



Supporting Online Material for

Bright Infrared Emission from Electrically Induced Excitons in Carbon Nanotubes

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Materials and Methods

Synthesis of nanoparticle catalysts

Fe nanoparticles were prepared by thermally decomposing $\text{Fe}(\text{CO})_5$ (*SI*). A solution of 0.196g $\text{Fe}(\text{CO})_5$ and 0.564g oleic acid in 5ml octyl ether was heated up and boiled under Ar protection for 30 minutes. After the solution cooled down to room temperature, 5ml ethanol was added. The solution was then centrifuged at 7200 rpm for 5 minutes to precipitate the formed Fe nanoparticles. After the solution was decanted, the nanoparticles were dispersed in hexane. The size of the nanoparticles was determined by TEM and AFM.

Synthesis of single-walled carbon nanotubes

The above hexane dispersion of the nanoparticles was diluted with hexane by approximately 10^6 . The solution was then deposited on a sample substrate. After the surface dried, the substrate was brought into a 1-inch quartz tube in a furnace and annealed at 700°C in the air for 15 minutes. After cooling down to room temperature, the substrate was then reheated in a 500 sccm H_2 flow. When the furnace temperature reached 900°C , 800 sccm CH_4 and 20 sccm C_2H_4 were added to initiate SWNT growth. The growth typically lasts 20 minutes and is terminated by switching off the CH_4 and C_2H_4 flow. The substrate is then cooled down to room temperature under H_2 protection.

Experimental setup and measurements

The IR emission from the CNTFETs was imaged using a liquid nitrogen-cooled HgCdTe detector-array mounted on a probe station which was used to simultaneously measure their electrical properties. The lateral resolution of the detector was diffraction-limited to $\sim 2 \mu\text{m}$. We measured the IR emission efficiency from the CNTFETs by integrating over their spectra. As in Ref. S2, we calibrated the detector and the IR collection optics against the emission from a blackbody emitter.

Exciton generation by carrier impact

In order to be able to generate an exciton, a charge carrier must be accelerated to an energy above the impact excitation threshold, before it is scattered inelastically by a phonon. We estimated the impact excitation probability using Fermi Golden Rule:

$$W_{k_1 k_2, k_1-q k_2+q} = \frac{2\pi}{\hbar} |M_{k_1 k_2 q}|^2 \delta(\varepsilon_{k_1}^c + \varepsilon_{k_2}^v - \varepsilon_{k_1-q}^c - \varepsilon_{k_2+q}^c), \quad (1)$$

where the matrix element $|M_{k_1 k_2 q}|$ involves both direct and exchange Coulomb interactions (S3) and was evaluated for the *free* electron-hole wavefunctions using a tight binding model with a hopping matrix element of $t=3$ eV and a dielectric constant $\varepsilon = 2$ for the surrounding medium (S4). The scattering rates in Fig. 2C and the inset of Fig. 3C (in the main text) were calculated using a self-consistent distribution function obtained from the Boltzmann equation as in (S5), but with both phonon (S5) and impact excitation scattering Eq. (1) included. The energy conservation law requires that the energy of the impacting electron $\varepsilon_{k_1}^c$ is larger than the energy

of the created electron $\varepsilon_{k_2+q}^c$ and hole $\varepsilon_{k_2}^v$. In addition, angular momentum conservation requires that the impacting electron must be able to populate the third CNT sub-band to create an electron and a hole in the first sub-band, and it must reach the fourth sub-band to create an electron and a hole in the second sub-band. This leads to a threshold energy of approximately $1.6 E_g$ for the first sub-band electron-hole pair excitation, where E_g is the tight-binding band-gap. It should be noted, however, that electron-hole correlations and band mixing effects in the two-particle exciton wavefunction (S4), not considered here, can influence the exciton production rate.

Generation of the second excited state via exciton-exciton annihilation

To understand the mechanism by which the E_{22} state is generated in our system, we have modeled its excitation by both direct impact and the process of excitation annihilation, i.e. as a result of a $E_{11} + E_{11} \rightarrow E_{22}$ bimolecular process. The relative importance of the two excitation mechanisms can be deduced by solving the following master equation for the number of the first n_1 (E_{11}) and the second n_2 (E_{22}) excitons:

$$\begin{aligned} \frac{dn_1}{dt} &= P_{11} - \gamma n_1(n_1 - 1) - \gamma_{1g} n_1 + \gamma_{21} n_2 \\ \frac{dn_2}{dt} &= P_{22} + \frac{\gamma}{2} n_1(n_1 - 1) - \gamma_{21} n_2 \end{aligned} \quad (2)$$

where P_{11} and P_{22} are the rates of E_{11} and E_{22} exciton production. If $n_1 > 1$, then the exciton annihilation rate constant $\gamma = 0.8 \text{ ps}^{-1}$ (S5, S6). If $n_1 < 1$, then $\gamma = 0$. The E_{11} non-radiative decay rate is $\gamma_{1g} = 0.01\text{-}0.06 \text{ ps}^{-1}$ (S5-S12), and the E_{22} decay rate has been measured (S12-S15) and calculated (S16) to be in the range of $\gamma_{21} = 1\text{-}25 \text{ ps}^{-1}$. For the second E_{22} exciton, we can neglect the non-radiative recombination channel involving direct decay to the ground state.

In the low field regime (i.e. small P_{11} and P_{22}), $n_1 < 1$ and the steady state solution of Eq. (2) is $n_1 = (P_{11} + P_{22})/\gamma_{1g}$ and $n_2 = P_{22} / \gamma_{21}$. In the high field regime, when the number of E_{11} excitons is larger than one (i.e. $P_{11} + P_{22} > \gamma_{1g}$), then the E_{22} exciton state can also be populated by the exciton annihilation mechanism, leading to:

$$n_1 = \frac{\sqrt{8\gamma(P_{11} + P_{22}) + (\gamma - 2\gamma_{1g})^2} + \gamma - 2\gamma_{1g}}{2\gamma} \quad (3a)$$

$$n_2 = \frac{P_{22}}{\gamma_{21}} + \frac{\gamma}{2\gamma_{21}} n_1(n_1 - 1) \quad (3b)$$

The first term in Eq. (3b) gives the contribution to n_2 (E_{22}) generated directly via the impact excitation process, whereas the second term gives the contribution from the exciton-exciton annihilation process. In Fig. 3C we plot the numbers n_2 of E_{22} excitons versus the numbers n_1 of E_{11} excitons from Eq. (3) for a realistic set of parameters: $\gamma = 0.8 \text{ ps}^{-1}$, $\gamma_{1g} = 0.03 \text{ ps}^{-1}$ and $\gamma_{21} = 10 \text{ ps}^{-1}$. We calculate the impact excitation rates r_{11} (r_{22}) for E_{11} (E_{22}) excitons, shown in Fig 2C and the inset of Fig. 3C in the main text, by averaging the scattering rate in Eq. (1) over the non-equilibrium distribution function, obtained from the solution of the Boltzmann equation. To relate P and r we need to know the number of electrons involved in impact excitation scattering, which is given by $\lambda_{scr}\rho$, where $\rho = I/ev$ is the charge carrier concentration and $\lambda_{scr} = 80 \text{ nm}$ is the screening length used in the simulation. Therefore, exciton production rate is equal to $P_{ii} = r_{ii}\lambda_{scr}\rho$. The results of simulations, shown in Fig 3C, indicate that the exciton-exciton annihilation process is primarily responsible for the E_{22} exciton production (more than 80% excitons for the typical electrical fields in the devices). We estimate exciton production rates of $P_{11} = 19.2 \text{ ps}^{-1}$ and $P_{22} = 4.9 \text{ ps}^{-1}$ for a 2 nm diameter tube in a field of 0.15 MV/cm at the suspended/supported interface junction, with a drive current of 3 μA and a charge carrier

velocity of 2×10^7 cm/s (SI7). The numbers of E_{11} and E_{22} excitons at this field at the junction are 8.2 and 2.9, respectively, These correspond to steady-state E_{11} and E_{22} exciton densities of 0.1 excitons/nm and 0.036 excitons/nm. We conclude that that current-induced impact excitation processes in the quasi-1D carbon nanotube devices are very efficient.

References:

- S1. Y. Li, J. Liu, Y. Q. Wang, Z. L. Wang, *Chemistry of Materials* **13**, 1008 (2001).
- S2. M. Freitag *et al.*, *Nano Lett.* **4**, 1063 (2004).
- S3. P. T. Landsberg, *Recombination in Semiconductors* (Cambridge University Press, Cambridge, 1991).
- S4. V. Perebeinos, J. Tersoff, Ph. Avouris, *Phys. Rev. Lett.* **92**, art. no. 257402 (2004).
- S5. F. Wang, G. Dukovic, L. E. Brus, T. F. Heinz, *Phys. Rev. Lett.* **92**, art. no. 177401 (2004).
- S6. Y.-Z. Ma, L. Valkunas, S. L. Dexheimer, S. M. Bachilo, G. R. Fleming, *Phys. Rev. Lett.* **94**, art. no. 157402 (2005).
- S7. Y.-Z. Ma *et al.*, *J. Chem. Phys.* **120**, 3368 (2004).
- S8. G. N. Ostojic *et al.*, *Phys. Rev. Lett.* **92**, art. no. 117402 (2004).
- S9. S. Reich, M. Dworzak, A. Hoffmann, C. Thomsen, M. S. Strano, *Phys. Rev. B* **71**, 033402 (2005).
- S10. O. J. Korovyanko, C.-X. Sheng, Z. V. Vardeny, A. B. Dalton, R. H. Baughman, *Phys. Rev. Lett.* **92**, art. no. 017403 (2004).
- S11. L. Huang, H. N. Pedrosa, T. D. Krauss, *Phys. Rev. Lett.* **93**, art. no. 017403 (2004).
- S12. A. Hagen, G. Moos, V. Talalaev, T. Hertel, *Appl. Phys. A* **78**, 1137 (2004).
- S13. C. Manzoni, *et al.*, *Phys. Rev. Lett.* **94**, 207401 (2005).
- S14. J. Kono, *et al.*, *Appl. Phys. A* **78**, 1093 (2004).
- S15. J.S. Lauret, *et al.*, *Phys. Rev. Lett.* **90**, 057404 (2003).
- S16. V. Perebeinos, J. Tersoff, Ph. Avouris, *Phys. Rev. Lett.* **94**, art. no. 027402 (2005).
- S17. Y. F. Chen and M. S. Fuhrer, *Phys. Rev. Lett.* (to be published).