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Efficient near-infrared up-conversion photoluminescence in carbon nanotubes

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Photoluminescence phenomena normally obey Stokes' law of luminescence according to which the emitted photon energy is typically lower than its excitation counterparts. Here we show that carbon nanotubes break this rule under one-photon excitation conditions. We found that the carbon nanotubes exhibit efficient near-infrared photoluminescence upon photoexcitation even at an energy lying >100–200 meV below that of the emission at room temperature. This apparently anomalous phenomenon is attributed to efficient one-phonon-assisted up-conversion processes resulting from unique excited-state dynamics emerging in an individual carbon nanotube with accidentally or intentionally embedded localized states. These findings may open new doors for energy harvesting, optoelectronics and deep-tissue photoluminescence imaging in the near-infrared optical range.
Photoluminescence phenomena normally obey Stokes’ law of luminescence, which states that the emission light wavelength (energy) is typically longer (lower) than its excitation counterpart. Up-conversion (or anti-Stokes) photoluminescence violates the Stokes’ law of luminescence owing to additional energy gain induced by multiple photon or thermal (phonon) energy absorption. This unique photon up-conversion phenomenon only occurs efficiently in certain materials such as rare-earth-doped materials and some organic dyes by virtue of their specific electronic structures. Its potential usefulness in various applications such as photovoltaic energy conversion, photoluminescence bioimaging, displays, lasers, and optical refrigeration of solids has attracted growing interest in recent years. However, especially in the near-infrared optical range, limitations in materials and combinations of excitation and emission photon energies available for efficient photon up-conversion have reduced its compatibility with a wide range of applications.

Single-walled carbon nanotubes (hereafter referred to as carbon nanotubes) consist of graphene sheets rolled up into quasi-one-dimensional tubular structures with diameters of the order of 1 nm. Depending on the rolling-up direction and their diameter defined by two indices \((n, m)\), nanotubes act as direct gap semiconductors with band gaps of the order of 1 eV and emit photoluminescence in the near-infrared optical range because of recombination of excitons (electron and hole pairs bound via attractive Coulomb interactions). Numerous distinctive luminescence properties of nanotubes and their applications have been uncovered over the past decade. However, this report reveals an additional remarkable characteristic of carbon nanotubes as photoluminescent materials.

Here, we demonstrate that carbon nanotubes are new up-conversion phosphors showing efficient near-infrared to near-infrared up-conversion photoluminescence at room temperature with an energy gain of up to a few hundreds of milli-electronvolts, corresponding to light wavelength shortening of a few hundreds of nanometres. This photon up-conversion does not originate from common coherent two-photon absorption or anti-Stokes Raman processes. The observed phenomena are attributed to efficient excitonic up-conversion processes gaining energy by absorbing high-energy (~100–200 meV) optical phonons characteristic in carbon nanotubes, although the phonon energy much exceeds the ambient thermal energy (only ~26 meV) and corresponding phonon number available for the up-conversion is considerably small. This apparently anomalous process stems from unique excited-state dynamics emerging in an individual carbon nanotube with accidentally or intentionally embedded localized states. These findings may lead to new opportunities for near-infrared and thermal energy harvesting, optoelectronics and deep-tissue up-conversion photoluminescence imaging using conventional silicon-based image sensors and low-cost near-infrared light sources.

Results

Optical imaging of the up-conversion light emission. Figure 1a shows an optical image of photoluminescence from (6,5)-rich carbon nanotubes dispersed in D₂O (Methods section) in a standard quartz cell. The incident photon wavelength (energy) was set to ca. 1,100 nm (1.13 eV) and the photoluminescence image ranging between 950 and 1,000 nm (1.24–1.31 eV) was selectively captured using optical filters. The power density of the collimated incident light equalled 200 mW cm⁻², which was too weak to induce coherent two-photon excitation photoluminescence.

Up-conversion photoemission spectra. Figure 2a compares photoemission spectra of nanotubes excited with 1.13 (1,100 nm; red curve) and 2.18 eV (568 nm; black curve) photons, respectively. The grey curve shows control data obtained for a nanotube-free surfactant solution excited at 1.13 eV. The emission peak detected at ca. 1.26 eV upon excitation at 2.18 eV (resonant with the second sub-band exciton energy \(E_{22}\) of (6,5) nanotubes) corresponds to the photoluminescence induced by exciton recombination in the first sub-band \((E_{11})\) of (6,5) nanotubes. The photoemission spectrum obtained at an excitation energy of 1.13 eV exhibited a peak at ca. 1.26 eV. The similar peak energies for excitation energies of 1.13 and 2.18 eV indicate that the photoemission mainly originates from (6,5) nanotubes.

Excitation power dependence. The excitation power density dependence was examined to clarify the origin of the observed light emission. Figure 2b compares excitation power dependence on the photoemission spectra from carbon nanotubes excited at 1.13 eV. The photoemission intensity was measured at 1.26 eV. The emission peak intensity increased as the excitation power increased, but no change in the peak wavelength was observed. The power density dependence was examined for excitation energies of 1.13 and 2.18 eV (Methods section). The power density dependence on the photoemission was clearly observed along the incident light path. We also confirmed that this light emission is excited at longer wavelength (lower energy) incident light (~1,100 nm).

Although the incident photon energy (wavelength) was considerably lower (longer) than the detected photon energy (wavelength), photoemission was clearly observed along the incident light path. We also confirmed that this light emission is excited at longer wavelength (lower energy) incident light (~1,100 nm).
Figure 2 | Excitation power and energy dependences of the up-conversion photoemission. (a) Photoemission spectra of carbon nanotubes excited at incident photon energies of 1.13 (1,100 nm, red curve) and 2.18 eV (568 nm, black curve). The gray curve is a spectrum taken for a carbon nanotube-free surfactant solution excited at 1.13 eV for comparison. The intensity was normalized so that the noise level appears to be comparable to the spectrum of carbon nanotubes excited at 1.13 eV (red curve). The excitation band width was 10 nm. (b) Excitation power density dependence of photoemission spectra excited at 1.13 eV. The spectra for excitation densities from 3 to 159 kW cm\(^{-2}\) are shown. Each spectrum is normalized by corresponding excitation power density. (c) Photoemission intensity (from data shown in b) plotted as a function of excitation power density. The dotted line corresponds to linear function for comparison. (d) Excitation photon energy dependence of the photoemission spectra. In b and d, each spectrum was vertically shifted for comparison, and corresponding excitation power densities (for d) or excitation photon energies (for d) are indicated on each spectrum for clarity. (e) Up-conversion photoemission intensity (red circles, from spectra in d) as a function of excitation photon energy, plotted together with normal photoluminescence spectrum at an excitation energy of 2.18 eV (black curve) for comparison. The dotted red curve is a guide to the eye. (f) Energy diagram for the observed photon up-conversion processes. Solid lines represent the ground (\(|0\rangle\)) and free exciton (\(|\text{ex}\rangle\)) states in carbon nanotubes. The dashed line corresponds to an intermediate state in the up-conversion process.

up-conversion photoemission. The spectral shape hardly changed with excitation power density variations (Fig. 2b). Figure 2c shows the up-conversion photoemission intensity as a function of excitation power density, revealing a weak sublinear dependence between these parameters. These observations exclude any possible photoemission induced by multiple-photon absorption (coherent or incoherent) or Auger recombination-mediated up-conversion\(^{28}\) as origins for the observed phenomena because these mechanisms usually display a superlinear (quadratic or more) excitation power dependence.

Excitation photon energy dependence. Next, the excitation photon energy dependence of the up-conversion photoemission spectra was evaluated (Fig. 2d). The up-conversion intensity strongly depended on the excitation photon energy (wavelength) but spectral shape and peak positions remain nearly intact upon excitation photon energy variations. This observation rules out the possibility that the up-conversion photoemission results from anti-Stokes Raman scattering because Raman processes induce clear peak shifts according to excitation energy changes.

The exclusion of these potential processes suggests that the observed up-converted photoemission is attributable to photoluminescence induced by one-photon absorption followed by an internal excitonic up-conversion process in a carbon nanotube. Therefore, the observed phenomena are referred to as up-conversion photoluminescence in the remainder of the manuscript. Let us now consider the mechanism that governs this efficient excitonic up-conversion. The excitation photon energy dependence of the up-conversion intensity may provide a clue to the mechanism. Figure 2e compares the observed up-conversion photoluminescence intensity (red circles) as a function of excitation photon energy with a normal (Stokes) photoluminescence spectrum (black curve) obtained at an excitation energy of 2.18 eV. The threshold excitation photon energy required to achieve an observable up-conversion photoluminescence reaching ca. 1.3 eV amounted to 1.03–1.08 eV. A diagram showing excitation and emission photon energies for the observed up-conversion processes is shown in Fig. 2f.

Temperature dependence. The threshold energy gain close to the maximum optical phonon energy (~0.2 eV) in carbon nanotubes\(^{29}\) and increasing up-conversion efficiency for smaller energy gain imply that phonon-assisted processes may induce internal up-conversion in carbon nanotubes. Therefore, temperature-dependent studies on the up-conversion photoluminescence were conducted. Figure 3a compares up-conversion photoluminescence intensities at 297 and 281 K at an excitation energy of 1.13 eV. The up-conversion photoluminescence intensity exhibited high
sensitivity to small temperature variations and increased with increasing temperature. Figure 3b shows the up-conversion (red open circles) and normal photoluminescence intensities (black open circles) as functions of temperature. Up-conversion and normal photoluminescence intensities displayed opposite trends with respect to temperature (Fig. 3b). The up-conversion photoluminescence intensity increased, whereas its normal counterpart slightly decreased when the temperature increased.

Figure 3c shows an Arrhenius plot of the up-conversion intensity (UCPL) divided by the normal photoluminescence intensity (PL) at the corresponding temperature. The solid line in Fig. 3c represents the Arrhenius equation ($I_{UCPL} / I_{PL}$) divided by the normal photoluminescence intensity ($I_{PL}$) at the corresponding temperature (red squares). $I_{UCPL}$ was divided by $I_{PL}$ to account for the temperature-dependent variation of $I_{PL}$. The black solid line represents the Arrhenius equation for an activation energy of 120 meV.

Carbon nanotubes with oxygen- and sp$^3$-defect-derived optically active localized (zero-dimension (0D)-like) states were prepared according to procedures originally developed by Ghosh et al. and Piao et al. with some modifications in selections of chemicals and experimental parameters, respectively (Methods section). Figure 4a,f compare the normal photoluminescence spectra of as-dispersed (black curves) and sp$^3$-defect (red curve) or oxygen-doped (blue curve; hereafter referred to as 0D-doped) carbon nanotubes. A relatively broad and intense photoluminescence band emerged around 1.1 eV after chemical treatment, whereas the original $E_{11}$ photoluminescence intensities decreased only slightly for 0D-doped nanotubes. Figure 4b–e,g–j show up-conversion photoluminescence spectra of as-dispersed (black curves) and 0D-doped carbon nanotubes (coloured curves) excited at 1.13, 1.08, 1.03 and 1.00 eV, respectively. Note that the 0D-doped nanotubes displayed a considerably enhanced up-conversion photoluminescence intensity compared with their as-dispersed counterparts regardless of origins of the localized states.

Intermediate states in up-conversion processes. Now that the up-conversion photoluminescence has been clearly attributed to phonon-assisted processes, the reason for the efficient phonon-assisted up-conversion with an energy gain reaching 5–10 $k_B T$ needs to be elucidated. The weak sublinear dependence of the up-conversion photoluminescence intensity on the excitation power density (Fig. 2c) may provide insight into this anomalous phenomenon. The sublinear dependence implies the existence of an intermediate state with finite lifetime causing state-filling-induced saturation effect. Because it lies at lower energy than the $E_{11}$ free exciton state, this state may be a mid-gap localized state unintentionally generated in carbon nanotubes during sample preparation because some types of these states are optically active and can be photoexcited directly by near-infrared photons.

To test this hypothesis, localized states were intentionally embedded in carbon nanotubes by chemical treatments and up-conversion photoluminescence changes were examined.

**Discussion**

We deduced the up-conversion quantum yield of the localized excitons to the free excitons using the difference between up-conversion photoluminescence intensities before and after intentional localized state doping (see Supplementary Discussion and Supplementary Fig. 9 for details). It was of the order of $10^{-1}$ for an energy gain of 120 meV even at room
temperature. This highly efficient phonon-assisted exciton up-conversion showing an energy gain much exceeding the thermal energy appears anomalous but may be understood as a consequence of rapid exciton migration along the nanotube axis\(^37\) as described below. The efficient exciton scattering by acoustic phonons\(^38\) or random extrinsic surface potentials\(^39\) that result in optical resonance in (6,5) carbon nanotubes for photoexcitation. The optical image of an individual nanotube shown in Fig. 1b was performed using an inverted microscope and a 1.4 NA, \(\lambda\) 100 objective under epi-illumination of the near-infrared incident light (1,075–1,125 nm, approximate power density of 4 kW cm\(^{-2}\)). For the microscopic imaging, the individually dispersed nanotubes were immobilized using an agarose gel matrix\(^47\). During spectral measurements shown in Figs 2–4, the nanotube dispersion was set in a quartz cell with optical path of 1 mm. Incident light was focused on the sample in the quartz cell as shown in Figs 2–4, the nanotube dispersion was set in a quartz cell with optical path of 1 mm. Incident light was focused on the sample in the quartz cell as shown in Figs 2–4, the nanotube dispersion was set in a quartz cell with optical path of 1 mm.

Finally, let us discuss the merits of the up-conversion excitation wavelength of the nanotubes lying in a specific near-infrared optical range (\(\lambda = 1,000–1,400\) nm). This wavelength range is known as second biological transparency window (NIR II), in which the light penetration depth into biological tissues is maximized, whereas photo-induced degradation and autofluorescence are minimized\(^38\). Indeed, carbon nanotubes are expected to serve as promising phosphors for NIR II deep-tissue imaging, and biocompatible and luminescent nanotube dispersion has already been developed\(^34\). A chief obstacle to this imaging approach has been the unsuitability of common silicon-based image sensors because of their vanishing sensitivity for NIR II photons. The up-conversion photoluminescence of the (6,5) carbon nanotubes with the inverted excitation (in the NIR II range) and emission (<1,000 nm, so-called NIR I range) wavelengths may solve this problem and facilitate deep-tissue bio-imaging by taking advantage of the large penetration depth of NIR II photons and common silicon-based image sensors (Supplementary Notes 3–5 and Supplementary Figs 5–8). Because up-conversion occurs as a one-photon process in carbon nanotubes, it does not require costly ultrafast high-power lasers and high-density excitation conditions unlike conventional multi-photon excitation imaging. Furthermore, up-converted photocarriers in carbon nanotubes may be directly extracted as electronic current by configuring photovoltaic devices because of their quasi-one-dimensional structures. Therefore, these findings may also lead to new routes for optoelectronics and heat and photon harvesting below the optical gap in the near-infrared region.

**Methods**

Sample preparation. (6,5)-rich CoMoCAT carbon nanotubes (Southwest Nanotechnologies, USA) were dispersed in D\(_2\)O in the presence of 0.2% (w/v) sodium dodecyl benzene sulfonate under moderate bath sonication for 60 min and vigorous sonication using a tip-type sonicator for 40 min before centrifugation at an acceleration of 130,000×g for 4 h (ref. 19). For the experiments shown in Fig. 4, additional localized states were embedded in carbon nanotubes by atomic oxygen\(^32\) or sp\(^3\)-defect doping\(^34\) that reduce the band gap and exciton energy locally. Oxygen- and the sp\(^3\)-defect-doped carbon nanotubes were prepared according to procedures originally developed by Ghosh et al.\(^12\) and Piao et al.\(^34\), respectively, with different chemical and experimental parameter selections\(^19\). In brief, the isolated nanotube dispersion was combined with a small amount of D\(_2\)O containing dissolved ozone and left under the illumination of a desk lamp (ca. 5 mW cm\(^{-2}\)) overnight, allowing moderate atomic oxygen doping to generate sparse oxygen-derived local states. To achieve sp\(^3\)-defect doping, the nanotube dispersion was combined with a small amount of D\(_2\)O containing dissolved organic 4-heptaldehyde\(^34\) and left in the dark for at least 10 days, allowing moderate sp\(^3\)-defect doping in carbon nanotubes to generate sparse sp\(^3\)-defect-derived localized electronic states. Optical absorption spectra of these samples are presented in Supplementary Fig. 1.

**Optical measurements.** Optical measurements were conducted using a broadband supercontinuum white light source (Fianium, SC450) for excitation. Incident light wavelengths were selected using a monochromator for normal Stokes emission measurements and optical filters for up-conversion photoemission measurements. The typical excitation band width was 10 nm for spectroscopic measurements and any unwanted stray light was carefully removed using multiple optical filters. Normal photoluminescence measurements were performed using monochromatic light at a wavelength of 568 nm (2.18 eV) that matches the \(E_2^\pm\) optical resonance in (6,5) carbon nanotubes for photoexcitation. The optical image showing up-conversion photoemission phenomena was performed using an electron multiplying charge coupled device camera (EMCCD). The microscopically up-conversion photoemission imaging of an individual nanotube shown in Fig. 1 was performed using an inverted microscope and a 1.4 NA, \(\lambda\) 100 objective under epi-illumination of the near-infrared incident light (1,075–1,125 nm, approximate power density of 4 kW cm\(^{-2}\)). For the microscopic imaging, the individually dispersed nanotubes were immobilized using an agarose gel matrix. During spectral measurements shown in Figs 2–4, the nanotube dispersion was set in a quartz cell with optical path of 1 mm. Incident light was focused on the sample in the quartz cell as shown in Figs 2–4. For spectral measurements shown in Figs 2–4, the nanotube dispersion was set in a quartz cell with optical path of 1 mm. Incident light was focused on the sample in the quartz cell as shown in Figs 2–4.
photoemission intensity as functions of excitation power density or temperature. The nanotube dispersion temperature was directly measured in a quartz cell using a dippen thin thermocouple. For the measurements of temperature dependence of nanotubes in the quartz cell were gradually cooled using iced water or allowed to warm up by natural convection. Optical spectra were acquired at temperatures ranging from 280 K to room temperature (ca. 300 K). The temperature typically varied by 1.5 K during each spectral measurement.

References

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

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