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Large scale, selective dispersion of long single-walled carbon nanotubes with high photoluminescence quantum yield by shear force mixing

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ABSTRACT

Selective dispersion of semiconducting single-walled carbon nanotube (SWCNTs) with conjugated polymers typically involves harsh sonication methods that damage and shorten the nanotubes. Here, we use simple high speed shear force mixing (SFM) to disperse nearly monochiral (6,5) SWCNTs with poly[(9,9-dioctylfluorenyl-2,7-diyl)-*alt-co*-(6,6′-{2,2′-bipyridine})] (PFO-BPy) in toluene with high yield and in large volumes. This highly scalable process disperses SWCNTs of exceptional quality with an average tube length of 1.82 μm and an ensemble photoluminescence quantum yield (PLQY) of 2.3%. For the first time for SWCNTs, we describe and apply absolute PLQY measurements, without the need for any reference emitter. We directly compare values for average SWCNT length, PLQY, linewidth and Stokes shift to other dispersion methods, including bath and tip sonication, as well as other sorting methods such as gel chromatography. We find that SFM results in dispersions of longer SWCNT with higher average PLQY than any other technique, thus making it an ideal method for sorting large amounts of long, high quality and purely semiconducting SWCNTs.

1. Introduction

Semiconducting single-walled carbon nanotubes (SWCNTs) are one of the rare carbon-based materials that exhibit stable near-infrared (NIR) luminescence. In combination with their extremely high charge carrier mobilities and mechanical flexibility, SWCNTs could find applications in electronics [1,2], medicine [3], and optical telecommunication [4,5]. The spectral position of their very narrow emission line can be tuned across the entire NIR (900–2000 nm) by choosing the appropriate nanotube chirality (n,m), thus covering all optical telecommunication bands [6]. While for optoelectronic applications monochiral and purely semiconducting SWCNTs are necessary, SWCNT growth still yields mixtures of various semiconducting and metallic nanotube species [7]. Hence post-growth sorting is needed to supply SWCNTs as a pure and defined starting material. Importantly, this process has to be scalable beyond the microgram-scale in order to become commercially viable. Among the various sorting techniques, such as gel chromatography [8], density gradient ultracentrifugation (DGU) [9], and aqueous two-phase separation [10], selectively wrapping SWCNTs with conjugated polymers leads to very pure semiconducting and even monochiral dispersions with comparatively low effort. For example, the polyfluorene copolymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-*alt-co*-(6,6′-{2,2′-bipyridine})] (PFO-BPy, see Fig. 1a) yields almost monochiral (6,5) SWCNT dispersions [11–13]. In general, polymer-sorted SWCNTs exhibit very low residual metallic content and little intertube interactions, which results in the highest photoluminescence quantum yields (PLQY) in undoped ensemble samples reported so far [12,14,15].

Typically harsh sonication methods are used to disperse nanotubes in order to break up the SWCNT bundles of the raw material and enable surfactant or polymer wrapping [16,17]. Sonication of SWCNTs has two major problems. First, it is known to damage the carbon lattice and shorten the SWCNTs [15,18], due to high local pressure and friction forces that follow sonication-induced

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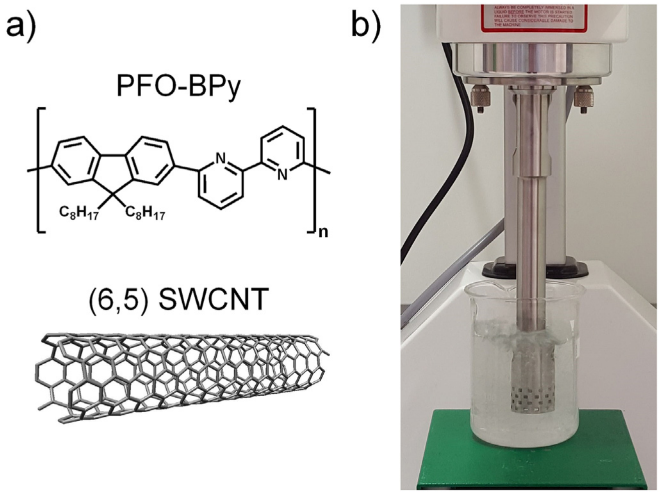

Fig. 1. (a) Molecular structure of copolymer PFO-BPy and (6,5) SWCNT. (b) Labscale shear force mixer used for dispersing large volumes of SWCNTs (cooling bath not shown). (A color version of this figure can be viewed online.)

cavitation. This is problematic because shorter nanotubes exhibit lower PLQY and, for example, in an SWCNT network field-effect transistor they necessitate more intertube charge transfers, which limits on-conductivity and effective mobility. Enrichment of the few remaining longer SWCNTs by size-exclusion chromatography, zonal fractionation or precipitation is time consuming and limited in maximum length (~1 µm) and concentration [19–21]. Second, sonication suffers from reproducibility issues and its scalability to industrially relevant quantities has not yet been shown. Other methods for the dispersion of SWCNTs include turbulent flow and mechanical force with (e.g. ball mill) or without (e.g. shear force mixer) grinding media [22]. Recently these dispersion methods have been investigated with regard to layered materials such as graphene [23] or MoS_2 [24]. The application of shear forces, for example by high speed shear force mixing (SFM) was found to be highly efficient as well as less damaging than sonication. Further, the scalability of SFM up to hundreds of liters was shown for liquid graphene exfoliation and is a well-understood industrial process for emulsions [25]. Despite its simplicity and low cost, SFM has not yet been applied for selective polymer dispersion of SWCNTs and only very rarely for the dispersion of SWCNTs in aqueous surfactant solutions [26]. This may be due to the misconception that it only yields small amounts of SWCNTs.

Here, we demonstrate that high speed SFM is suitable for large-volume, high-yield, high-quality and highly selective dispersion of carbon nanotubes by polymer wrapping using (6,5) SWCNTs as an example system. In particular, SFM yields large amounts of exceptionally long SWCNTs. These SWCNTs exhibit a considerably higher PLQY than previously reported ensemble averages, thus confirming the high quality of the shear force dispersed SWCNTs. Furthermore, for the first time for SWCNTs, the absolute PLQYs were measured directly and without any reference emitter for low and high concentrations. We compare these PLQY values with those of SWCNTs dispersed by different sonication methods and confirm the superior properties of shear-force mixed SWCNT dispersions.

2. Experimental

2.1. SWCNT dispersion and recycling

All (6,5) SWCNT dispersions were prepared from the same CoMoCAT® raw material (Sigma Aldrich 773735, Lot #14J017A1). According to the supplier, this CoMoCAT material has a maximum carbon content of 95%, of which 93% are SWCNTs. 40% of the nanotubes are (6,5) SWCNTs resulting in a total of ~35 wt% of the raw material. For polymer-wrapping with SFM, 0.5 g/L PFO-BPy (American Dye Source, $M_W = 34$ kg/mol) were dissolved in 140 mL toluene before adding 0.38 g/L CoMoCAT raw material. Hence, a maximum of 17 mg (6,5) SWCNTs was in the initial dispersion. SFM using a Silverson L5M-A mixer was then applied at maximum speed (10,230 rpm) for a given time. The temperature was kept constant at 20 °C with a cooling bath. The dispersion step was followed by centrifugation at 60,000 g (Beckman Coulter Avanti J26XP centrifuge) for 45 min with an intermediate supernatant extraction and centrifuge tube exchange after 15 min. For SWCNT recycling the pellet obtained after centrifugation and supernatant extraction was reused instead of raw CoMoCAT material. Fresh toluene (140 mL) and polymer (0.5 g/L) were added to the pelletized nanotubes and SFM was repeated.

For comparison, 10 mL (20 mL) of toluene with 2 g/L (0.5 g/L) PFO-BPy and 1.5 g/L (0.38 g/L) CoMoCAT were used for dispersions employing bath (tip) sonication for 6 h (5.5 h). During the treatment with the ultrasonic bath (Bandelin Sonorex Digitec DT 102 H) or the tip sonicator (Sonics Vibra Cell, pulsed mode at 20% power output) the temperature was kept constant at 20 °C. Again, the dispersion step was followed by centrifugation at 60,000 g for 45 min with an intermediate supernatant extraction and centrifuge tube exchange after 15 min.

Surfactant suspended (6,5) SWCNTs were prepared from the same CoMoCAT material similar to previous work [17]. Briefly, 15 mg raw material was suspended in 2 wt% aqueous sodium dodecyl sulfate (SDS, Merck) solution by tip sonication (Weber Ultrasonics, 35 kHz, 500 W, in continuous mode at ~20% power output) for 1 h at 15 °C. After sonication, the suspension was centrifuged at 100,000 g for 1 h and carefully decanted. Due to the high affinity of (6,5) to the Sephacryl-S200 gel (Amersham Biosciences) at 1.6 wt% SDS the concentration was adjusted by addition of water before being applied to a gel column in a one-column approach. 1 wt% sodium cholate (Sigma Aldrich) was used as the eluent. DGU was performed in a 1 wt % sodium cholate solution with a stepped density gradient of Iodixanol (from bottom to top of the centrifuge tube) 40 wt%/30 wt% + (6,5) SWCNTs/20 wt %.

2.2. Length measurements

The length distribution of the dispersed SWCNTs was determined by recording tapping-mode atomic force microscopy (AFM) images (Bruker Dimension Icon) of well-separated SWCNTs on a polished silicon wafer. Dispersions were directly spin-coated onto the wafer and residual polymer or surfactant was washed off with THF. The lengths of more than 200 nanotubes per sample were analyzed.

2.3. Optical characterization

Absorption spectra were recorded with a Varian Cary 6000i spectrometer with an optical path length of 10 mm. For photoluminescence excitation-emission (PLE) maps of the SWCNT dispersion the spectrally separated output of a WhiteLase SC400 supercontinuum laser source (Fianium Ltd.) was used for excitation and spectra were recorded with an Acton SpectraPro SP2358 (grating 150 lines/mm) spectrometer with an OMA-V InGaAs line camera (Princeton Instruments) and corrected for background and wavelength-dependent sensitivity/excitation power.