Quantum-coupled radial-breathing oscillations in double-walled carbon nanotubes

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Van der Waals-coupled materials, ranging from multilayers of graphene and MoS2 to superlattices of nanoparticles, exhibit rich emerging behaviour owing to quantum coupling between individual nanoscale constituents. Double-walled carbon nanotubes provide a model system for studying such quantum coupling mediated by van der Waals interactions, because each constituent single-walled nanotube can have distinctly different physical structures and electronic properties. Here we systematically investigate quantum-coupled radial-breathing mode oscillations in chirality-defined double-walled nanotubes by combining simultaneous structural, electronic and vibrational characterizations on the same individual nanotubes. We show that these radial-breathing oscillations are collective modes characterized by concerted inner- and outer-wall motions, and determine quantitatively the tube-dependent van der Waals potential governing their vibration frequencies. We also observe strong quantum interference between Raman scattering from the inner- and outer-wall excitation pathways, the relative phase of which reveals chirality-dependent excited-state potential energy surface displacement in different nanotubes.
Electronic and vibrational coupling in the nanoscale governs many important physical processes, such as energy transfer in photosynthesis\(^1\), charge separation in heterojunctions\(^2\) and thermal transport through interfaces\(^3\). Quantum coupling between nanostructures is also crucial for understanding emerging properties in van der Waals-coupled superstructures, such as multilayer of graphene and superlattice of nanoparticles. Double-walled carbon nanotubes (DWNTs), a coaxial composite of two single-walled carbon nanotubes (SWNTs), provide a unique model system for quantitative study of such nanoscale coupling, because the structural and physical properties of DWNTs are precisely defined individually, but richly varied among different species\(^4\)-\(^12\). Specifically, a SWNT is uniquely defined by its chiral indices \((n, m)\). A DWNT, composed of two SWNTs, is fully defined by chiral indices \((n_o, m_o)/(n_i, m_i)\) of the coaxial outer-/inner-walls\(^10\)-\(^12\). Its electronic and vibrational properties, however, can differ profoundly from those of the constituent SWNTs owing to tube–tube interactions.

Radial-breathing mode (RBM) oscillation is a signature vibration of one-dimensional nanostructures. It is widely used for characterizing carbon nanotubes\(^13\)-\(^17\), and can be sensitively measured at the single-nanotube level using resonance Raman spectroscopy\(^18\)-\(^20\). In SWNTs, the RBM oscillation frequency \(\omega_{\mathrm{RBM}}\) uniquely determines the nanotube diameter \(D\) following a simple scaling law \(\omega_{\mathrm{RBM}} = 228/D\) \((\text{nm cm}^{-1})\)\(^21\). The RBM behaviour in DWNTs, however, is drastically different owing to strong inter-tube coupling. The coupling effects in DWNTs have been actively investigated for over one decade\(^4\)-\(^9\), but they are still poorly understood. In this letter, we systematically study quantum-coupled RBM oscillations in chirality-defined DWNTs by simultaneously determining structural, electronic and vibrational properties of individual nanotubes with combined single-tube electron diffraction\(^11\),\(^12\), Rayleigh scattering\(^22\),\(^23\) and Raman scattering\(^18\)-\(^20\) techniques.

We show that mechanical coupling between the walls lead to collective oscillation modes with concerted inner- and outer-wall vibrations in DWNTs. Oscillation frequencies of the coupled RBM modes can be quantitatively described by a coupled oscillator model, where the coupling originates from the van der Waals force between the inner and outer tubes. Different DWNTs, which have different inner- and outer-wall separations, allow us to probe the inter-tube van der Waals interactions at an effective pressure that can be both positive and negative and at gigapascal level. The coupled RBM oscillations also exhibit unusual electron–phonon interactions. They always appear in pairs in resonance Raman spectra, because each RBM mode couples to electronic resonances in both walls. Furthermore, Raman amplitudes from inner- and outer-wall excitation channels can interfere quantum mechanically. Relative interference phase between the two Raman channels enabled us to examine the displaced excited-state potential energy surface in SWNTs and its dependence on the nanotube chirality.

### Results

#### Experimental design

Figure 1 shows the schematic illustration of our experimental design. We utilized the SiO\(_2\)/Si wafer with open slit as our base substrate, where suspended carbon nanotubes are directly grown on (See Methods for more details). Transmission electron microscope (TEM) beam and laser beam can both go through the slit. This design enables the combination of TEM electron diffraction, Rayleigh scattering and Raman scattering techniques to probe the structural, electronic and vibrational properties of the same individual nanotubes. In addition, the use of the as-grown suspended nanotubes makes it possible to exclude the substrate effects and ensures to probe the intrinsic physical properties of carbon nanotubes.

Figure 2 displays electron diffraction patterns, Rayleigh scattering and Raman scattering spectra for two representative individual DWNTs. Electron diffraction patterns (Fig. 2a,c) unambiguously determine the DWNT chiral indices \((n_o, m_o)/(n_i, m_i)\) to be \((27, 5)/(18, 5)\) and \((31, 4)/(15, 13)\). Electronic transitions of the two DWNTs are obtained from the Rayleigh scattering spectra (insets in Fig. 2b,d, respectively), in which prominent optical resonances can be observed. By comparing the optical resonances in Rayleigh spectra of DWNTs to that of the constituent SWNTs, we can assign the resonance peaks to inter-subband electronic transitions of either inner- and outer-wall nanotubes because tube–tube interactions in DWNTs produces only a small shift (tens of meV) of the electronic transition energies\(^24\). We measure the RBM oscillations of DWNTs using resonant Raman scattering. Two well-defined RBM peaks are observed in the resonant Raman spectra of the \((27, 5)/(18, 5)\) and \((31, 4)/(15, 13)\) DWNTs (Fig. 2b,d). The laser excitation energy \((1.96 \text{ eV})\) is marked by dashed line in the figure insets showing the Rayleigh scattering spectra. We have studied 35 DWNTs with well-defined Rayleigh scattering resonances (that can be assigned to each tube components) and TEM diffraction data. Of these DWNTs, 13 have one or more electronic transitions in resonance with our Raman excitation lasers. RBM Raman peaks are observed in, and only in, these 13 tubes. We summarized in Table 1 their chirality and Raman data. Our DWNTs have relatively large diameters, with inner-wall diameter \(D > 1.5 \text{ nm}\) in all the nanotubes.

There are two striking features in the RBM Raman data of these (relatively large diameter) DWNTs. (1) Frequencies of the two RBM oscillations in DWNTs, denoted as \(\omega_{\mathrm{RBM}}\) and \(\omega_{\mathrm{RBM}}\), are respectively much higher than the RBM frequencies of the constituent outer- \((\omega_{\mathrm{RBM}})\) and inner-wall SWNTs \((\omega_{\mathrm{RBM}})\) (for example, Fig. 2b,d). If this blue shift is attributed to a simple increase of ‘effective’ restoration force, this restoration force has to increase by as high as 35%. (2) The resonant peaks almost always appear in pairs in resonant Raman spectra: there are either no RBM peak (in 21 tubes) or two RBM peaks (in 13 tubes). Only one nanotube has just one RBM peak. This behaviour is quite surprising, because conventional picture suggests that resonance enhancement of the inner- and outer-wall RBM oscillations are largely independent\(^5\),\(^7\) and most nanotubes should have a single RBM peak even excited resonantly. To understand the unusual RBM behaviour in DWNTs, we have to realize that tube–tube interactions in these DWNTs are not small perturbations. Instead, they qualitatively change the DWNT RBM oscillations by strongly mixing the inner- and outer-wall vibrations: the
observed lower-($\omega_L$) and higher-frequency ($\omega_H$) RBM modes are collective oscillations with concerted in-phase and out-of-phase motion of the two walls.

**Inter-wall van der Waals interactions in DWNTs.** The collective RBM oscillations of a unit-length DWNT can be modelled by a coupled mechanical oscillator with five parameters: $m_i$, $k_i$, $m_o$, $k_o$ and $k_c$ (Fig. 3a)\(^\text{25}\). The unit-length mass of the inner- and outer-walls ($m_i$ and $m_o$) can be obtained directly from the tube chiral indices, and the unit-length intrinsic force constant of the two walls ($k_i$ and $k_o$) can be obtained from RBM frequencies of isolated SWNTs (Supplementary Note S1). The only unknown parameter is the coupling force constant $k_c$, which characterizes the van der Waals interaction between the two walls of the DWNT. Using a single value of $k_c$ for any given DWNT, we can simultaneously reproduce the in-phase ($\omega_L$) and out-of-phase RBM vibration frequencies ($\omega_H$) (Fig. 3b,c). For different DWNTs, the coupling constant $k_c$ vary significantly.

The **tube-dependent $k_c$** provides a unique way to examine how the van der Waals interaction varies with the separation between the inner- and outer-wall tubes. The unit-length coupling force
Quantum interference in resonance Raman process in DWNTs. Unlike separated inner- and outer-SWNTs RBM excitations (illustrated in Fig. 4a), the collective DWNT oscillations $\omega_i$ and $\omega_H$ contain both inner- and outer-wall motion, and they couple simultaneously to electronic transitions in both walls (Fig. 4b). Therefore, both coupled RBM oscillations will be resonantly excited if an electronic transition of either wall matches the excitation photon energy. This leads to the unusual behavior that we observed experimentally: the RBM Raman modes are mostly either not observable (in 21 tubes) or appearing in pairs (in 13 tubes) in resonant Raman scattering spectra of DWNTs.

The collective RBM oscillations in DWNTs couple to the electronic excitations quantum mechanically, and it leads to interesting quantum interference between the inner- and outer-wall excitation pathways. With such quantum interference even non-resonant contribution can become important, and Raman intensities of the coupled RBM oscillations in DWNTs are described by the superposition of Raman amplitudes from inner- and outer-wall excitation pathways as

$$I_L = |M_i R_i(\omega_i | o_L) + M_o R_o(\omega_o | o_L)|^2$$

and

$$I_H = |M_i R_i(\omega_i | o_H) + M_o R_o(\omega_o | o_H)|^2$$

Here, $\langle o_i | o_L | o_H \rangle$ is the inner(out)er-wall component of the coupled RBM mode $o_i(o_L)$, and its value can be calculated directly from a quantized coupled mechanical oscillator model illustrated in Fig. 3a (Supplementary Note S2). $R_i(o)$ and $M_i(o)$ denotes, respectively, the electronic resonance factor and Raman matrix element of the inner(out)-wall SWNT excitations. The resonance factor $R_{i(o)}$ can be obtained from Rayleigh scattering spectra of the DWNTs, which probe directly the optical resonances of both the inner- and outer-wall nanotubes (Supplementary Note S3). The Raman matrix element $M_{i(o)}$ characterizes how the phonon couples to the photo-excited exciton in the inner(out)-wall nanotube. For simplicity, we will assume that $M_i$ and $M_o$ have the same magnitude and focus on their relative sign, $s = \text{sgn}(M_i/M_o)$. This simplification emphasizes the importance of the phase factor, which determines whether the quantum interference is constructive or destructive for the coupled RBM oscillations.

To compare with the experiment quantitatively, we use the Raman intensity ratio $I_L/I_H$ because it does not depend on an absolute determination of Raman cross-section. The ratio has the form of $I_L/I_H = \frac{\sum R_i(o_L(o_H)) + R_o(o_L(o_H))}{\sum R_i(o_i(o_H)) + R_o(o_i(o_H))}$ in our approximation. In Table 1, we listed the measured Raman intensity ratio $(I_L/I_H)_{\exp}$ together with calculation results including the quantum interference $(I_L/I_H)_{\text{N}}$. Nice agreement between the theory and experiment is achieved when, and only when, the quantum interference effect is fully included using the correct $s$ parameter.

We take a closer look at the Raman quantum interference using (40, 1)/(22, 14) DWNT as an example (Fig. 4c). The $s$ parameter, which characterizes the relative sign between Raman matrix elements $M_i$ and $M_o$, depends sensitively on the chirality of the inner- and outer-SWNTs. Its value is related to the relative motion direction of the inner- and outer-wall nanotubes immediately after the optical excitation. A physical picture of this process in outer- and inner-SWNTs is provided by recalling Frank–Condon effects (Fig. 4e): the excited state has a displaced potential energy surface compared with that of the ground state. The displacement is extremely small (~1 fm), but is essential for the exciton–phonon coupling. Upon optical excitation, the SWNT lattice, initially at the ground-state equilibrium
configuration, relaxes based on the excited-state potential energy surface and sets off the RBM vibration. In (40, 1)/(22, 14) DWNT the potential energy surface displacements of inner- and outer-walls displace are opposite with an \( s = -1 \) (refs 30,31).

To determine the RBM oscillation interference, we also need to include the resonance phase factor. For (40, 1)/(22, 14) DWNT, the phase factors are nearly opposite for the (non-resonant) inner- and (resonant) out-wall pathways with 2.33 eV photon excitation (Fig. 4d). The opposite resonance phase factors together with the opposite excited potential energy surfaces (e), will drive the inner- and outer-walls to vibrate mostly in the same direction after the optical excitation, and enhance the out-of-phase oscillation \( \omega_L \) while suppress the in-phase oscillation \( \omega_H \) owing to quantum interference (g). It leads to significantly enhance \( I_L/I_H \) at our Raman excitation energy 2.33 eV (dashed line), as observed experimentally.

We further plot the calculated RBM Raman intensity of the (40, 1)/(22, 14) DWNT at different excitation energies without (Fig. 4f) and with the quantum interference (Fig. 4g), which displays the variation of quantum interference effects with the excitation laser energy.

**Discussion**

Our observed \( s \) parameter shows that the relative displacement of the excited-state potential energy surface varies with the SWNT chirality, and it can be described by a simple family pattern: the excited-state potential energy surface is displaced inwards for transitions on one side of the zig–zag cut through K point of the graphene Brillouin zone, which includes even transitions of
mod\((n - m_3) = 1\) semiconducting, odd transitions of mod \((n - m_3) = 2\) semiconducting and higher branch transitions of non-armchair metallic nanotubes. The displacement is outwards for all other transitions. This is the first observation of family non-armchair metallic nanotubes. The displacement is outwards (12).

The ability to combine structural, electronic and vibrational characterization on the same individual DWCNTs allows us to systematically investigate quantum-coupled mechanical oscillations and their unusual interactions with electronic excitations for the first time. We show that van der Waals interaction, usually treated as a weak perturbation, can actually produce quantum phenomena in coupled nanostructures that have only been observed in covalent material previously. With exact structural determination, we are able to determine the separation-dependent van der Waals coupling between nanotube walls and the excited-state potential energy surfaces of constituent nanotubes. Such approach can also be used to explore other composite nanostructures. It will enable quantitative understanding of van der Waals interactions and the electronic and vibrational couplings in the nanoscale.

Methods

In our experiment, we use suspended DWCNTs that are free of substrate effects and compatible with both TEM and single-tube optical spectroscopy techniques. Long suspended nanotubes were grown by chemical vapour deposition (CVD) across open slit structures (\(~30 \times 500 \mu m\)) fabricated on silicon substrates(3,2). We use Fe nanoparticles as catalysts and methane in hydrogen\((CH_4:H_2)\) as gas feedstock, and control the size of catalyst particles to achieve the selective abundance of DWCNTs(3). We determine chiral structures of DWCNTs using electron diffraction with nano-focused 80 keV electron beams in a JEOL 2100 TEM(1,2). Utilizing the slits edges as markers, the same individual nanotubes can be identified in an optical microscopy setup. To determine electronic transitions of these individual nanotubes, we use Rayleigh scattering spectroscopy with a fibre-laser-based supercontinuum light source covering the spectral range from 450 to 900 nm (refs 22,23). To determine RBM vibration and electron–phonon coupling in these individual nanotubes, we use resonant Raman scattering spectroscopy by Rayleigh scattering. Our instrumental resolution for RBM Raman frequency is \(~2 \text{ cm}^{-1}\).

References


Acknowledgements

This study was supported by NSF CAREER grant (No. 0846648), NSF Centre for Integrated Nanomechanical Systems (No. ECC-083219), NSF Grant No. DMR10-1006184, DOE Contract No. DE-AC02-05CH11231 and DOE Molecular Foundry (No. DE-AC02-05CH11231); and by the MOST (Grant No. 2012CB933003), CAS (Grant Nos. KJCX2-YW-M13 and KJCX2-YW-W35) and NSF (Grant Nos. 11027402, 10973844 and 20791395) of China.

Author contributions


Additional information

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Liu, K. et al. Quantum-coupled radial-breathing oscillations in double-walled carbon nanotubes. Nat. Commun. 4:1375 doi: 10.1038/ncomms2367 (2012).