

Sonochemical Degradation of N-Methylpyrrolidone and Its Influence on Single Walled Carbon Nanotube Dispersion

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Supporting Information

Experimental Section

Materials and instruments: Semi-purified HiPco SWNTs were purchased from Unidym™ [Carbon Nanotubes, CA90425, US (Lot no. P0261)] and used as received. HPLC and anhydrous NMP were purchased from Sigma Aldrich. NMP (HPLC grade) was used as received and anhydrous NMP was de-gassed by freeze-thaw in liquid nitrogen (x 5) before use. All sonication in this experiment was carried out with 20 ml of NMP in a 30 ml glass vial. The sonicator tip was placed into the NMP about 2 cm from the bottom of vial for each experiment in order to minimise variations in power output. Sonication was carried out with 150 W power output (20% of the total output, GEX 750 ultrasonic processor with a 5 mm titanium alloy Ti-6Al-4V microtip, SONICS & MATERIALS INC, Newtown, US). The power output of the sonic probe was tested with DI water in a polystyrene insulation set up before use. A 3 L ice bath was used for each sonication. Centrifugation was performed with L-90k Optima ultracentrifuge, Beckman Coulter with a SW41 Ti rotor at 41,000 rpm, 200,000 g, for 2 hours. The top 50 % of the supernatant was collected for analysis. A control experiment was carried out with an identical procedure but omitting the sonication (the same sonic probe was simply immersed into 20 ml of NMP for 2 hrs with a 3 L ice bath).

HiPco SWNT dispersion: HiPco SWNTs (2mg) were mixed with 20 ml of NMP in a glass vial. The same sonic probe described above was then immersed into the NMP/SWNTs mixture, cooled with an ice bath and sonicated for 2 hours. The SWNTs/NMP mixture turned into a black dispersion within 10 seconds of initial sonication. After that the dispersion was allowed to stand overnight and top fraction (ca. 12 ml) was transferred into a centrifuge tube for centrifugation. After centrifuging the dispersion at 41,000 rpm, 200,000 g, for 2 hours, the top 50 % of the supernatant was collected as a HiPco dispersion.

Atomic Force Microscopy (AFM): AFM micrographs were taken in tapping mode using a Digital Instruments Multimode VIII AFM with a Nano-scope IV controller. All AFM micrographs were recorded with a resolution of 512 lines and with a typical scanning speed of 1 Hz. All micrographs were processed using NanoScope Analysis v 1.40 (R2Sr), Bruker Corporation. 3 µL of dispersion or NMP were drop-cast onto a clean silicon wafer surface (5 x 5 mm, Agar Scientific, UK). The wafers were then dried *in vacuo* overnight at room temperature, then heated to 200 °C to aid complete removal of residual NMP prior to AFM characterization.

UV-vis spectroscopy: The UV-vis spectra were acquired using a Lambda 950 spectrophotometer (Perkin Elmer, Waltham, MA, USA) with a 1 cm path length quartz cuvette. All spectra were recorded from 250 to 800 nm with 1 nm resolution.

Thermogravimetric Analysis (TGA): TGA was carried out with Pyris 1 TGA (Perkin-Elmer). Each sample was first annealed at 200 °C under nitrogen for 60 min to ensure complete removal of residue NMP, then heated from 200 to 850 °C in either air/nitrogen with a heat rate of 10 °C/min.

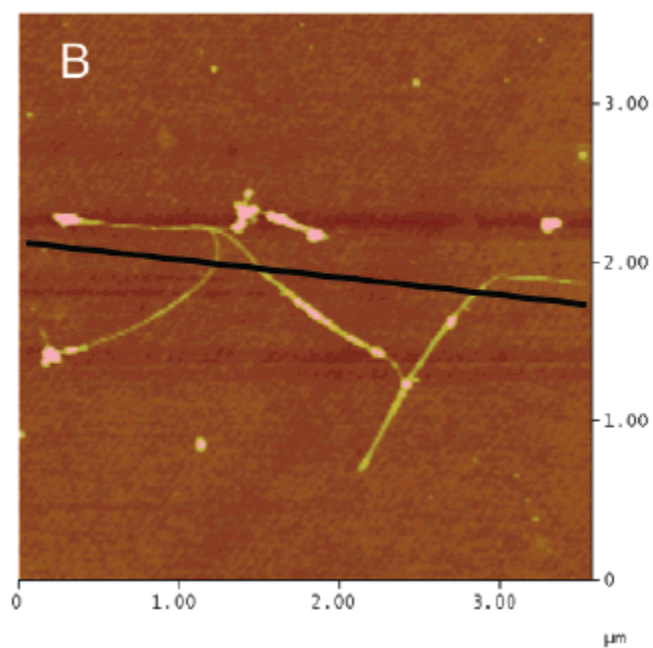


Figure S1. AFM image of SWNTs prepared from a N-methyl pyrrolidone (NMP) SWNTs dispersion.¹ (Reprinted from **ref 1** with permission from the publisher. Copyright @ 2006, American Chemical Society)

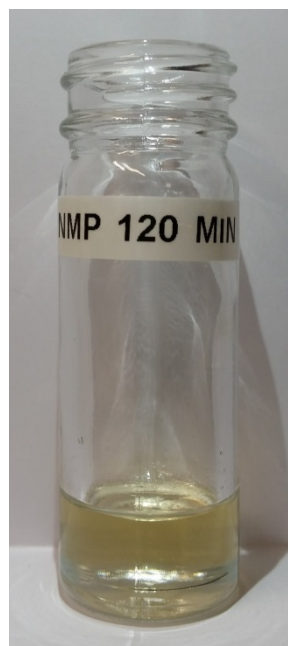


Figure S2. Photograph of anhydrous NMP sonicated for 120 min under nitrogen.

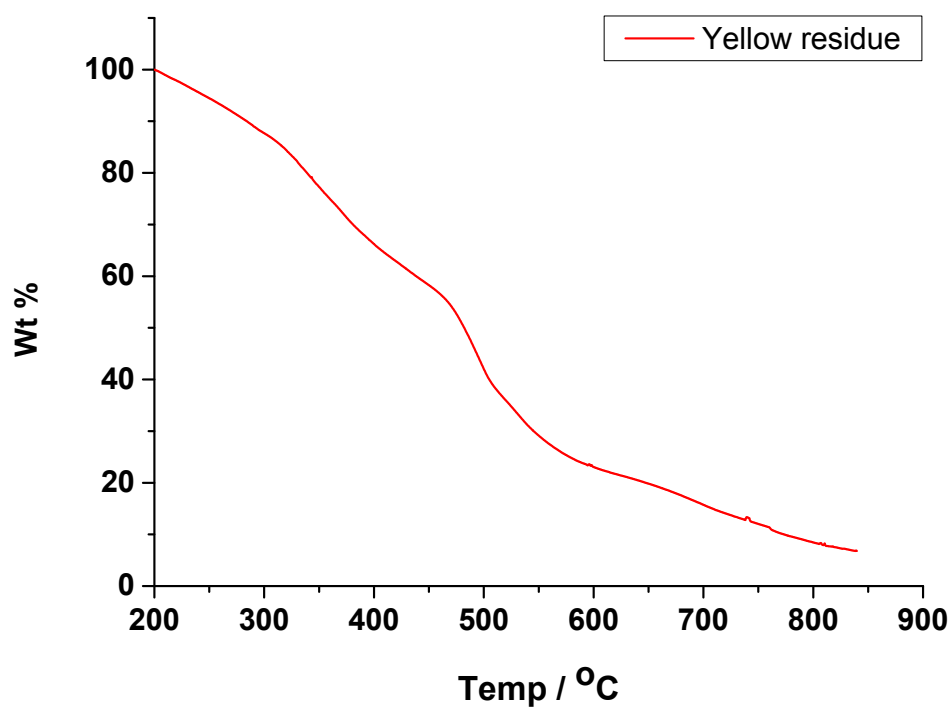


Figure S3. TGA (under air) of the yellow residue isolated from 120 min sonicated NMP.

The TGA was carried out under air and 95 % of the material combusted before 850 °C, confirming that the yellow residue is predominantly organic, rather than metal or metal oxide.

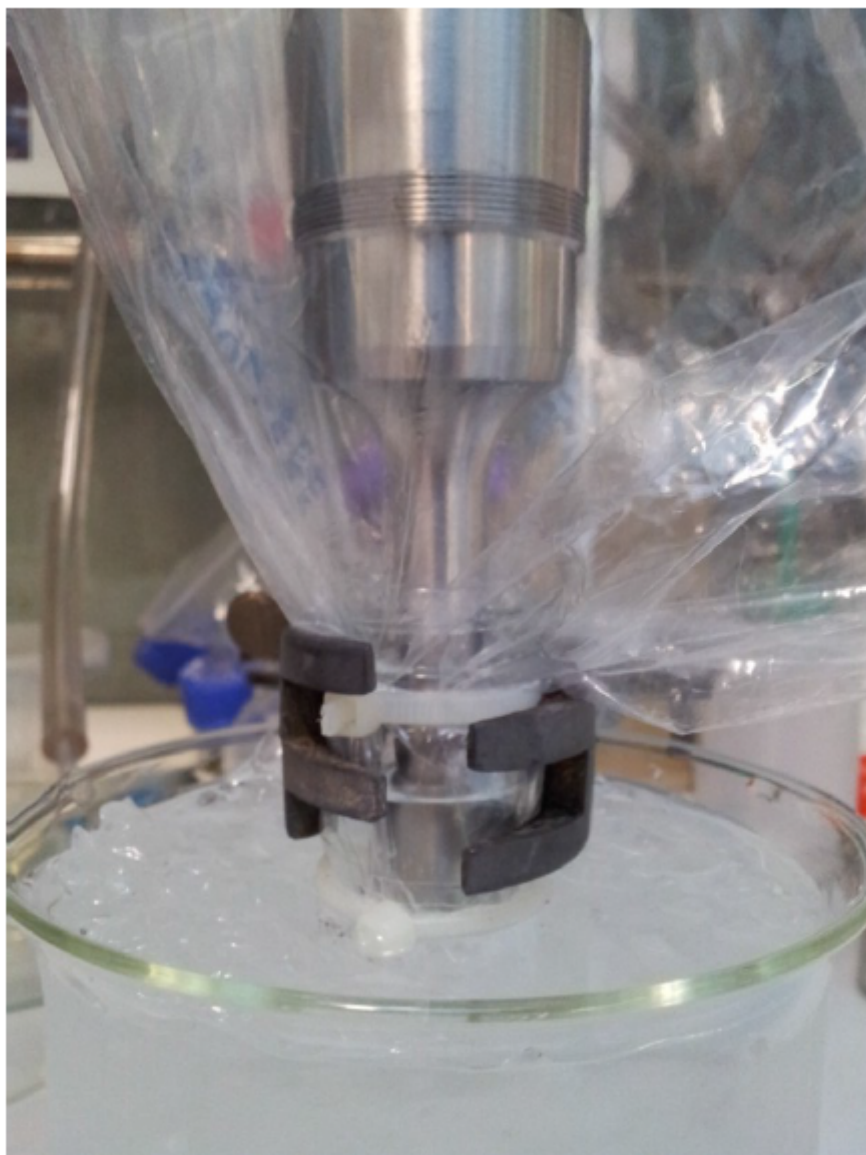


Figure S4. Photograph of the sonication set up for anhydrous NMP.

The sonication probe and the glass vial containing the anhydrous NMP was placed in a polypropylene (PP) bag which was connected to a nitrogen inlet. The ice bath was placed outside the PP bag to avoid water vapour condensing into the NMP.

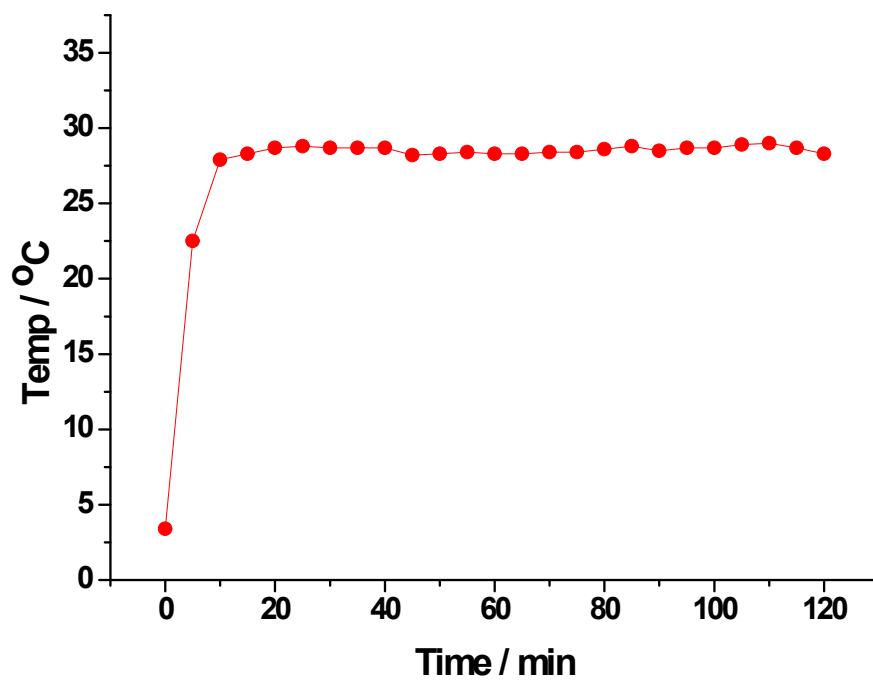


Figure S5. Temperature profile of NMP sonication (0 – 120 min)

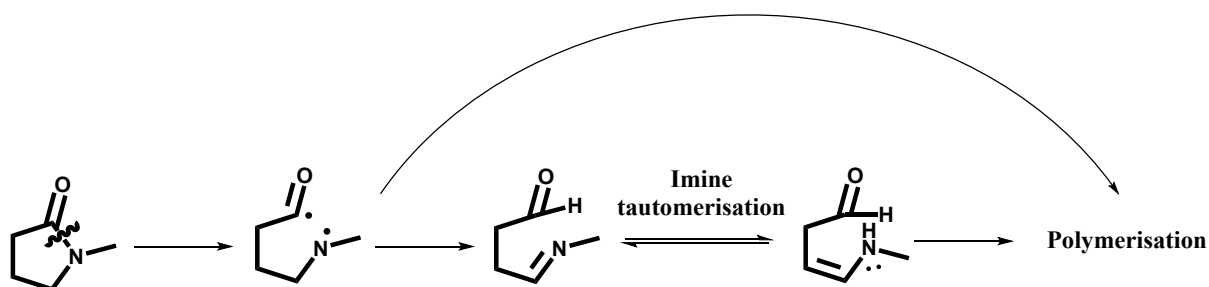
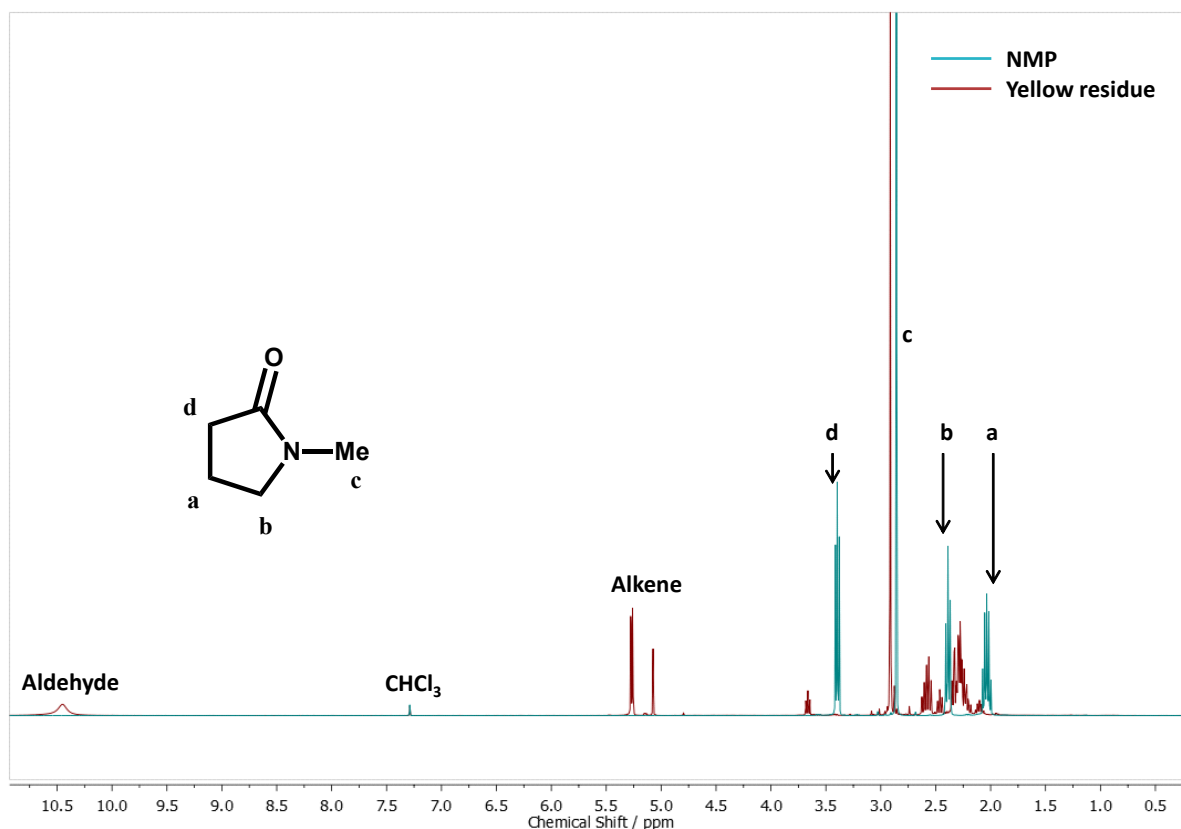


Figure S6. (top) ^1H NMR spectrum of NMP and the yellow residue isolated from NMP, NMP signals assignment from SDBS database, AIST. CDCl_3 solvent peak at 7.29 ppm. Possible newly formed aldehyde proton and alkenyl proton at 10.45 and between 5.0 – 5.5 ppm respectively. (bottom) Possible NMP sonochemical degradation pathway. Since ^1H NMR confirmed the present of aldehyde in the NMP degradation product/polymer, the only possible bond to cleave in the lactam ring sonochemically is, therefore, the amide linkage, to give two neutral radicals on carbonyl and amine. The signal at 5.0 – 5.5 ppm in the ^1H NMP spectrum suggests the present of alkene, therefore, the ring-opened NMP may rearrange via proton transfer to form aldehyde and imine (which can then undergo imine tautomerisation² to form enamine -N=C=C-). The radical reaction intermediate and the rearranged imine/enamine can both self polymerise or co-polymerise to give a complex, possibly cross-linked structure. The appearance of a possible N-H bond and the shift in the carbonyl stretch, in the FTIR data, are consistent with this suggestion.

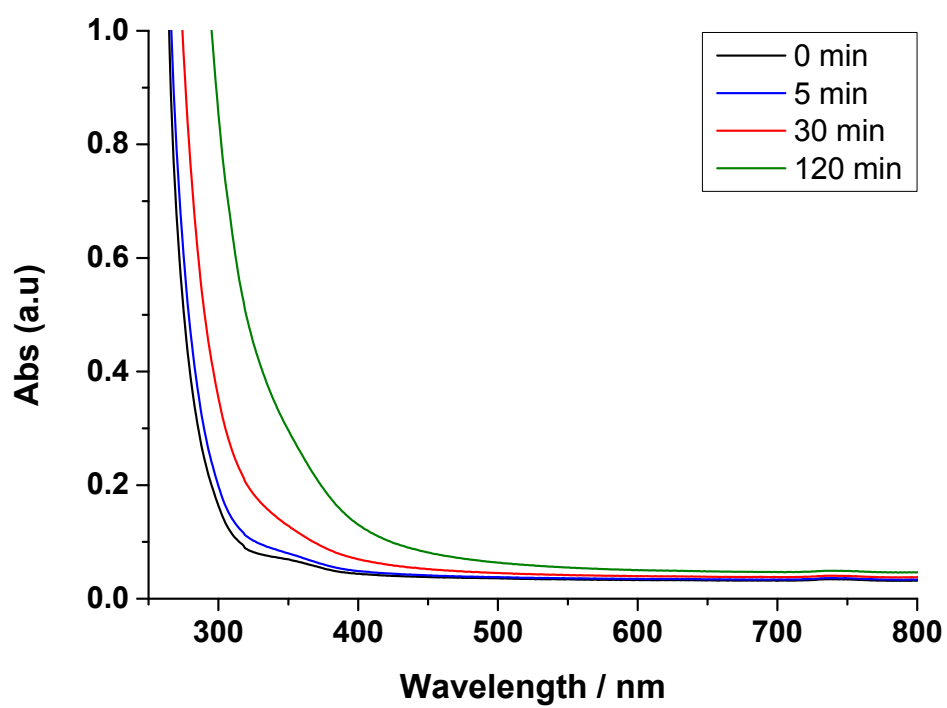


Figure S7. UV-vis spectra of NMPs with increasing sonication time (0, 5, 30 & 120 min)

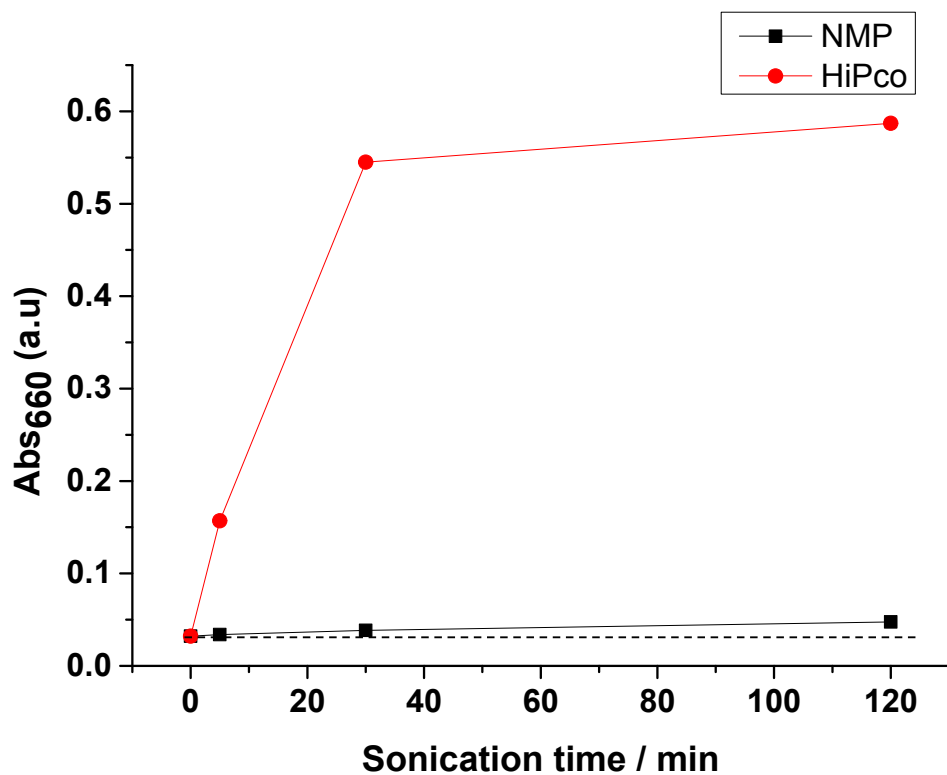


Figure S8. Optical absorbance at 660 nm (Abs_{660}) of sonicated NMP and HiPco SWNT dispersions with sonication time from 0 to 120 min. Dotted line denotes a constant solvent background for NMP SWNT dispersions, as commonly used in the literature.

Reference

1. S. Giordani, S. D. Bergin, V. Nicolosi, S. Lebedkin, M. M. Kappes, W. J. Blau and J. N. Coleman, *The journal of physical chemistry B*, 2006, 110, 15708-15718.
2. R. A. Clark and D. C. Parker, *Journal of the American Chemical Society*, 1971, 93, 7257-7261.