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Effect of medium dielectric constant on the physical properties of single-walled carbon nanotubes

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ABSTRACT

The photophysical properties of semiconducting single walled carbon nanotubes (SWNTs) in different environments are analyzed by steady-state and time-resolved photoluminescence (PL) spectroscopy. The PL emission of SWNTs shows a red shift with the increase of the dielectric constant of the environments. The solvatochromic shift depends on the structural properties of the nanotubes and reaches almost 100 milli-electron volts in the case of (7,5) tubes. These experimental results allow deriving a relationship between the PL shift and the structure of SWNTs. Moreover, the dynamics of 'bright' excitons in semiconducting SWNTs and the effect of the medium on the decay of the excitons are discussed by using time-resolved spectroscopy.

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1. Introduction

Single-walled carbon nanotubes (SWNTs) can be pictured as a graphene sheet rolled into a cylindrical shape and are considered as a very important candidate for the study of one-dimensional systems. The structure of SWNTs is identified by the chiral index that specifies the diameter and chiral angle. The chiral index (n, m) also indicates the electronic structure of SWNTs by a relation following which nanotubes possessing chiral indices satisfying $(n - m) = 3q$ (q integer) are metallic or semi-metallic while all the others are semiconducting. The optical properties of SWNTs are of great importance not only because they can help in the understanding of their fundamental physical properties, but also because of the potential application of SWNTs in nano-phonic devices [1–5]. The excitonic nature of SWNT photoexcitation has been revealed by using two photon spectroscopy [6] and the excitonic properties such as size, binding energy, and dynamic have been investigated by several spectroscopic techniques [7–9]. The effect of the environment on the photophysical properties of SWNTs has also attracted specific research interest in the last few years. Lefebvre et al. demonstrated blue-shifted PL emission from suspended carbon nanotubes compared to that from dispersed SWNTs [10]. Ohno et al. [11] and Kappes et al. [12] compared the PL emission of suspended (or as-grown) SWNTs in different media and described the PL shifts resulting from dielectric screening effects. The study of the role of the dielectric screening in SWNTs photophysics requires that the SWNTs are individually dispersed. In this respect SWNTs dispersed in aqueous solution have been

very important for the study of the exciton physics of carbon nanotubes [13–15]. Recently, polyfluorene homo- and co-polymers have attracted specific interests due to their unique selectivity towards semiconducting SWNTs. Moreover, the SWNTs with narrow diameter distribution obtained with poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) shows much higher fluorescence quantum yield than the aqueous counterpart [16–19].

Here we study semiconducting SWNTs excitons in different environments. SWNTs were dispersed in toluene with the aid of PFO, and then mixed with different organic solvents. We observed that the PL peaks of the single nanotubes shows a red shift and the emission intensity decreases with increasing of the dielectric constant of the environment. The relationship between the solvatochromic shifts and the structural properties of SWNTs is derived. From the study of the dynamics of 'bright' excitons in semiconducting nanotubes we obtain evidences of structural-dependent fluorescence efficiency of individual carbon nanotube.

2. Experimental

All the solvents in this study were purchased from Sigma–Aldrich and were used as received: cyclohexane, chloroform (CHCl_3), chlorobenzene, toluene (Tol), o-dichlorobenzene (oDCB), p-xylene, dichloromethane (CH_2Cl_2), tetrahydrofuran (THF).

The properties of the solvents are shown in the supporting information (SI Table 1).

HiPco SWNTs (<15 wt.% ash content) from Unidym were used as received. For the preparation of SWNT dispersions, dry nanotubes were added to 10 mL of polymer solution in a weight ratio of 1 mg SWNT to 3 mg polymer and the mixture was sonicated for 4 h in a tabletop ultrasonic bath (VWR, The Netherlands). After

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sonication, the crude solution was ultra-centrifuged at 45 k rpm (160,000g) for 1 h to obtain an optimal SWNT dispersion [20]. The supernatant ($\approx 50\%$) was removed and mixed with different solvents at the ratio of 1 to 9 (v/v), then followed by mild sonication for 1 min in order to achieve homogeneity.

Steady-state and time-resolved photoluminescence (PL) measurements were performed, exciting the solutions at 760 nm by a 150 fs pulsed Kerr mode locked Ti-sapphire laser. PL emission of SWNTs was measured with an InGaAs detector. The time-resolved PL of the SWNT dispersion was recorded by a Hamamatsu streak camera working in synchroscan mode with photocathode sensitive in the near infrared spectral range. All the measurements were performed at room temperature and the spectra were calibrated for the instrumental response.

3. Results and discussion

Because of the miscibility of toluene, the polymer-wrapped SWNT dispersion can be mixed with many organic solvents with different dielectric constants. The time-integrated PL spectra of the dispersed SWNTs are shown in Fig. 1. The peak wavelength of each species of SWNTs was obtained by fitting the spectral profile with Lorentzian line shape.

Fig. 2 shows the solvatochromic shift (ΔE_{11}) of five kinds of semiconducting SWNTs depending on the dielectric constant of the environment. Solvatochromism refers to the change of fluorescence emission energy due to the change of solvent polarity (or dielectric constant). Dipole–dipole interaction between the fluorophore and solvent molecules lowers the energy of the excited state of the fluorophore. In general, the emission shifts towards lower energy with the increase of the solvent polarity. In this study, ΔE_{11} is defined as the difference of the optical transition energy of carbon nanotubes in the specific medium (E_{11}^{media}) with respect to that in vacuum (E_{11}^{vac}). The optical transitions in vacuum were calculated based on the equation [13]: $E_{11} = \frac{1241}{(61.1+113.6 \times d)} - A \times \left(\frac{\cos(3\theta)}{d^2}\right)$, where d and θ are the diameter and chiral angle of the SWNTs, respectively. The value of A depends on the structure of the SWNTs, which is 0.032 eV nm^2 for (7,5), (8,6) and (9,7) nanotubes and -0.077 eV nm^2 for (7,6) and (8,7) nanotubes, respectively. The dielectric constant (ϵ) of the solvent mixtures was calculated by using the equation as reported by Lou et al. [21]. The PL of dispersed SWNTs shows a red shift up to 0.095 eV with increasing of the dielectric constant of the environments. This result is in good agreement with a previous report from Ohno et al. [11]. The second observation is that the smaller diameter nanotubes show larger shifts compare to the larger diameter ones, implying a strong dependence of the solvatochromic shifts of the PL of the SWNTs on the structure of the tubes.

Fig. 1. PL spectra of dispersed SWNTs in different environments.

Fig. 2. Solvatochromic shifts of SWNTs in different environments as a function of dielectric constant.

Fig. 3. PL intensity of SWNTs as a function of dielectric constant. The dash lines are power law fits.

The PL emission intensity of semiconducting SWNTs (I_{SWNT}) in different environments is summarized in Fig. 3. A clear trend with the intensity of the PL of the single tube decreasing with the increase of dielectric constant of the media, with no dependence on the SWNT structure is observed. The dependence can be described using a power law $I_{\text{SWNT}} \propto \epsilon^{-0.8}$ (dashed lines in Fig. 3), which is comparable to that derived by Ziegler et al. ($I_{\text{SWNT}} \propto \epsilon^{-0.5}$) [22]. Such observation can be interpreted as the result of similar “solvent microenvironment” where carbon nanotubes reside in. Polymer (or surfactant) shows minor effect on the PL emission and the solvatochromic shifts of nanotubes. Two sets of experimental data show significant deviation from the trend that corresponds to the SWNT dispersion mixed with CH_2Cl_2 and CHCl_3 , respectively. Recently other authors [14,22], reported a strongly reduced PL intensity of SWNTs dispersed in CHCl_3 . These authors attributed the quenching either to the polarity of the solvent or the presence of SWNT bundles [23]. Our results cannot be explained only with the polarity of the solvent. In fact the emission of SWNTs in THF (mixed with toluene), which is more polar than CHCl_3 , does not show remarkable deviation from the trend in contrary with what is shown in CHCl_3 (mixed with toluene). A possible alternative explanation is the instability of the polymer wrapped SWNTs in CHCl_3 . The superior solubility of PFO in CHCl_3 compare to toluene might induce aggregation and precipitation of the wrapped SWNTs.

As we showed above, the solvatochromic shifts of SWNTs depend strongly on the structural properties of nanotubes. Based on Onsager polarity functions, the solvatochromic shifts of carbon nanotubes can be written as:

$$\Delta E_{11} = -K \frac{\Delta \alpha_{11}}{R^3} f(\epsilon, \eta)$$

In which K is fluctuation parameter, $\Delta\alpha_{11}$ is the change in polarizability, R is the SWNT radius, $f(\epsilon, \eta)$ is Onsager polarity function, ϵ is the dielectric constant and η is the refractive index of the media [24]. Being a quasi-1D material, SWNTs show highly anisotropic polarizability. The longitudinal component ($\alpha_{||}$) is more than one order of magnitude larger than the transverse component ($\alpha_{\perp}$) [25]. As a result, the PL emission from semiconducting SWNTs, also the spectral shifts, is dominated by the longitudinal component. The change in polarizability is also primarily determined by the longitudinal component ($\Delta\alpha_{11} \approx \alpha_{11||}$). So far, there have been several reports describing the relationship between the longitudinal component of the polarizability and other physical quantities. One of them expresses the longitudinal polarizability as: $\alpha_{11||} = kR^a(E_{11}^{vac})^b$, where k is a constant in a certain environment, R is the SWNT radius, E_{11}^{vac} is the optical transition energy in vacuum, a and b are integer. However, the value of a and b is still controversial and several values have been proposed by different authors [14,22,26–29].

The solvatochromic shifts of the SWNTs in three different environments (oDCB (mixed with Tol), THF (mixed with Tol), pure Tol) or in pure toluene are demonstrated in Fig. 4(a)–(f), in which (a, b) correspond to $(-2, -3)$, $(-1, -2)$, $(1, -2)$, $(0, -1)$, $(0, -2)$ and $(2, 0)$, respectively. Surprisingly, scaling relationship between the diameter of the tubes and the solvatochromic shifts can be derived in all the cases and no family dependent behavior was observed (highlighted in Fig. 4 (c), (type I, $(n - m = 3q + 1)$, (7, 6) and (8, 7) tubes) and (type II, $(n - m = 3q + 2)$, (7, 5), (8, 6) and (9, 7) tubes)). The unexpected agreement is probably due to a narrow diameter distribution of SWNTs species studied.

The dynamics of the ‘bright’ excitons in SWNTs in different environments was investigated with the aid of a high-resolution streak camera (~ 3 ps), sensitive in the near infrared range. The measured PL decays can be accurately fitted with a bi-exponential function: $A_1 \exp(-\frac{t}{\tau_1}) + A_2 \exp(-\frac{t}{\tau_2})$, in which τ_1 and τ_2 are the short and long decay components, and A_1 and A_2 are the weight of the two components, respectively. This bi-exponential behavior is ascribed to non-radiative process. It has been observed the measurements of SWNT ensembles and also in measurements of individual SWNT synthesized using HiPco method [30]. Lounis et al. recently reported a monoexponential PL decay with τ in the range of 10–30 ps in the case of CoMoCat carbon nanotube [31] and reasoned as it is the result of the generation of defect during the nanotubes growth process. Fig. 5 (a) shows the fitting results of the PL decays of (7, 5), (7, 6) and (8, 6) tubes in different media, the error bar for the lifetime data is less than 10% in most cases. We further define an effective lifetime (τ_{eff}) using the average $\tau_{eff} = \frac{(A_1 \tau_1 + A_2 \tau_2)}{(A_1 + A_2)}$, in which the contribution of weight (A_1 and A_2) are also taken into account. The effective lifetime of the (7, 5), (7, 6) and (8, 6) nanotubes remain almost constant at 15–20 ps in most environments (Fig. 5(b)). An exceptional case is the SWNT dispersion mixed with CH_2Cl_2 , where the effective lifetime decreased to less than 10 ps. All the fitting results are summarized in the supporting information SI table 2 and SI Fig. 1. Another interesting observation is that the effective PL lifetime (τ_{eff}), which is proportional to the fluorescence efficiency of carbon nanotubes, of (7, 6) carbon nanotubes (type I) is always shorter (10%) than that of (7, 5) and (8, 6) tubes (type II), which indicates a structural-dependent PL lifetime and efficiency in SWNTs. A recent study

Fig. 4. Solvatochromic shifts for SWNTs as a function of nanotube structure ($\alpha_{11||} = kR^a(E_{11}^{vac})^b$), in which (a, b) corresponds to (a) $(-2, -3)$ (from Ref. [21]); (b) $(-1, -2)$ (from Ref. [13]); (c) $(1, -2)$ (from Ref. [25]); (d) $(0, -1)$ (from Ref. [26]); (e) $(0, -2)$ (from Ref. [27]); (f) $(2, 0)$ (from Ref. [28]).

Fig. 5. (a) Short (red) and long (blue) decay component of (7,5), (7,6) and (8,6) nanotubes as a function of dielectric constant of the environment; (b) effective lifetime of (7,5), (7,6) and (8,6) nanotubes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

demonstrates that the decay of “bright” excitons in carbon nanotube is influenced by the extrinsic effects such as the defect density, the length of tubes, etc. [31]. However, we can safely exclude those effects in this study because these three kinds of nanotubes experienced identical treatment and were characterized in the same environments. Carbon nanotubes bundling, which favors energy transfer from large band-gap to small band-gap tubes [17] and shortens the lifetime of large band-gap tubes, does not play a role in this case because (7,5) tubes have larger band gap and longer lifetime than (7,6) tubes. It then leads to the hypothesis that the lower fluorescence efficiency of (7,6) tubes compare to (7,5) and (8,6) tubes is related to the intrinsic property of carbon nanotubes. This finding is in good agreement with previous studies on individual SWNT [32,33] and demonstrates the advantage of PFO wrapped SWNTs for the understanding of the photophysics of SWNTs.

4. Conclusions

The photophysical properties of semiconducting SWNTs dispersed in different environments having a variety of dielectric constants were studied. The PL emission energy of nanotubes shows red shifts with the increase of the dielectric constant of the media. Time resolved PL results show different effective lifetimes for different species of SWNTs. This is an indication of chirality-dependent fluorescence efficiency.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemphys.2012.11.003>.

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