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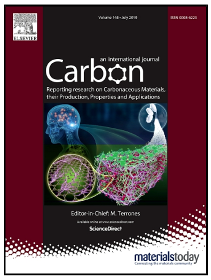

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Direct injection of SWCNTs into liquid after supercritical nitrogen treatment

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Abstract:

We developed a novel robust technique to produce high-quality dispersions of debundled SWCNTs in aqueous solutions. Direct injection of SWCNTs treated with supercritical nitrogen into the aqueous surfactant solution facilitates the dispersion process without the need of extensive ultrasonication. According to photoluminescence and absorbance measurements, the mild ultrasonic treatment of such dispersions resulted in a higher yield of individual SWCNTs, compared to pristine tubes and tubes collected after the supercritical treatment in the form of powder.

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High quality SWCNT dispersions, containing either individual tubes or small bundles, are of a great importance for many technological applications, including biosensors, optical devices and conductive films [1]. However, strong van der Waals interaction between tubes together with their large surface area and high aspect ratio force SWCNTs to form bundles to minimize their free surface energy [2, 3, 4]. Several techniques are used to prepare homogeneous dispersions of SWCNTs in aqueous solutions. They are based on covalent and noncovalent modification of SWCNTs, respectively including partial oxidation by strong inorganic acids and surface coverage with surfactants or polymers. [5]. Partial oxidation of SWCNTs results in the formation of various functional groups (hydroxyl, carboxyl, *etc.*), which stabilize SWCNT aqueous dispersions [5]. However, this approach leads to substantial alteration of SWCNT electronic properties, which are vital for the majority of applications. To preserve intact SWCNT structures and electronic properties, various surfactants can be used to cover the tube surface and thereby to protect the tubes from agglomeration [3, 4, 6]. However, to get high quality SWCNT dispersions by separating bundles into individual tubes, detrimental ultrasonication process is required [7].

Here we propose a novel technique to improve dispersion of SWCNTs in aqueous media by direct injection of SWCNTs treated in supercritical nitrogen into aqueous surfactant solution. Exfoliation of SWCNT bundles is caused by rapid expansion of supercritical nitrogen intercalated inside the bundles [8]. The tubes after the supercritical conditions immediately enter the solution are covered by the surfactant before they form bundles. This technique significantly decreases the time necessary for dispersion of SWCNTs from powder, increases the yield of debundled nanotubes in aqueous dispersions and decreases their damage in comparison to prolonged ultrasonication.

In our study, we utilized the as-received HiPco SWCNTs (NoPo Nanotechnologies India Private Ltd.). For the supercritical treatment, we used a home-built system consisting of a high-pressure Supercritical 24 pump (SSI, PA, USA), a 25 ml stainless steel high-pressure chamber (Waters Corp, MA, USA) equipped with an electrical heating jacket (Industrial systems, Smolensk, Russia), a wide-bore ball valve (Hy-Lok, Busan, South Korea) and a 500 ml stainless steel collection chamber (Waters Corp, MA, USA). 50 mg of SWCNTs were placed into the high-pressure chamber and exposed to supercritical nitrogen conditions (40°C and 150 atm. for 30 minutes). Then, the pressure was released in less than a second by opening the wide-bore bottom valve. The flow from the chamber was directed either to an empty stainless-steel chamber (dry spraying method) or to 2% sodium dodecyl sulfate (SDS, ≥ 98.5% chemical grade) 100 ml water solution (direct injection method) as shown in Fig. 1. After the nanotube flow was released to the collection chamber, we observed the pressure increase from the atmospheric one to 7 and 10 bar for the dry spraying and direct injection method, respectively.

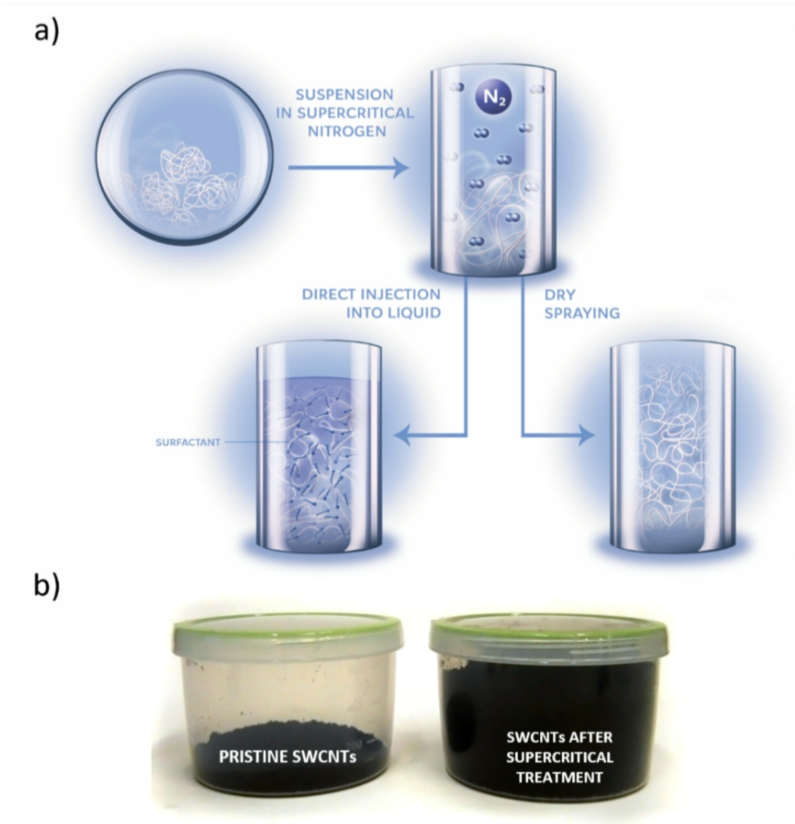

Figure 1. a) Schematic diagram of two methods: direct injection into liquid, leading to the formation of the SWCNT dispersion, and dry spraying method, resulting in the loose

SWCNT powder; b) a photograph of SWCNT powders of the same amount (2 g) before and after supercritical nitrogen treatment.

The comparison of Raman spectra of the as-received (pristine) SWCNTs and dry sprayed SWCNT powder did not reveal any significant changes in the structure due to the supercritical treatment (Fig. 2). All spectra demonstrate relatively low D and high G band intensities with the I_G/I_D intensity ratio of 7.4 for pristine SWCNTs and 6.8 for the nanotubes treated at the supercritical conditions.

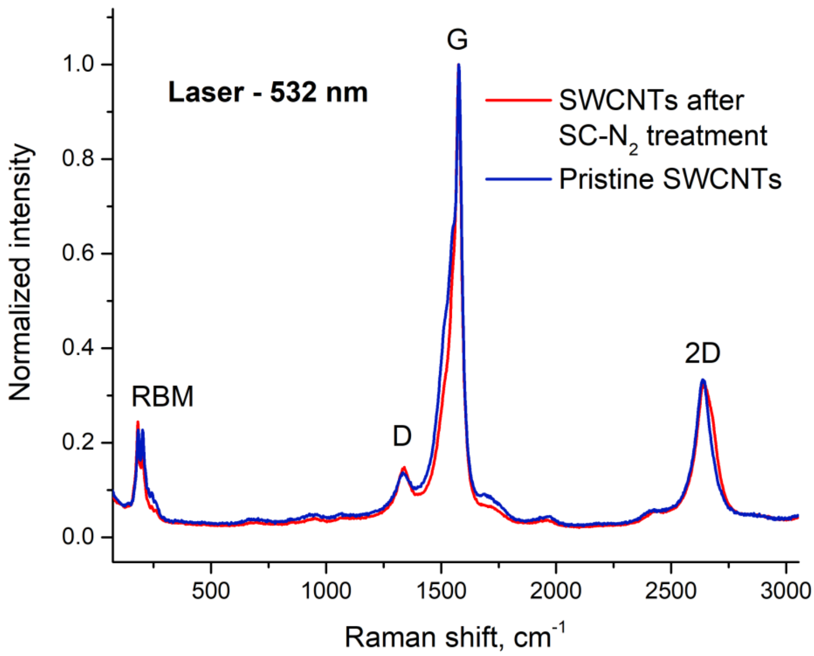

Figure 2. Raman spectra of pristine SWCNTs and tubes after the supercritical nitrogen treatment (a dry spraying method).

A spectrum of SWCNT dispersion obtained immediately after the direct injection into the SDS solvent (Perkin-Elmer Lambda 1050 spectrometer) does not reveal the features corresponding to individual tubes [9] and was not stable over time. Therefore, we performed ultrasonic treatment using Branson 450 horn sonicator with a power of 80 (20%) and 120 W (30%) from 1 to 3 hours at the frequency of 20 kHz (Fig. 3a). It was found that the sonication at 80 W for 1 hour was not enough to get a good dispersion, whereas 3 hours ultrasound treatment at any power was difficult to maintain due to the increased foam formation. 120 W for 2 hours in a continuous regime resulted in a good dispersion of the SWCNTs according to optical absorption spectra and was selected as an optimal condition for further studies. It is worth mentioning that we deliberately avoided centrifugation to keep the initial concentration of the SWCNTs and investigate the effect of stability of the SWCNT dispersions.

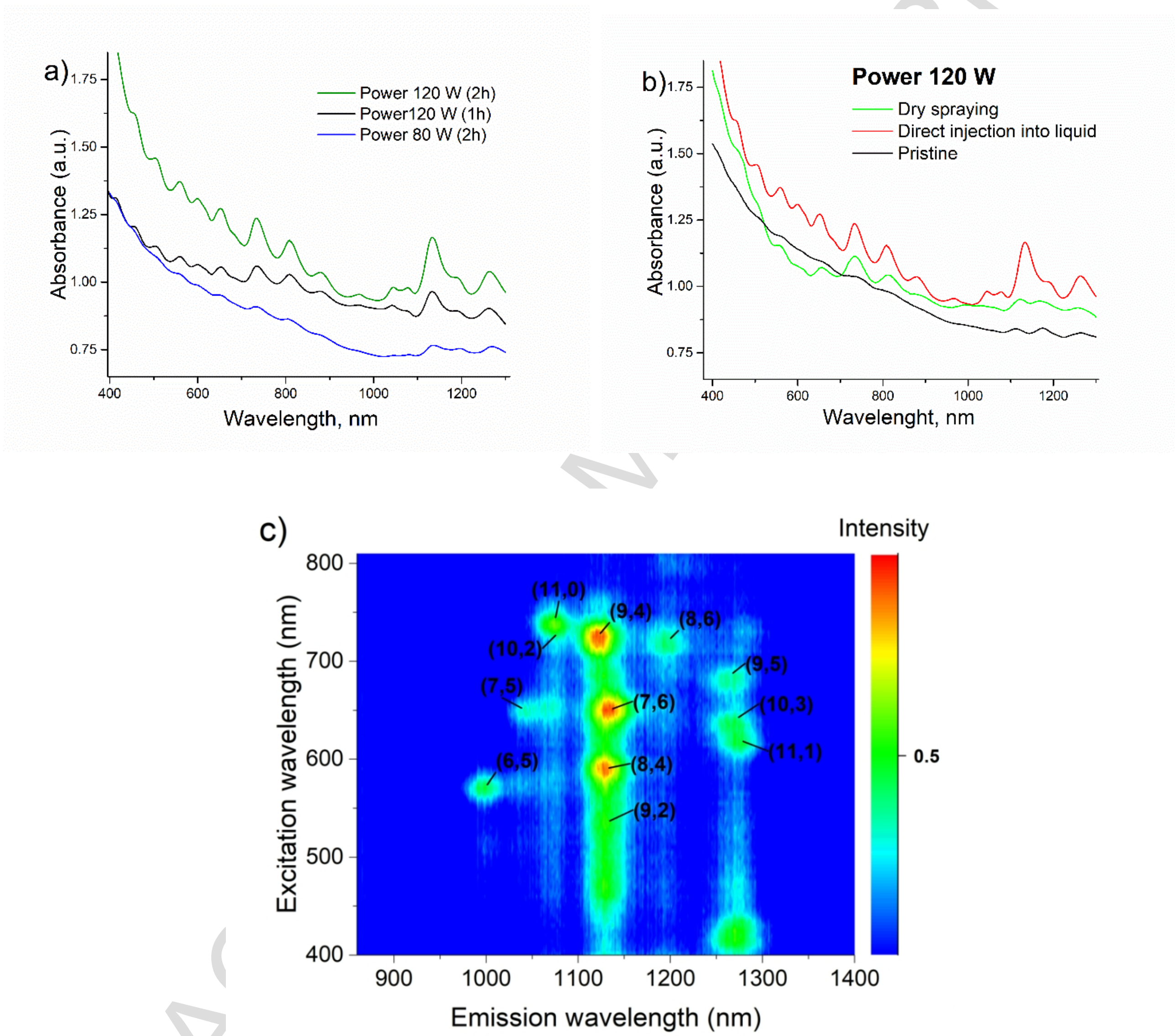

Figure 3. Absorbance spectra of a) SWCNT dispersions after direct injection and sonication at different conditions, b) dispersions obtained after sonication (120 W, 2 hours) from pristine SWCNTs, from SWCNT powder after dry spraying and after direct injection and c) PL map of the SWCNT dispersion obtained after direct injection into liquid.

To examine the influence of the supercritical treatment we compared the spectra of dispersions obtained from pristine, dry spraying sample and after the direct injection into liquid after the sonication at optimal conditions (Fig. 3b). The ultrasonication of the pristine SWCNTs did not lead to the formation of homogeneous dispersion (Fig. 3b), which furthermore was unstable in time. We observed rapid sedimentation of the SWCNT bundles after the sonication. The improved dispersion was obtained only with the novel technique of the direct injection of SWCNTs into a surfactant solution. The dry spraying method allowed us to produce the dispersion better in quality than that from the pristine tubes, however still worse than by the direct injection technique. This can be explained by a rapid bundle formation in a dry state after the spraying the SWCNTs from supercritical conditions into the powder form. The effect of the supercritical conditions can be attributed to the penetration of nitrogen fluid inside the SWCNT aggregates and deagglomeration of bundles during supercritical nitrogen suspension expansion [7].

PL measurements help to examine the quality of the SWCNT dispersions, since only individual semiconducting SWCNTs can emit light in dispersions [10]. The only dispersion, which was obtained by the direct injection of the SWCNTs into the solution, expressed high PL intensity under the investigated conditions (Fig. 3c). According to PL map (HORIBA Nanolog-4 equipped with InGaAs near-IR array detector), maximum signal was observed for individual SWCNTs with the following chiralities: (7,6), (9,4), and (8, 4). These results are in a good agreement with absorption spectra (Fig. 3b).

In summary, we proposed a novel technique of direct injection of SWCNT suspension in supercritical nitrogen into aqueous solutions of the surfactant. This technique provides high quality SWCNT dispersion (after short sonication), compared to the pristine SWCNTs or nanotube powder collected by the dry spraying method. Consequently, the supercritical nitrogen treated SWCNTs injected into a low-concentration surfactant solution exhibit enhanced debundling effect along with a formation of individual nanotubes after 2 hours sonication at 120 W power.

Conflict of Interests: The authors state that they have no conflict of interests.

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