

Electron-Transfer Reduction of Cup-Stacked Carbon Nanotubes Affording Cup-Shaped Carbons with Controlled Diameter and Size

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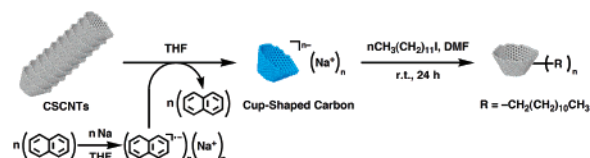
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Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991,¹ considerable efforts have been devoted to exploring potential applications of this promising material.^{2,3} Critical for the practical realization of applications is the control of CNTs' diameter and size in an integrated device. However, it still remains a significant challenge to control the diameter and size of CNTs.^{4,5} In this context, the cup-stacked carbon nanotubes (CSCNTs) consisting of truncated conical graphene layers have merited special attention.⁶ The cup-stacked structure provides a hollow tubular morphology, composed of cup-shaped carbon units with diameters ranging from 50 to 150 nm and lengths of up to 200 μm ,⁶ in contrast with conventional carbon nanotubes made up of seamless cylinders of hexagonal carbon network. In addition, the availability of reactive edges on the outer and inner surface of cup-shaped carbons to chemical functionalization or surface modification will open up new ways to utilize them in electronic, catalytic, and photovoltaic applications.^{7,8} The ball milling processes are reported to result in a decrease in the average lengths of pristine CSCNTs (up to 200 μm) into 7 μm after 24 h milling.⁹ However, individual cup-shaped carbons with the controlled diameter and size have yet to be obtained.

We report herein that the electron-transfer reduction of CSCNTs with sodium naphthalenide and the subsequent treatment with 1-iodododecane results in electrostatically destacking CSCNTs to afford individual cup-shaped carbons with controlled diameter and size, as shown in Scheme 1.¹⁰

The CSCNTs used in the present study were a gift from GSI Creos Corporation, Japan. They were purified according to the previously reported procedure.¹¹ The CSCNTs with larger diameter (ca. >50 nm) were removed as follows: Purified CSCNTs were suspended in CHCl_3 (5 mg/mL, 10 mL) by mild sonication (i.e., 70 W for 15 min). After centrifugation for 15 min at 1880g, the supernatant was filtered over a PTFE membrane (pore size = 0.1 μm).¹² Sodium naphthalenide¹³ in tetrahydrofuran (THF) was poured over CSCNTs (50 mg) and stirred overnight at room temperature under inert atmosphere. The mixture was filtered over a PTFE membrane (pore size = 0.1 μm) and washed repeatedly with distilled THF until it remained colorless. The residual solid was dried in vacuum at 100 $^\circ\text{C}$ for 24 h. The progress of electron transfer from naphthalene radical anion to CSCNTs was easily detected by monitoring the UV-vis-NIR absorption spectrum (Figure S2). The absorption band around 500–900 nm due to the naphthalene radical anion completely disappeared after reduction of CSCNTs with sodium naphthalenide. We have also examined the *solid-state* electron spin resonance (ESR) spectra of pristine and reduced CSCNTs to confirm the reduction of CSCNTs by sodium naphthalenide (Figure S3). The pristine CSCNTs were ESR silent at 298 K. This indicates no impurity in the CSCNTs sample. In contrast, reduced CSCNTs exhibit a broad signal at 298 K together with a sharp signal ($g = 2.0025$) which is virtually the same as

Scheme 1



that observed in K-doped graphite ($g = 2.0027$).¹⁴ The broad ESR signal and its small g value as compared to the free spin value (2.0023) are diagnostic of the delocalized electron on the carbon nanomaterials.¹⁵

The reduced CSCNTs were treated with 1-iodododecane to obtain dodecylated CSCNTs as follows: 1-Iodododecane (2 mL) and the reduced CSCNTs were mixed in deaerated DMF under inert atmosphere using a glovebox. The reaction mixture was stirred overnight at room temperature. The suspension was filtered over PTFE membrane (pore size = 0.1 μm) and washed with hexane and methanol. The residual solid was dried at room temperature. The comparison of the IR spectra of CSCNTs before and after the reactions with sodium naphthalenide and the subsequent treatment with 1-iodododecane revealed the attachment of the dodecyl groups to CSCNTs after the reaction with 1-iodododecane, that is, C–H vibrations of the attached dodecyl groups [$\nu(\text{C–H})$: 2918 and 2850 cm^{-1}] (Figure S4).¹⁶ In addition, the elemental analysis afforded a chemical formula of $\text{C}_{161}(\text{C}_{12}\text{H}_{25}) \cdot 0.3(\text{C}_3\text{H}_7\text{NO})$, and this indicates that one dodecyl group is attached per 161 carbon atoms.¹⁷

The scanning electron microscopy (SEM) images of pristine CSCNTs,¹⁸ reduced CSCNTs, and dodecylated CSCNTs revealed that the stacked structure of pristine CSCNTs with micrometer scale (Figure 1a) were disassembled after reduction with the naphthalene radical anion to form individual cup-shaped carbons (Figure 1b). The size remained the same after the treatment of the reduced CSCNTs with 1-iodododecane to produce dodecylated CSCNTs (Figure 1c).

The transmission electron microscopy (TEM) is then applied to observe the changes in the stacked structure of pristine CSCNTs by the reduction of CSCNTs with the naphthalene radical anion more clearly, as shown in Figure 2.¹⁹ The cup-stacked structure of pristine CSCNTs (Figure 2a) is disassembled to individual cup-shaped carbons with similar diameters (ca. 50 nm) and lengths (ca. 100 nm) after the reduction with the naphthalene radical anion (Figure 2b). The individual cup-shaped structure is also clearly observed in the TEM image of dodecylated CSCNTs (Figure 2c).²⁰

Dynamic light scattering (DLS) measurements provide a powerful tool for determining the mean size of the destacked carbons generated by electron-transfer reduction with sodium naphthalenide and/or the subsequent treatment with 1-iodododecane *in solution*.²¹ DLS in THF (Figure 3) clearly indicates that the mean size of purified CSCNTs (>6000 nm) decreases drastically when they are reduced and dodecylated to show narrow size distribution with the

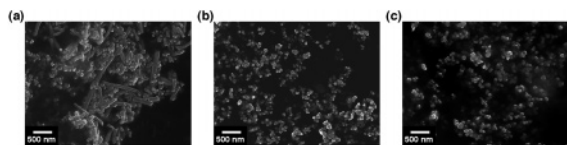


Figure 1. SEM images of (a) pristine CSCNTs, (b) reduced CSCNTs, and (c) dodecylated CSCNTs.

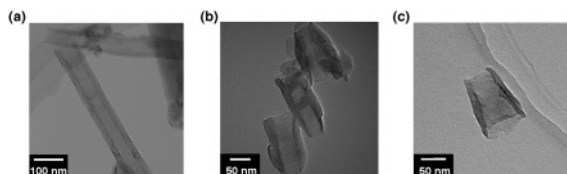


Figure 2. TEM images of (a) pristine, (b) reduced CSCNTs, and (c) dodecylated cup-shaped carbons; scale bar = 100, 50, and 50 nm, respectively.

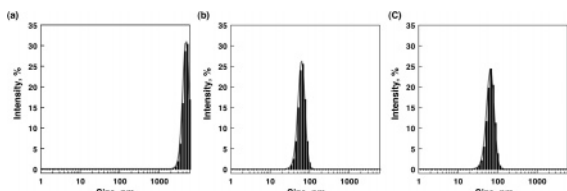


Figure 3. Size distribution diagrams of (a) pristine CSCNTs, (b) reduced CSCNTs, and (c) dodecylated cup-shaped carbons in THF at 25 °C.

Table 1. Mean Size of Dodecylated Cup-Shaped Carbons in Various Solvents, Solvent Viscosity, and Relative Permittivity

solvent	viscosity ^{a,b} η (mPa·s)	relative permittivity ^a ϵ_r	size (nm) ^c
tetrahydrofuran	0.456	7.52 (22 °C)	62.5 ± 14.1
tetrachloroethylene	0.844	2.27 (30 °C)	54.6 ± 9.5
chloroform	0.537	4.81 (20 °C)	46.0 ± 9.4
acetonitrile	0.369	36.64 (20 °C)	4350 ± 920
benzonitrile	1.267	25.90 (20 °C)	5500 ± 180

^a From ref 23. ^b Values at 25 °C. ^c Average size determined by DLS.

mean size of 59.1 ± 12.4 and 62.5 ± 14.1 nm, respectively.²² DLS measurements were also performed in various solvents, and the mean sizes of dodecylated cup-shaped carbons are listed in Table 1 with solvent viscosity and relative permittivity.²³ The mean size of dodecylated cup-shaped carbons is not related to solvent viscosity, but the mean size increases generally with increasing the solvent relative permittivity because of the more favored aggregation of dodecylated cup-shaped carbons by the hydrophobic interaction of dodecyl groups in polar solvents.

High dispersibility of dodecylated cup-shaped carbons in THF was maintained after 1 day in air, whereas the suspension of pristine CSCNTs in THF precipitated in 1 h (Figure S6).

In conclusion, CSCNTs were *efficiently* destacked by the electron-transfer reduction with sodium naphthalenide to produce individual cup-shaped carbons with controlled diameter and size.⁹ Addition of 1-iodododecane to reduced cup-shaped carbons leads to functionalized cup-shaped carbons, which are stable in air and highly dispersible in nonpolar solvents for a long time.

Acknowledgment. We thank Prof. H. Mori and Dr. T. Sakata for helpful advice and discussion in the TEM measurements in the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University.

Supporting Information Available: TEM images of CSCNTs after centrifugation (S1), UV-vis spectra (S2), ESR spectra (S3), IR spectra

(S4), TEM images of dodecylated CSCNTs with low magnification (S5), and photographs of THF suspension of pristine CSCNTs and dodecylated cup-shaped carbons (S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The change in the diameter distribution of CSCNTs by the centrifugation is shown by TEM images in Supporting Information S1.
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- Elemental Analysis: Anal. Calcd for $C_{161}(C_{12}H_{25})_0.3$ (DMF): C, 93.42; H, 1.29; N, 0.20. Found: C, 93.42; H, 1.29; N, 0.22. This indicates that one dodecyl group is attached per 161 carbon atoms. Since the ratio of the edge carbons to the sidewall carbon with diameter of 50 nm and length of 100 nm is ca. 500, the dodecyl groups must be attached not only to the edges but also to the sidewall.
- Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6700F microscope.
- TEM images were collected on a HITACHI Model H-800 transmission electron microscope operating at an accelerating voltage of 200 kV. We prepared the TEM samples from the diluted suspension to prevent aggregation between individual cup-shaped carbons in the gradual evaporation process of solvent. The results were quite reproducible, confirming the homogeneity of product.
- The TEM image of a lower magnification is shown in Supporting Information S5, where a number of individual cup-shaped carbons are seen in contrast with the stacked structure before the reduction.
- Dynamic light scattering (DLS) measurements were performed using a LB-500 particle size analyzer (Horiba, Japan).
- A DLS instrument used in this study has a range between 1 and 6000 nm, and thereby any structures over the limit cannot be detected.
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