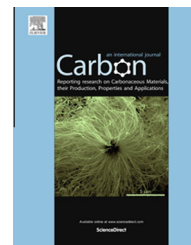


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# Overcoming the quality–quantity tradeoff in dispersion and printing of carbon nanotubes by a repetitive dispersion–extraction process



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## ABSTRACT

Dispersion–printing processes are essential for the fabrication of various devices using carbon nanotubes (CNTs). Insufficient dispersion results in CNT aggregates, while excessive dispersion results in the shortening of individual CNTs. To overcome this tradeoff, we propose here a repetitive dispersion–extraction process for CNTs. Long-duration ultrasonication (for 100 min) produced an aqueous dispersion of CNTs with sodium dodecylbenzene sulfonate with a high yield of 64%, but with short CNT lengths (a few  $\mu\text{m}$ ), and poor conductivity in the printed films ( $\sim 450 \text{ S cm}^{-1}$ ). Short-duration ultrasonication (for 3 min) yielded a CNT dispersion with a very small yield of 2.4%, but with long CNTs (up to 20–40  $\mu\text{m}$ ), and improved conductivity in the printed films ( $2200 \text{ S cm}^{-1}$ ). The remaining sediment was used for the next cycle after the addition of the surfactant solution. 90% of the CNT aggregates were converted into conductive CNT films within 13 cycles (i.e., within 39 min), demonstrating the improved conductivity and reduced energy/time requirements for ultrasonication. CNT lines with conductivities of  $1400\text{--}2300 \text{ S cm}^{-1}$  without doping and sub- $100 \mu\text{m}$  width, and uniform CNT films with 80% optical transmittance and  $50 \Omega/\text{sq}$  sheet resistance with nitric acid doping were obtained on polyethylene terephthalate films.

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## 1. Introduction

Carbon nanotubes (CNTs) have a unique one-dimensional nanostructure, and characteristic properties including a high specific surface area, high electrical conductivity and carrier mobility, high tensile strength and mechanical flexibility, and high chemical and thermal stabilities; these properties

make them attractive for various applications, including flexible electronics [1–4], and batteries/capacitors [5–8]. Individual CNTs display these highly desirable properties to their maximum extent; in contrast, ensembles of CNTs typically show significantly inferior properties, due to the junctions between the CNTs [9–11]. The dry printing process—in which aerosols of single-wall CNTs (SWCNTs) synthesized via floating-

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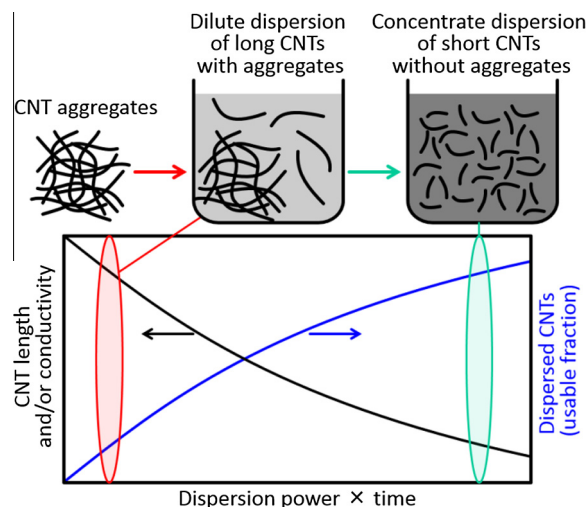
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catalyst chemical vapor deposition (CVD) are directly captured by membrane filters, or deposited on plastic films—is a smart approach for the production of high-quality SWCNT films without any damage or contamination [12–15]. Very high performances of 84 and 86  $\Omega/\text{sq}$  at 90% optical transmittance (at 550 nm, excluding the absorption by the base films) were reported for transparent conductive films (TCFs) made using this method after doping with  $\text{NO}_2$  and  $\text{AuCl}_3$ , respectively [13,14]. On the other hand, the wet printing process is advantageous in terms of its scalability and its applicability to CNT aggregates produced using any method [16–21]; however, wet printing methods sometimes result in damage and contamination of the CNTs during the process of dispersing the CNTs in liquids. Chlorosulfonic superacid can be used to dissolve SWCNTs without the application of any external forces to the solution (using methods such as ultrasonication), yielding superior performances of 60  $\Omega/\text{sq}$  at 90.9% optical transmittance (excluding the absorption by the base film); this high performance is due to the absence of any damage resulting from ultrasonication, the absence of any surfactant residue in the films, and the high degree of p-type doping by the superacid [16]. However, water-based solution methods are much more popular, because of the safety of the processing and materials used [17–21].

Extensive research efforts have been dedicated to the investigation of milder dispersions of CNTs, and the printing of more conductive CNT films [17–21]. CNTs are often dispersed in water using ultrasonication, and the use of various dispersants, including Triton-X [17,18], sodium dodecyl sulfate (SDS) [19,20], sodium cholate (SC) [20,21], and sodium dodecylbenzene sulfonate (SDBS) [20], has been investigated. Encouraging values have been reported for TCFs made using SWCNTs doped with nitric acid; a sheet resistance of 30  $\Omega/\text{sq}$  was achieved at >70% optical transmittance for SWCNT films prepared on quartz glass substrates using vacuum filtration and transfer [16], and sheet resistances of 70 and 69  $\Omega/\text{sq}$  were achieved at 80% optical transmittance for SWCNT films prepared on polyethylene terephthalate (PET) films using spray coating [19,20]. However, such films are often made using some fraction of the SWCNTs remaining in the supernatant after the centrifugation of mildly dispersed SWCNTs. Significant amounts of expensive SWCNTs ( $\sim 1000 \text{ USD g}^{-1}$ ) are thus wasted; this is a crucial issue that must be solved to achieve practical, inexpensive CNT devices.

In this work, we propose a repetitive dispersion–extraction process to overcome this quality–quantity tradeoff (Fig. 1). CNTs were mildly dispersed and centrifuged, and the supernatant was used to make CNT films. The sediment was then reused (with the addition of a surfactant solution) and mildly dispersed in the next cycle. To examine in detail the effects of changing the dispersion time, the experiments were performed using a batch process. Almost complete conversion ( $\sim 90\%$ ) of the as-produced CNT aggregates to CNT lines with attractive properties (conductivities of  $\sim 2000 \text{ S cm}^{-1}$  without doping, and sub-100  $\mu\text{m}$  line width) was realized via vacuum filtration of the dispersions on membrane filters with a metal mask [12,13], and subsequent transfer to PET films. Encouraging properties of 105 and 50  $\Omega/\text{sq}$  (without and with nitric acid doping, respectively) with 80% optical



**Fig. 1 – Schematic illustrating the quality–quantity tradeoff inherent in the dispersion of CNTs. (A color version of this figure can be viewed online.)**

transmittance (at 550 nm, excluding the absorption by the base film) were realized for the uniform CNT-TCFs on PET films.

## 2. Experimental

### 2.1. Repetitive process for the dispersion and extraction of CNTs, and evaluation of their dispersion state

The repetitive CNT dispersion–extraction process is illustrated schematically in Fig. 2. As-produced CNTs synthesized via floating-catalyst CVD, the so-called eDIPS method [22] (MEIJO eDIPS, EC grade; Meijo Nano Carbon Co., Ltd., Nagoya, Japan), were used in this work without any purification. The CNTs had a carbon purity of  $\sim 98 \text{ wt}\%$ , determined by X-ray fluorescence spectroscopy (XRF; Rigaku ZSX Primus 2, Akishima, Japan), and the number of walls and diameter varied from one to three and around 1 to 3 nm, respectively, observed by transmission electron microscope (TEM; JEM-2100F; JEOL, Akishima, Japan) (see [Supplementary data, Table S1 and Fig. S1](#)). 100 mg of SDBS (Sigma Aldrich, St. Louis, MO, USA) was dissolved in 20 mL of deionized water held in a 50 mL glass bottle. The as-received CNT aggregates were torn into small pieces using tweezers, and 2 mg of the aggregates was added to the bottle (Fig. 2a). The bottle was then placed in a bath-type sonicator (VS-50R, VELVO-CLEAR, Tokyo, Japan) and sonicated at 30 W and 45 kHz for various times of 3, 10, 30, and 100 min, with the sample solution undergoing convection in the bottle (Fig. 2b). After sonication, the sample in the bottle was centrifuged at 3500 rpm for 20–30 min (Fig. 2c). 15 mL of the supernatant was used to make the CNT films (Fig. 2d), while 5 mL of the sediment was used for the next cycle, after the addition of 15 mL of a 0.5 wt% aqueous solution of SDBS (Fig. 2a). This cycle was repeated until the CNTs were dispersed almost completely ( $\sim 90\%$ ). The concentration of CNTs in the supernatant was determined by measuring the optical absorbance at 550 nm, using ultraviolet–visible spectrophotometry (UV–vis; V-630,

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