Proposed strategy to sort semiconducting nanotubes by band-gap

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Abstract

We propose a strategy that uses a tunable infra-red source and an alternating non-linear potential defined by an electrode to sort a suspension of assorted semiconducting nanotubes. The band-gap scales with the inverse of the nanotube diameter, hence the infra-red frequency can be tuned to create excitons in some of the nanotubes; these excitons will be polarized by the potential. Since, a polarized exciton is a dipole, the excited nanotubes will experience a net force and may then diffuse towards the electrode, unlike the other nanotubes. We discuss experimental parameters such as IR intensity, electrode design, and potential frequency for a pilot experiment to sort nanotubes with lengths $\approx 0.5\,\mu m$. The basic physics of the system has been illustrated using a Hartree model applied to nanotubes with nanoscale lengths. The calculated exciton binding energy suddenly drops to zero and the force on the nanotube increases dramatically when the exciton disassociates as the nanotube moves towards the electrode. The quantum adiabatic theorem shows that excitons will be adiabatically polarized for potential frequencies typical for experiments $\approx 1-10\,MHz$. The analysis indicates that the manipulation of nanotubes with nanometer lengths requires nanoscale electrodes.

1. Introduction

The unexpected discovery of another state of carbon in single-walled carbon nanotubes [1] (SWNTs) has attracted a great deal of theoretical and technological interest. SWNTs can be semiconducting or metallic [1] depending on their chirality and diameter, and may be combined to create exotic devices. Typically an assortment of SWNTs bound by strong van-der-waals forces are created, thus individual SWNTs are hard to manipulate. Recently, SWNT ropes were separated in water (containing a surfactant) by sound waves and centrifugation [2]. The resulting suspension contained SWNTs with an average diameter and length of 0.7 and 130 nm, respectively. The process has been fine-tuned for different solvents and surfactants to increase the average SWNT length to 500 nm [3]. Metallic and semiconducting SWNTs have subsequently been separated [4] by alternating current (AC) dielectrophoresis [5]. This paper proposes theoretically a strategy for sorting the remaining semiconducting SWNTs according to radius and chirality.

An electrode defines an alternating exponentially decaying potential in the suspension, and laser pulses or continuous wave radiation excite electron–hole ($e-h$) pairs. Since the band gap conveniently scales with the inverse of the diameter (where a diameter between 0.6 to 1.6 nm corresponds to $0.4-1.0\,eV$) the laser frequency can be tuned to select some nanotubes [6]. The external potential frequency is "slow" so that the e–h hole pairs are polarized adiabatically, but also "fast" enough to prevent the build up of a surface charge and its associated electrophoretic force. The e–h pairs are expected to initially screen the external potential [7] which will recover as the exciton density decays. The remaining excitons, as in the p–n junction of a nanotube solar cell [8], shall disassociate and migrate to opposite ends. The excitonic dipole experiences a net time average force and the host nanotube may then diffuse towards the electrode, whereas the inert nanotubes

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will remain in place; this is the essence of the separation strategy which can be classified as light-induced AC dielectrophoresis (LID).

We shall discuss experimental parameters to manipulate nanotubes with length of the order of 1 μm. The exact simulation of the movement of the nanotubes towards the electrode is beyond the scope of this paper, which is best performed in conjunction with actual experiments. The trends of the separation process however shall be illustrated by considering nanotubes with nano-scale lengths. The exciton dipole shall be calculated using a simple Hartree model to estimate the force on a bare nanotube.

2. Reasonable experimental parameters

The proposed experiment requires nanotubes to be adequate photoconductors. The nanotube photoconductivity depends on the balance between the expected balistic transport of electrons and holes with the high exciton binding energy in such quasi-1D wires. Photoconductivity measurements of nanotubes suspended in methanol under continuous wave near infrared (IR) illumination [9] show that nanotubes exhibit reasonable photoconductivity for modest incident light intensities and source to drain voltages. Moreover, recent experiments [8] confirm that the photocurrent is associated with excitons rather than interband processes [10].

The following parameters from Ref. [9] are suggested as starting values for a pilot experiment to test LID. The nanotube suspension on an inert substrate should have a maximum thickness of 15 μm and a light intensity of $0.1\,W\,cm^{-2}$ should provide an adequate electron–hole creation rate without evaporating the liquid. Recent photoconductivity measurements on a single nanotube shows that a light intensity of $1\,kW\,cm^{-2}$ produces a $10^{-10}\,A$ photocurrent with 0.5 V across a 0.5 μm nanotube. The actual exciton creation rate cannot be estimates since a fraction of excitons will recombine. Assuming the exciton creation rate is linear [11] with the light intensity then $0.1\,W\,cm^{-2}$ will drive a current of around of 6.24×10^4 electrons/holes s^{-1} (this is for a 0.5 μm nanotube between source and drain). Since the electrons and holes are confined to the nanotube no current can flow and we can consider the latter figure crudely as the exciton creation rate. The AC field will polarize the electron(s) and hole(s) when the field is strong enough. These will then recombine as the field approaches zero. The polarization of the nanotube can only be estimated by solving a complex time-dependent many-body problem and is beyond the scope of this paper.

Since the dielectrophoretic force scales with the objects volume it was historically thought that the Brownian motion experienced by sub-micron particles could not be overcome, restricting the application of dielectrophoresis to larger objects. The advancements in lithographic techniques however, has made it possible to fabricate

electrodes with feature sizes of 1 μm. The electrodes must be fabricated to manipulate nanotubes with lengths of the order of 0.5 μm, and many designs can be used. The electric field can be maximized by applying a high voltage or by a strong curvature in the electrode shape. Triangle shaped electrodes have been used to manipulate submicron DNA and viruses [12] and "cages" for molecules with sizes of the order of 10 nm have been constructed using triangle electrode pairs with a 500 nm gap [13]. In addition a nano-pipette electrode has been used to define a strong electric field over several microns to manipulate DNA [14].

The semiconducting nanotubes will experience positive or negative dielectrophoresis depending on the AC frequency of the electrode(s). The windows in frequency space for which the semiconducting nanotubes are attracted or repelled to the electrode depends on the solvent used. LID should be performed when the attractive dielectrophoretic force experienced by unexcited semiconducting nanotubes is comparable to the random Brownian force from the fluid. The inert nanotubes will then feel a weak attraction towards higher potential, in contrast to the excited nanotubes which can in principle experience a strong attraction to the electrode. The frequencies 1 MHz and 10 KHz can be used when using water and 2-propanol (IPA) as solvents, respectively [15].

Clearly for a nanotube with length L the applied potential must vary significantly over L to separate the excitons; this implies that for nanotubes shorter than some critical length LID using existing electrodes would be impossible. The increase in the Brownian force and the reduced photon capture cross-section with decreasing L shall also inhibit the applicability of LID. Nanoscale electrodes made from nanotubes are also being developed and maybe used in future to manipulate nanoscale nanotube fragments. The applicability of LID for sub 50 nm nanotubes is of fundamental and technological interest. We shall investigate this nanoscale limit for LID using a simple Hartree model.

3. Simple Hartree model

The time dependent Hamiltonian for an electron and hole on the surface of a nanotube with positions r_1 and r_2 with masses m_1 and m_2 has the form

$$H = p_{r_1}^2/2m_1 + p_{r_1}^2/2m_1 + V_C(r_1, r_2) + V_{ext}, \qquad (1)$$

where the external potential $V_{ext} = e(t/T)(V_0 e^{-kz_1} - V_0 e^{-kz_2})$, V_c is the attractive Coulomb potential, and V_0 and k are constants determined by the gate bias and geometry. Within one cycle the external potential increases adiabatically from zero to its full value for $0 < t < T$ during the polarization time T. The adiabatic regime implies, that instantaneous eigenstates can be calculated using an effective time independent Hamiltonian.

In an effort to illustrate the physical trends of the system we have calculated the adiabatic exciton ground state using a simple Hartree model by assuming a separable