Supporting Information

Adverse effect of PTFE stir bars on the covalent functionalization of carbon and boron nitride nanotubes using Billups-Birch reduction conditions

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Scheme S1. Functionalization reactions for multi-walled BNNTs and single-wall CNTs that were stirred with either a glass stir bar (gf) or a PTFE stir bar (Tf). Similar reactions were carried out to produce control experiments, where 1-bromododecane was not added; such reactions produced controls stirred with a glass stir bar (gc) or stirred with a PTFE stir bar (Tc).

Figure S1. On the left: PTFE stir bars after being used in the Billups-Birch reaction. On the right: an unused PTFE stir bar.
Figure S2. DTG curves for gf-CNTs and Tf-CNTs.

Figure S3. XPS survey scan of pristine CNTs, PTFE-stirred functionalized CNTs (Tf-CNTs), and glass-stirred functionalized CNTs (gf-CNTs).
Table S1. Detailed information on the binding energies within the C1s peak for each CNTs sample.

| Sample | Binding Energy (eV) | FHWM | Percent area (%) |
|--------|---------------------|------|------------------|
| CNTs   | C=C 284.65          | 0.98 | 61.24            |
|        | C-C 285.57          | 0.97 | 9.05             |
|        | C-O 286.71          | 2.07 | 14.58            |
|        | C=O 288.89          | 1.70 | 6.12             |
|        | π-π* 291.02         | 2.36 | 9.01             |
| gf-CNTs| C=C 284.62          | 1.08 | 69.98            |
|        | C-C 285.59          | 1.11 | 11.88            |
|        | C-O 286.73          | 1.47 | 7.82             |
|        | C=O 288.20          | 1.71 | 4.51             |
|        | π-π* 290.62         | 2.19 | 5.81             |
| Tf-CNTs| C=C 284.55          | 1.08 | 62.83            |
|        | C-C 285.61          | 1.18 | 16.76            |
|        | C-O 286.88          | 0.98 | 3.90             |
|        | C=O 288.06          | 1.09 | 3.56             |
|        | C-F₂ 289.55         | 1.53 | 10.15            |
|        | π-π* 290.60         | 1.96 | 2.80             |

STATISTICAL RAMAN SPECTROSCOPY

This statistical approach to CNTs functionalization was first published by Hirsch and co-workers.\(^1\)

The Raman defect index (RDI) provides information on the mean degree of functionalization by calculating the length of the vector from the origin to the intersection between \(x_c^{532}\) and \(x_c^{785}\) [Eq. (1)].

\[
RDI = \sqrt{(x_c^{785})^2 + (x_c^{532})^2} \quad (Eq. 1)
\]

Where \(x_c^{532}\) and \(x_c^{785}\) are the maxima of the Gaussian peak fitted to the histogram while exciting the CNTs samples at 532 nm and 785 nm, respectively.

The Raman homogeneity index (RHI) is calculated as the reciprocal product of the width of each Gaussian, \(w^{532}\) and \(w^{785}\).

Figure S4. Histograms resulting from the Raman mapping showing the D/G ratio at 532 nm and 785 nm excitation for pristine CNTs, glass-stirred control CNTs (gc-CNTs), and PTFE-stirred control CNTs (Tc-CNTs).
Figure S5. (a) FTIR, (b) TGA, and (c) statistical Raman spectroscopy of pristine CNTs, glass stirred control CNTs with additional PTFE (gc-CNTs+PTFE), and glass stirred functionalized CNTs with additional PTFE (gf-CNTs+PTFE).
Figure S6. BNNTs powders obtained after reaction, work-up and drying where it is clear that those that were in contact with PTFE during the reductive conditions became darker.

Figure S7. XPS survey scan of pristine BNNTs, glass-stirred functionalized BNNTs (gf-BNNTs), and PTFE-stirred functionalized BNNTs (Tf-BNNTs).
Table S2. Detailed information on the binding energies within the B1s, N1, and C1s peaks for each BNNTs sample.

|       | Binding Energy (eV) | FWHM | Percent area (%) |
|-------|---------------------|------|------------------|
| BNNTs | B1s                 |      |                  |
|       | B-C                 | -    | -                |
|       | B-N                 | 190.6| 1.58             | 91.29             |
|       | B-O                 | 192.09| 1.32          | 8.71              |
|       | N-B                 | 398.43| 1.60         | 86.23             |
|       | N-C/N-O             | 399.69| 1.66         | 13.77             |
|       | C1s                 |      |                  |
|       | C-B                 | -    | -                |
|       | C-C                 | 284.86| 1.30        | 84.06             |
|       | C-O                 | 285.87| 1.40        | 12.84             |
|       | C=O                 | 288.51| 1.36        | 3.10              |
| gf-BNNTs| B1s              |      |                  |
|       | B-C                 | 189.99| 1.21         | 13.68             |
|       | B-N                 | 190.64| 1.60         | 77.01             |
|       | B-O                 | 192.17| 1.37         | 9.31              |
|       | N1s                 |      |                  |
|       | N-B                 | 398.31| 1.60         | 90.54             |
|       | N-C/N-O             | 399.68| 1.69         | 9.46              |
|       | C1s                 |      |                  |
|       | C-B                 | 284.06| 1.32         | 5.61              |
|       | C-C                 | 284.81| 1.30         | 83.35             |
|       | C-O                 | 285.99| 1.35         | 11.04             |
| Tf-BNNTs| B1s               |      |                  |
|       | B-C                 | 190.08| 1.29         | 4.91              |
|       | B-N                 | 190.77| 1.55         | 81.67             |
|       | B-O                 | 192.10| 1.50         | 13.42             |
|       | N1s                 |      |                  |
|       | N-B                 | 398.35| 1.65         | 87.36             |
|       | N-C/N-O             | 399.68| 1.79         | 12.64             |
|       | C1s                 |      |                  |
|       | C-B                 | 283.82| 1.12         | 7.55              |
|       | C-C                 | 284.27| 1.48         | 77.50             |
|       | C-O                 | 286.27| 1.83         | 14.95             |
Figure S8. Region in the B1s that corresponds to the π-π* shake-up satellite attributed to sp² hybridization for pristine BNNTs, glass-stirred functionalized BNNTs (gf-BNNTs), and PTFE-stirred functionalized BNNTs (Tf-BNNTs). The B-N peak at 190.6 eV of each sample was normalized to the same intensity so that the intensities of these satellites were comparable.

References

1. Hof, F.; Bosch, S.; Englert Jan, M.; Hauke, F.; Hirsch, A., Statistical Raman Spectroscopy: A Method for the Characterization of Covalently Functionalized Single-Walled Carbon Nanotubes. Angew. Chem. Int. Ed 2012, 51 (47), 11727-11730.