have revealed the existence of efficient energy transfer between the hosts and LLCCs enabled by their strong excited state interaction, and the insensitivity of the excitation relaxation dynamics to the external temperature. This knowledge is pivotal to understanding nanoscale device properties such as stability, optical response efficiencies, and energy relaxation pathways.

For a complex conjugated system with congested electronic responses, such knowledge is not easily attainable with other more traditional methods, such as time-resolved absorption and reflection spectroscopies. To the best of our knowledge, this is the first experimental report on the nonequilibrium dynamics for a combined system of sp2/sp3-hybridized carbon allotropes.

2. Results and Discussion

Figure 1a depicts a LLCC encapsulated in a host DWCNT (LLCC@DWCNT) and an empty DWCNT. Due to the Peierls distortion,[21] the LLCC has a stable polyene-like structure (≡C≡C≡), as opposed to a cumulene-like structure (≡C≡). The unit cell of the polyene-like structure contains two carbon atoms providing two electrons, which completely fill up the valence band. This results in a semiconducting nature of the LLCs with excitons as the fundamental optical excitations. Raman scattering spectra of the samples (see Figure 1c) show the presence of the typical G-modes at ≈1590 cm−1 for both LLCCs@DWCNTs as well as pristine DWCNTs. The weak mode observed for both samples at ≈1750 cm−1 most likely originates from combination scattering involving the radial breathing mode (RBM, spectra of the RBM modes can be found in Figure S1, Supporting Information) and the G-mode, similar to that observed in graphite and other nanotubes.[19] The presence of the linear carbon-chains is evidenced by the appearance of Raman peaks at ≈1840 cm−1 for LLCCs@DWCNTs corresponding to the typical stretching vibrations of LLCs.[10,11,14c,20] This carbon-chain band is well separated from those of DWCNTs, providing a unique experimental access to investigate the excited state dynamics in the time-resolved resonant measurements. Before performing the time-resolved Raman measurements, we first characterize the steady state resonant Raman response of LLCCs@DWCNTs over a wide range of photon energies. Detailed Raman spectra recorded at various wavelengths are presented in Figure S2 in the Supporting Information. The resonance profile obtained from the phonon peak centered around 1840 cm−1 is presented in Figure 1d. It shows a clear resonance around 2.2 eV with a full width at half maximum of 0.3 eV, and a tail extending below 1.8 eV, consistent with previously reported results of confined LLCs.[20,21]

In the time-resolved Raman measurements, we first applied a resonant pump at 2.1 eV and a probe at 2.4 eV (512 nm). The transient changes in the Raman response have been recorded in the 1500–2000 cm−1 spectral window covering both the DWCNT G-mode and the LLCC stretching mode. The room temperature time-resolved Raman spectra of pristine DWCNTs and LLCCs@DWCNTs are recorded using a moderate pump intensity of around 25 μJ cm−2 and are presented in Figure 2a,c respectively. Immediately after optical excitation, the intensity of all phonon modes shows a significant reduction for both samples. The reduction observed here cannot be explained as direct population of coherent phonons by the pump pulse, otherwise we would expect an enhanced signal as the Raman signal is proportional to the phonon population number. Also, in most materials coherent phonons only last for a few picoseconds, as demonstrated in low dimension materials,[22] whereas herein the signal of LLCs persists until 100s of ps timescale. Thus, the signal reduction is a direct consequence of bleaching of the electronic ground state by the pump excitation pulse, which reduces the resonant enhancement of the Raman probing signals, thus providing a direct measurement of electronic excited state populations.[16c,23] To demonstrate the pump induced effect more clearly, the lower panels of Figure 2b,d show the difference Raman spectra for DWCNTs and LLCCs@DWCNTs obtained by subtracting the −5 ps spectra. The DWCNT G-bands around 1590 and 1750 cm−1 show a rapid recovery within a few ps for both pristine DWCNTs and LLCCs@DWCNTs. The initial intensity reduction ratio of the LLCC stretching mode (1840 cm−1) of LLCCs@DWCNTs is significantly larger than that of the DWCNT modes, indicating a stronger suppression of the resonance enhancement for LLC. The most surprising observation, however, is that the LLCC mode recovers much slower than the DWCNT modes, taking about
Figure 1. a) Illustration of a DWCNT and a confined LLCC@DWCNT. b) Sketch of the time-resolved Raman scattering setup. Green, red, and broad colorful lines indicate the Raman probe, the pump, and the Raman scattered signal, respectively. M: mirror, GR: grating, CCD: charge coupled device, BS: beam splitter, BL: beam block, MO: microscope objective, ST: sample stage. c) Steady-state Raman spectra of DWCNTs and LLCCs@DWCNTs measured using a 532 nm continuous laser as excitation source. d) Resonance Raman profile of LLCCs obtained from the intensity of mode 1840 cm\(^{-1}\) relative to 1590 cm\(^{-1}\); the blue solid line is a guide to the eyes.

Figure 2. Time-resolved Raman scattering spectra of the pristine DWCNTs and LLCCs@DWCNTs recorded at various pump-probe delay times. a) Raman spectra of pristine DWCNTs. b) Difference Raman spectra of pristine DWCNTs. c) Raman spectra of LLCCs@DWCNTs. d) Difference Raman spectra of LLCCs@DWCNTs. To highlight the relatively small amplitude from the LLCC mode, the spectra in (a) and (c) are plotted using a logarithmic intensity scale.
Figure 3. Normalized relaxation dynamics of phonon Raman scattering in pristine DWCNTs and LLCCs@DWCNTs for the phonon bands at a) 1590 cm$^{-1}$, b) 1750 cm$^{-1}$, and c) 1840 cm$^{-1}$. The inset in (c) shows an expanded view of the short time range. Symbols are experimental data and red lines are multiexponential fits.

Figure 4. Excitation energy dependence of the relaxation dynamics of the LLCC mode and the population efficiency. a) Representative decay dynamics observed for excitation energies far below (1.27 eV, 1.49 eV), at (2.11 eV), and far above (2.69 eV) the resonant transition energy. The inset shows the short time dynamics. b) Extracted optical bleaching percentage of the ground state at 1 ps. The blue dashed line is the resonance profile taken from Figure 1d.

100 ps, suggesting a relaxation mechanism different from the DWCNT modes.

Figure 3 shows the time evolution of the various phonon modes obtained by integrating the transient signal over the corresponding spectral region (shaded regions in Figure 2b,d). The 1590 and 1750 cm$^{-1}$ modes show identical multiexponential recovery dynamics for which a global fitting yields that 80% of the signal decays with a time constant of 0.3 ps, and 20% with a time constant of 2.7 ps. Similar relaxation dynamics were observed for the 1590 cm$^{-1}$ peak for carbon nanotubes made in different batches (Figure S3, Supporting Information). We note that the observed fast decay dynamics for the DWCNTs are consistent with previous observations on multiwalled carbon nanotubes which reported a similarly short lifetime of around 1 ps.[24]

It is clear that the decay dynamics of the LLCC stretch mode is substantially slower than that of the DWCNT modes. Fitting a multiexponential decay function to the data yields time constants of $\approx 7$ and $\approx 80$ ps, with amplitudes of 35% and 55% respectively. A small part of the transient signal (10%) shows no decay at all in the measured time window. Alternatively, an exponential decay with a log-normal distribution of the relaxation rate can also fit the observed dynamics perfectly (Figure S4, Supporting Information). More discussion on the mechanism of the relaxation dynamics and the multiexponential nature will follow later on when presenting the temperature and excitation intensity dependent measurements. For convenience in describing the dynamics, we adhere to the multiexponential fitting procedure for all decay dynamics discussed in the following.

Since we always excite the hosts and the confined LLCCs simultaneously, the much slower dynamics of the LLCC mode compared to their hosts suggest that excitation energy should flow from DWCNTs down to LLCCs if there is energy transfer between them. Due to the ps time resolution of our Raman probing, the current single excitation energy data do not allow to resolve a direct energy transfer between the DWCNTs and the LLCCs if the process is very fast. To further investigate the intricate optical transition and relaxation dynamics, we carried out excitation energy dependent measurements of the LLCCs relaxation dynamics from the 1840 cm$^{-1}$ mode. While fixing the probing energy at 2.4 eV, the excitation photon energy was tuned over a wide range from 2.8 to 1.2 eV. A few representative relaxation dynamic curves are presented in Figure 4a, in which all curves are normalized to the pre-zero Raman signal and to the pump excitation photon density. The maximum reduced signal amplitude (around 1 ps) is converted into the ground state bleaching ratio by taking the changes of Raman response into account as described in previous reports,[16e,25] and is presented in Figure 4b. More decay curves at specific excitation energies are presented in Figure S5 in the Supporting Information.

Several significant points are revealed from the photon energy dependent excitation results. First, dynamics at all the different excitation energies are very similar and can be globally described well using three decay components with the same time constants, with small variations in the component amplitudes (Figures S5 and S6, Supporting Information). This indicates that, independent of the excitation energy, all signals originate from excitation of the same species. Second, in the middle energy range, the resonance profile obtained from the time resolved experiments
fit well to that from the steady state measurements, confirming the strong resonance effect around 2.2 eV. Third, at lower excitation energies, we still observe a substantial LLCC response signal. Understanding this phenomenon is very challenging due to absence of data on the excited state spectra and dynamics of the confined LLCCs from any other experiments. The much broader responses may come from some low energy dark states of the LLCCs that become bright when interacting with the DWCNTs, from some intrinsic resonant states with lower density of the LLCCs below 2.2 eV, or from a very fast energy transfer from the hosts to the LLCCs. High time-resolution experiments are required to further distinguish these possibilities. Fourth and most significantly, on the high energy side around 2.7 eV, where the steady state measurements do not show an observable resonance, the observed population effect is even more enhanced. This unambiguously indicates that there is significant energy transfer from the excited host DWCNTs to the confined LLCCs. Since the photoluminescence states of the host DWCNTs lie in the infrared region, one does not expect a Förster-type energy transfer but rather a Dexter-type. A Dexter-type energy transfer is indeed expected in view of the strong overlapping of the molecular orbitals due to the small radius of the inner tube of the DWCNTs. Intriguingly, the population amplitude at ≈2.7 eV excitation is even larger than at the resonance excitation of LLCs at ≈2.1 eV. A possible origin for this surprising observation lies in the much higher density of states available for both the LLCs (dark state) and the host tubes in the near UV region, making the near UV excitation very efficient in bleaching the LLCC through DWCNT-LLCC energy transfer which subsequently decays to the lowest excited LLCC state at 2.2 eV thereby bleaching the resonance enhancement of the LLCC phonon response.

We now return to recovery mechanisms of the observed exciton relaxation dynamics of LLCs. To shed more light on this we have performed temperature dependent measurements on the relaxation dynamics at the fixed excitation energy of 2.1 eV and at around of ≈25 μJ cm⁻². As shown in Figure 5, the dynamics is nearly temperature independent below 150 K but speeds up only at for higher temperatures. Figure 5b shows the temperature dependence of the two time constants obtained from multieponential fits. Since no luminescence has been detected at any temperature, we can assume that the dominant decay mechanism is nonradiative and has most likely, in view of the temperature dependence, an optical phonon-assisted nature. We therefore fitted the temperature dependent decay rates using a phonon occupation model

\[ \tau^{-1}(T) = \Gamma_0 + \Gamma_1(T) + \Gamma_2(T) \]  

where \( \Gamma_0 \) represents a constant contribution originating from the impurities and defects, \( \Gamma_1(T) \) represents a contribution from low energy acoustical phonons, which is proportional to \( T \), and \( \Gamma_2(T) \) represents the contribution from high frequency optical phonons. Under the assumption of fast optical phonon relaxation (usually around 2 ps for carbon nanomaterials) and quasi-equilibrium between the acoustic phonons, \( \Gamma_1(T) \) is proportional to the Bose-factor \( \frac{1}{\exp \left( \frac{\hbar \omega_0}{k_B T} \right) - 1} \). From the fit we obtain \( \omega_0 \approx 1800 \text{ cm}^{-1} \) for \( r_1 \) and \( \omega_0 \approx 1820 \text{ cm}^{-1} \) for \( r_2 \), indicating that the high energy optical phonon modes of the LLCs play an extra role in the exciton relaxation dynamics at higher temperatures.

For the nonexponential nature of the recovery dynamics, there could be several reasons: 1) diffusion assisted recombination at defects or sample ends as those observed in other 1D systems; 2) exciton-exciton annihilation reaction; and 3) a wide range distribution of the LLCs with different length and of the different type host DWCNTs. In the first two situations the dynamics is strongly dependent on the exciton diffusion. However, the observation that the dynamics is nearly temperature independent below 150 K ruling out this possibility, since the diffusion constant is expected to be linearly dependent on temperature according to the Einstein relation. We also performed a set of experiments varying the pump power-density by one order of magnitude. These experiments show identical dynamics (Figure S7, Supporting Information), confirming once again the lack of exciton diffusion as well as the lack of an important contribution from exciton-exciton annihilation processes to the dynamics. Considering that the dynamics could also be well described by an exponential decay with a log-normal distribution of the relaxation rate (Figure S4, Supporting Information), we thus assign the origin of the nonexponential dynamics to inhomogeneity which may include variations of the length of LLCs, different type of host DWCNTs as well as possible variations in bonding between the host and the LLC.

3. Conclusion

In conclusion, we have systematically investigated the optical transition and the excitonic population dynamics in the LLCs@DWCNTs by steady state and time-resolved resonance Raman spectroscopy. Combining the advantages of the good
resolution capability in both frequency and time-domain, we have successfully discriminated dynamic signals from different constituents and observed short and long-lived excited state population lifetime of the host DWCNTs and the confined LLCCs, respectively. The optical response of the LLCCs was observed to be in a wide energy range far below 2.2 eV, and an efficient Dexter-type energy transfer was identified from the excited DWCNTs to the LLCCs with excitation energy at the near UV side (≈2.7 eV) by comparing to the steady state resonant transition of LLCCs, indicating the presence of strong excited state interactions between the two carbon allotropes. The observed temperature dependence of the dynamics show that the exciton recombination is dominated by defects and optical phonon-assisted processes, whereas the power dependent experiments showed that exciton-exciton recombination does not play any significant role.

4. Experimental Section

Sample Preparation: Samples consisting of carbon-chains inside the double wall carbon nanotubes (LLCCs@DWCNTs) were produced by annealing the enhanced direct injection pyrolytic synthesized single-walled carbon nanotubes (eDIPS SWCNTs) at 1460 °C in high vacuum (<10^{-4} mbar) for 1 h. Details of the synthesis and characterization can be found in refs. [12b,29].

Steady State Raman Scattering Spectroscopy: Typical steady state Raman spectra of the LLCCs@DWCNTs and the DWCNTs were measured using a commercial Raman spectrometer (Princeton Instruments IsoPlane) equipped with a deep-cooled back-illuminated charge coupled device. A continuum wave 532 nm laser with 0.5 mW power was used for experiments. A microscope objective with numerical aperture 0.4 (Olympus MPLFLN, 20x) was used to focus the laser beam onto the sample. Wavelength dependent resonance Raman measurements were performed by using the time-resolved setup described below.

Time-Resolved Raman Scattering Spectroscopy: Details of the time-resolved resonance Raman scattering spectroscopy method are described in refs. (25,30). Briefly, an integrated ultrafast laser system (Light Conversion PHAROS) with two outputs of the fundamental 1030 nm pulses (compressed 300 fs and chirped 150 ps) pumps two optical parametric amplifiers (Light Conversion) to generate wavelength tunable laser pulses for selective excitation (~300 fs) and narrow-bandwidth laser pulses for Raman probing (~1.5 ps), respectively, the measured cross correlation of pump and probe is around 1.7 ps, which determines real time resolution of our setup. The laser repetition rate is 100 kHz. The widely tunable pump pulse allows to cover a photon energy range from the near ultraviolet to the near infrared. This output is also used as light source for the steady state resonance Raman measurement mentioned above. The Raman probe laser pulses were sent to a 4f-pulse shaper to narrow the line width down to ≈10 cm⁻¹ and suppress background light. The Raman probe pulse energy used is around 3 μJ cm⁻², which is usually around ten times weaker than the pump pulse energy. The major scheme of the time-resolved Raman scattering spectroscopy setup/experiment is illustrated in Figure 1b. To reduce background signal originating from the strong optical pump, a perpendicular linear polarized pump and probe laser pulses are used in the experiments with the pump light blocked by a polarizer in front of the spectrometer. In order to avoid possible optical damage of the sample and to improve the signal to noise ratio, the laser spot size on the sample was defocused to ≈80 μm in diameter. At each delay time point, a complete Raman spectrum was accumulated for 20 s. The transient changes were determined by comparing the spectra recorded at a given time after, to the spectrum recorded at negative delay time (≈−5 ps) before pump-probe time overlap. For all measurements, samples were mounted in a Helium cooled cold-finger cryostat with vacuum condition maintained at ≈10⁻⁶ mbar.

Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors.

Keywords

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