Efficient Toroidal Formation of Sorted Metallic and Semiconducting Single-Walled Carbon Nanotubes via General Pickering Emulsion

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ABSTRACT: Single-walled carbon nanotubes (SWNTs) with a toroidal/coiled geometry-shaped structure sustain innovative preference to future technology material. The toroidal shape can be used in designing nanoelectronic devices for various prospective applications such as tactile sensors, electromagnetic absorbers, and energy storage devices. In this study, we demonstrate the fabrication of toroidal geometry shapes of metallic (m-) and semiconducting (s-) SWNTs, which can be revealed by simply mixing a few solutions in the correct ratio, both oil-in-water (hydrophobic) and water-in-oil (hydrophilic) emulsion processes. Herein, the letter communicates the formation of pure m- and s-SWNTs (metallic and semiconducting) by annular, obtained from gel column chromatography, via the emulsion approach. We have also studied the surfactant sodium dodecyl sulfate removal of sorted species from a gel column by a simple method named as chloroform/methanol/water extraction.

INTRODUCTION

Single-walled carbon nanotubes (SWNTs) and their extraordinary properties can be deemed a tremendous milestone for nanomaterials and nanotechnology. Numerous researches have been conducted to find the potential applications of SWNTs in various fields such as nanomedicines, energy storage devices, textiles, sensors, and so on. Actually, the extraordinary properties of SWNTs are also extensively associated with their geometric structure, that is, hexagonal and nonhexagonal networks. Diverse forms of SWNTs including straight, branched, tori, and coiled have been considered and possess exclusive properties for prominent innovations. Among the different geometric shapes of SWNTs, coil/tori-shaped SWNTs drag massive attention because of their significant properties such as persistent current ($I_P$), magnetic response, high mechanical strength, superelasticity, and conducting behavior. In 1994, toroidal carbon nanotubes (CNTs) were observed experimentally at 700 °C over silica-endorsed carbon monoxide (CO) catalyst by the catalytic decomposition of acetylene. The tori geometry structure attained significant attention, and several approaches (catalyst, gas atmosphere, and temperature) have followed to synthesize the tori/coil CNTs.

Many studies have been conducted to investigate the structural models of tori CNTs to investigate their thermodynamic stabilities. The work of Iliha et al. showed that the tori CNTs are found to be more stable than the C$_{60}$ fullerene, comparing the cohesive energies. Additionally, many numerical simulations have demonstrated that the toroidal SWNTs (TSNs) exhibit quantum interference effect in charge transport under an external magnetic field or electromagnetic field, along their potential use as a macroscopic molecular toroid/coil with the molecular Aharonov–Bohm oscillator, spin-polarized current injector, detection of biopolymers, and metal–insulator transition switching. Recently, gold nanoparticles (Au NPs) were deposited on CNT rings for theragnostic applications. Nevertheless, the experimental studies and applications of TSNs have been dilatory as the theoretical investigations. Continuous exploration is made on the toroid closure, such as via self-organized coating, covalent ring-closure reaction, templating in polymer shell, and oil-in-water and water-in-oil emulsions. However, the toroid structures of SWNTs were previously fabricated by gas phase or liquid suspension techniques. The adjustment and variation in parameters (gas and temperature) can be tailored to manage in controlling the structure of toroidal CNTs. In 1996, Kaneto et al. and Shen et al. worked on the electrical conductivity of single-carbon microcoils at room temperature. Recently, Chiu et al. worked on the high conductivity of tori-shaped CNTs at low temperature. In addition, numerous studies have also been conducted to explore the electronic properties of the tori CNTs. The work...
of Akagi et al. demonstrated the calculation of the band structure and electronic density of tori CNTs that would be metallic (m-), semiconducting (s-), or semimetallic, depending on the arrangement of pentagons and heptagons. The zigzag toroidal carbon nanowire (TCNW) with m-TSN, the $I_{pc}$ in the primary carbon ring are concealed by those in resultant TCNW; TCNW with s-TSN, $I_{pc}$ exhibits the same response as that in their primary carbon rings. Thus far, coil/tori CNTs can be formed by the mixture of s-SWNTs and m-SWNTs that are firmly packed in small bundles. Notably, to manifest and harvest the superiority of a TSN, especially its unique quantum interface and spin transport characteristic, it must constitute either m-SWNTs or s-SWNTs purely, as proposed in the numerical simulation. To the best of our knowledge, we can find the fabrication of s-SWNTs or m-SWNTs by structural simulation, but there is no effort on the synthesis of toroidal s-SWNTs or m-SWNTs experimentally.

In this study, we report a fabrication method of pure m- and s-SWNTs into a coil/tori geometry shape by an emulsion process, as shown in Figure 1. First, there are several wet approaches for the solution phase separation of m- and s-SWNTs, such as electrophoresis, density gradient ultracentrifugation (DUG), polymer wrapping extraction, and gel column chromatography. Gel column chromatography has the advantages of scalable throughput with highly pure m-SWNTs and s-SWNTs, where more than 20 isolated chiralities have been sorted out. Ideally, it can provide a range of specific chiralities for SWNT fabrication that would allow comprehensive studies of charge transport of SWNTs under an external field. The bending of SWNTs into a coil or tori closure can be achieved via sonication, covalent ring closure, templating in a polymer shell, colloidal mask, emulsion, and by incorporating pentagons and heptagons into the hexagonal network. Notably, we demonstrate the fabrication of m-SWNTs and s-SWNTs from annular high-pure s-SWNTs and m-SWNTs, obtained from gel column chromatography, via the emulsion process. We are particularly interested in considering the compatibility of the emulsion with the gel column chromatography, scalability, controllable tori radii, and minimal surface modification. Second, the sorted species showed hydrophilic behavior because of the coverage of SDS, an anion surfactant that used to disperse the nanotubes and control the interaction with gel beads during the sorting process. Apparently, the removal of SDS is critical to induce the formation of the tori structure. SDS acted as a spacer, blocking the van der Waals interaction and II–II stacking that stabilized the tori structure when the SWNT bundle was forced to coil into a tori in the emulsion droplet. Hence, it is critical to remove the SDS surfactant. SDS can be merely removed from SWNTs by alcohol washing, filtration, and chloroform/methanol/water (C/M/W) extraction. In this experiment, C/M/W extraction was applied to remove the SDS coating. Consequently, the sorted metallic and semiconducting nanotubes were successfully coiled into a tori topology with a diameter of ∼150–200 nm. Of note, it remains a challenge to develop the coiling and uncoiling of SWNT tori into a reversible process. Till now, there are only limited works performed to refine the geometry shape of nanostructured m- and s-SWNT tori.

RESULTS AND DISCUSSION

By Liu et al., numerous methods have been presented for the fabrication of novel nanotori from the Marangoni effect, hole nucleation mechanism, two-dimensional gas bubbles, and breath figures method. Huang and co-workers experienced the rapid evaporation of mixed droplets to compress the dissolved graphene oxide sheets into warp/bend spheres. The nanostructures were initially confined by the polymer shells and droplets. Then, they compressed when the droplets changed in shape or shrunk in volume. Thus, in this process, collapsing generates shock waves that exert force to bend the CNT bundles. In the shape formation of the nanostructure, interfaces played a significant role. The interfaces are either the polymer–solution interface, the solution–air interface, or...
Figure 2. Successful coiling of hydrophobic SWNTs into TSNs via the oil-in-water emulsion (a) and schematics illustrating the coiling process of a ring (b–h). TEM images of TSNs obtained by the emulsion method, mixed rings, and uncoiled CNT at scale bars of 50 nm, 0.2 μm, 20 nm, and 0.5 μm. More than 80% SWNT rings (diameter 90–120 nm) were obtained by using an emulsion.

the interface between different densities. Notably, the general interaction between the emulsion droplets and nanofilms is focused in this study. The oil droplets (nonpolar) should be first solubilized and the oil-carrying solvent should be miscible with water. The common solvents can be either DMF or N-methylpyrrolidinone (NMP). In addition, mixing DMF and water without oil did not show any bending; too much quantity of oil also did not work. Thus, this present system gives us unexpected outcomes without using polymers and emulsifiers. The results confirmed that rings formed inside the suspended oil droplets before the polymer.

Furthermore, the diameter of the rings can be controlled by the droplet size. The droplets serve as templates for coiling. When the droplet size is sufficiently small, it can exert significant force on the entrapped nanostructures, causing their deformation. However, if the droplet is either too small, it cannot coil into a ring, or if too large, it folds or twists, forming loose/curled or 8-shaped rings. Notably, the droplet size can be controlled by varying the ratio of oil with DMF [toluene/DMF or 1,2-dichlorobenzene (DCB)/DMF]. We suspect that bath sonication also has a great influence on the droplet size.

In this study, the tori morphology was formed by an emulsion process. The emulsion process is simply performed with water, NMP/DMF, and toluene/DCB. Generally, SWNTs interact with the nonpolar soluble oil, and the oil-carrying solvent should be miscible with water. During the coiling process, toluene plays an essential role in the tori/coil structure of SWNTs. The stability of the emulsion system is strongly dependent on the size of particles and the interfacial energy of the oil-in-water and water-in-oil interfaces. Competition occurs between the elastic energy trying to maintain the straight SWNT shape and the interfacial energy to keep a curved water-in-oil interface. Herein, we coined the SWNT bundles into tori at a large scale in an oil-in-water emulsion process. SWNTs can be coined into tori in the presence of a surfactant, and it is also well known as the "solvent-shifting" method, both in oil-in-water and water-in-oil emulsions. Without the need of polymer encapsulation, the method is now simpler and more scalable. The hydrophobic SWNTs were coined into tori with their diameter ranging from ~90 to 100 nm. The formation of tori is due to the bending of SWNT bundles at the oil-in-water interface. The procedure of the formation of SWNT tori is clearly shown in Figure 2.

TSN were formed by following oil-in-water emulsion interface Figure 2a. SWNTs were dispersed in DMF through tip ultrasonication, resulting in a dark suspension. At this point, the SWNTs were in the form of bundles, and then a small amount of oil was added in the surfactant. In addition, water was injected in a single shot and the surfactant turned cloudy. After this, the final solution was isolated by centrifugation. As shown by TEM (Figure 2b), the SWNTs were in the form of parallel bundles, and there was no self-coiling of the SWNT bundles. Thus, the structural variety of the coil/tori was observed (Figure 2c–h), such as 0-shaped, racket-shaped, and 8-shaped tori geometry shapes. The resultant coil/tori were stable and did not uncoil after being dispersed in either oil or water because of the II–II stacking among the SWNTs.

We have investigated the formation of mixed species of SWNT tori via the emulsion process. Several parameters were studied comprehensively to obtain a controllable tori/coil size and yield, as to build a solid foundation for m- and s-SWNT tori formation. Next, we moved on to the m- and s-SWNT tori formation via the emulsion process. Before performing tori synthesis, we carried out the sorting of metallic and semiconducting species. The sorting of SWNTs by their electronic and atomic structures in liquid phase is of paramount importance for the use and application of SWNTs. Several separation methods are introduced, such as polymer extraction, ion-exchange chromatography, aqueous two-phase extraction, gel chromatography, DUG, and DNA wrapping chromatography. Most recently, innovative metallic and semiconducting separation is done using gel column chromatography. Gel column chromatography offers simple, high-throughput, and high-purity m- and s-SWNTs at an affordable cost and short time span. Moreover, gel column chromatography has hitherto been progressively pioneering in species sorting and very promising, and it has effectively sorted out more than 20 isolated species of high purity and several optical isomers from SWNTs. Thus, gel column chromatography is a suitable approach for m- and s-SWNT sorting for tori/coil synthesis.

We carried out gel column chromatography as reported by Tanaka et al. by using dextran exclusion gel (sephacryl-200) beads as the gel medium. SWNTs were dispersed in 1% SDS surfactant and flowed through the gel column. The unbound fraction was collected as the metallic species. The extraction of the semiconducting species from the gel column was performed by flushing with 5% SDS. The different chiralities in the semiconducting species have different affinities to the gel beads. As the result, a weaker affinity was obtained at the lower level of the gel column, whereas a higher affinity was bound to the higher level of the gel column. The affinity difference also
realized the extraction of single-chirality (enriched) SWNTs. The different colors of the obtained semiconducting species indicated the enrichment in certain chiralities. Thus, the purity of metallic and semiconducting species is high.

As the result, the metallic species were bound to the gel beads, thereby allowing the extraction of metallic and semiconducting species.

The absorption peaks for HiPco SWNTs were around 300−450, 650−950, and 950−1350 nm, which correlated to the third, second, and first optical transitions of the semiconducting species, and were designated as $S_{33}$, $S_{22}$, and $S_{11}$, respectively. The absorbance peak of 450−650 nm is the first optical transition of metallic species and designated as $M_{11}$. As compared with the unsorted SWNTs (before separation), the enrichment of the semiconducting SWNTs was clearly observed in the rinsed portion (blue spectrum) and the metallic SWNTs were clearly concentrated in the $M_{11}$ region (red spectrum). From the UV−vis spectra (Figure 3a), it is observed that the SWNTs have broad absorption in the $S_{22}$, $S_{11}$, and $M_{11}$ regions because they contain two-thirds of semiconductors and one-third of metals. For s-SWNTs, the $S_{22}$ and $S_{11}$ bands are significantly stronger/sharper in the absence of the metallic band. In contrast, m-SWNTs show significant enhancement in the $M_{11}$ band in the absence of the $S_{22}$ and $S_{11}$ bands. For s-SWNTs, the absence of the $M_{11}$ peak indicates that they are highly enriched with semiconducting SWNTs, the condition which is the same for m-SWNTs in the $M_{11}$ region. Figure 3a clearly evidences the enrichment in the semi-
conducting and metallic species. For semiconducting SWNTs, the S_{22} and S_{11} bands are significantly stronger. In contrast, metallic SWNTs show significant enhancement in the M_{11} band in the absence of the S_{22} and S_{11} bands.

By careful investigation of the UV-vis spectra and Raman spectra, we found that s-SWNTs and s-TCNs are different in patterns (Figure 3c). From the UV-vis spectra, it is observed that the intensity of s-TSN peaks in the region of S_{11} highly enhances and sharpens. In comparing the radial breathing mode (RBM) of s-TCN to s-SWNTs, we observed a slight red shift under 532 nm excitation, whereas a single RBM peak had been intensively increased.

As we discussed above, the properties of SWNTs are strongly dependent on their geometric structures and are explained by the chiral index \((n_1, n_2)\). Hence, in tiny SWNT cylinders, two-thirds are semiconductors and one-third are metals. Today, many SWNT-based applications need only one or a specific type of tube such as a semiconducting tube for transistors. Thus, the SWNT chiral index is the current focus of the researcher. In principle, to measure the chiral index and properties of the SWNTs, we performed photoluminescence, and Raman scattering was performed to identify the metallic and semiconducting SWNTs. Hence, it is important to know even a small change in the tube’s environment. Raman scattering of the RBM will be changed by different surfactants which create variations in the RBM intensity. The surfactant creates a minor influence on frequency (diameter) and the excitation energy axes. The interaction between the nanotubes and the surrounding environment-related effects can affect the RBM frequency.

To examine the surfactant-based changes in the Raman spectra, we measured the sorted m- and s-SWNTs by using 532 and 785 nm laser excitations. We identified the left and right RBM intensities as that of m-SWNTs and s-SWNTs between 150 and 350 meV. In the region of s-SWNTs, we identify several branches of excitation energy, and the peaks (11,1), (10,0), and (9,1) lie at \(\alpha\)RBM 256.0, 291.4, and 306.2, respectively. m-SWNTs are mostly in the region of (15,0); so, the peaks (7,7) and (13,0) lie at \(\alpha\)RBM 247.8 and 230.8, respectively. Hence, it is clearly indicated that m-SWNTs and s-SWNTs in aqueous solution are wrapped with SDS, as shown in Figure 4.

The next step toward the formation of TSN is to coil the sorted m- or s-SWNT fraction into the topology of toroid by following the emulsion procedures as shown by Wang et al. and Chen et al. The tori formation originates from the liquid/liquid interface-induced SWNT bending. The tori are stabilized by van der Waals interaction and II–II stacking. We found that in the presence of surfactants, neither water-in-oil (w/o) emulsion nor oil-in-water (o/w) emulsion has led to the formation of TSNs. We elucidate that surfactants act as spacers that screen or block the tori from stabilizing by the van der Waals interaction and II–II stacking. Lukaszczuk et al. have proposed a surfactant-free post-treatment that is highly compatible to gel column chromatography. The sorted fraction is introduced to HCl to convert the sodium salt to deoxycholic acid, followed by hot ethanol washing to dissolve the deoxycholic acid that covers the nanotube surface. We are curious and interested in searching for an alternative approach. Again, SDS has been widely used for protein solubilization and separation of protein by SDS polyacrylamide gel electrophoresis. C/M/W extraction was reported as an effective manner for SDS removal from protein.

In determining the organic solvent precipitation for the effective removal of SDS, we carried out C/M/W extraction and acetone extraction. Dialysis against water has also been carried out for reference purpose. From the FTIR spectra in Figure 3b, it is observed that both C/M/W and acetone extractions are effective in SDS removal. However, we found that only the species sorted by C/M/W extraction could be coiled into tori. Before this, we have studied the synthesis of m- and s-TSNs and their properties (magnetic and optical) by simulation. We have succeeded in m-TSN and s-TSN fabrication with the additional step of surfactant removal. Thus, the major difference in our approaches is that nanofilaments are included by the process (emulsion) and transformed in shape. The FTIR spectra revealed that the surfactants are fairly removed but at the cost of introduction of carboxylic groups (1640 cm\(^{-1}\)) during acid hydrolysis (Figure 5).
3d). We have tried other surfactant removal protocols, such as acetone washing, dialysis, C/M/W extraction, and acid hydrolysis with ethanol washing, but only the latter two methods have led to the formation of TSNs.

The TSNs are constituted of a few to tens of nanotubes that bundle together and form a torus. The walls of nanotubes are clearly observed under a higher magnification. The significant difference between the m- and s-TSN and SWNT tori was the circumference of the SWNT tori which was knowingly longer. Possibly, we can say that SWNT bundles were longer and flexurally strong. Therefore, numerous factors could be involved in the formation of the tori structure, such as the length of SWNT bundles before formation, the bundled amount of SWNTs, and the wobbling interaction between the complex and dynamic SWNT tori, and contract polymers during the coiling procedure.

The TEM images (Figure 5a–h) revealed that the m-SWNTs and s-SWNTs are coiled into tori topology (“O-shaped”) with the diameter of ∼150–200 nm. Semiconducting TSNs exhibit diamagnetism at a small magnetic flux, which is in great contrast with the paramagnetism of metallic TSNs. An applied magnetic flux is known to induce tori current in molecules and persistent current in mesoscopic tori. The physical origin of persistent current is the cyclic boundary condition of the electronic system. The electronics structure calculated from the tight-binding model could be divided into these following types: a metallic, a narrow-gap semiconducting (Eg < 1 meV), and a wide-gap semiconducting (Eg > 1 eV). When TSN are threaded by a uniform perpendicular magnetic field, the persistent currents only exist in metallic and a narrow-gap semiconducting TSNs.

Toluene played an important part in the coiling process; so, in both experiments (hydrophobic and hydrophilic), toluene was used. Coil/tori were formed in both cases. Theoretical studies revealed that the dependence of the electronic structure of TSN wires/bundles is based on the number of particles, which has been changed by the outer TSN coating and differs from the particles of inner SWNT tori.

It is well known that the wave nature manifests itself only when the device size is comparable to the wavelength and the absence of inelastic scattering. Therefore, the observation of quantum interference phenomenon in the mesoscopic structure, in particular TSNs which show all the spin and charge transport features of graphene coil because of the additional degree of freedom in electron motion along the smaller torus circumference, has become the interest of all. Studies revealed that the dependence of the electronic structure in both experiments (hydrophobic and hydrophilic), toluene played an important part in the coiling process; so, in both experiments, hydrophobic and hydrophilic, toluene was used. Coils/tori were formed in both cases. Theoretical studies revealed that the dependence of the electronic structure of TSN wires/bundles is based on the number of particles, which has been changed by the outer TSN coating and differs from the particles of inner SWNT tori.

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■ CONCLUSIONS

In this report, we have addressed the mixed species in TSN by the hydrophobic emulsion process. Second, the raw SWNT bundles are sorted into m- and s-SWNTs via gel column chromatography. The sorted SWNTs showed a hydrophilic behavior because of the coverage of SDS, an anion surfactant that used to disperse the nanotubes and control the interaction with gel beads during the sorting process. Hence, SDS removal is critical to induce the formation of tori. C/M/W extraction was applied to remove the SDS coating. As the result, the sorted metallic and semiconducting nanotubes were success-fully coiled into tori topology with a diameter of 150–200 nm. In addition, we have shown that the C/M/W extraction is effective in SDS removal for nanotubes, and its tori/coil formation process has not been communicated elsewhere. Throughout the ring formation process, from species sorting to SDS removal and tori closure, minimal chemical modification has been exerted on the SWNTs. It is utterly significant because gel column chromatography has hitherto been progressively pioneering in species sorting and very promising, and it has effectively sorted out more than 20 isolated species and several optical isomers from SWNTs. Therefore, the integration could provide loads of species for tori formation which would facilitate the fundamental study in transport mechanism and electrical properties.

■ MATERIALS AND METHODS

Purified-grade HiPco SWNTs with a length of 0.1–1.0 μm and diameter of 0.8–1.2 nm were purchased from NanoIntegris, Canada. All chemical reagents were used as purchased without any additional distillation. All other chemicals were purchased from Sigma-Aldrich. Deionized water was also used in all reactions. The sorting of metallic and semiconducting nanotubes followed the work reported by Hirano et al. Gel column chromatography enables the easy separation of SWNTs into metallic and semiconducting species at considerable throughput and resolution.36 However, the sorted species were covered with SDS, an anion surfactant that used to disperse the nanotubes and control the interaction with gel beads during the sorting process. The TEM images were collected by a JEM-1400 (JEOL) at 100–200 kV.

Mixed Species Tori Formation via Emulsion. SWNTs (0.04 mg/mL) were redispersed in DMF by tip sonication (400 W) for 4 h. Next, 10 μL of toluene was added in 1 mL of the obtained solution of SWNTs under sonication. Next, 5 mL of water was injected to the mixture at one shot to trigger the emulsion process under bath sonication. The mixture turned into a whitish color immediately and then turned into a transparent color. The emulsion was kept at room temperature for 20 min. After 20 min, the solution was isolated with a centrifuge at 12 000 rpm for 30 min and the final product was collected. This final product was characterized by TEM and Raman spectroscopy. Tori/coil with a size of ∼90 nm was obtained and characterized by TEM. If the added toluene was increased to 20–40 μL, then the diameter of SWNT was also increased to ∼180–290 nm, respectively.

Metallic and Semiconducting Nanotube Sorting. The sorting of metallic and semiconducting nanotubes followed the work reported by Hirano et al. First, we dissolved SWNTs in SDS under tip sonication for 1 h at 400 W power. Then, we performed ultracentrifugation at 215 000g for 30 min to remove impurities. After centrifugation, we collected the supernatant for further use. Next, to make the filtration column, a plastic syringe was plugged with cotton, and then 5 mL of dextran exclusion gel was placed as a medium for gel filtration. The black suspension which was achieved after ultracentrifugation was dispersed in the column with 1% SDS. By SDS washing, we successfully collected metallic SWNTs. Metallic SWNTs were covered well by surfactant molecules when compared to semiconducting SWNTs, resulting in weaker interactions with the gel, and therefore metallic SWNTs were collected in unbound fractions passing directly through the column. A 0.5 wt % SDS was further used to remove the metallic SWNTs. After this, we can add different

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wt % (1, 0.5%) of SDS disposed in the tube to get the different chiralities of the metallic SWNTs.

Next, we washed the column to obtain different chiralities of semiconducting SWNTs. A 0.5 wt % deoxycholate (DOC) was added to the column to wash down the semiconducting SWNTs. The same process was repeated, and after this, different wt % (1, 0.5%) of DOC were added to collect the different chiralities of the semiconducting SWNTs. Metallic SWNTs are mostly near-red to wine red in color with different chiralities, and semiconducting SWNTs are near sky-blue in color with different chiralities.

C/M/W Washing for SDS Removal. This washing methodology was reported by Wessel and Flügge.61,62 First, 2 mL of solvent containing sorted SWNTs was mixed in 8 mL of methanol. Next, 2 mL of chloroform and 6 mL of water were added for phase separation. Then, the solution was vortexed until homogeneous and centrifuged for 10 min at 5000 rpm. The sorted SWNTs were localized at the interphase. The upper supernatant was removed carefully, and then 6 mL of methanol was added to the lower chloroform phase. Again, the mixture was centrifuged for 10 min at 10 000 rpm. The upper supernatant was carefully removed. The C/M/W ratio was 1:4:3 (v/v/v).

Emulsion for Metallic and Semiconducting TSNs. SDS removal nanotubes (metallic or semiconducting) were then redispersed in DMF (0.08 mg/mL) by tip sonication (400 W) for 4 h. A 10 μL of toluene was added into 1 mL of the contained solution and vortexed to give a homogeneous mixture. Next, 5 mL of water was injected into the mixture at one shot to trigger the emulsion process under bath sonication. The solution turned into a whitish color immediately and then turned into a transparent color, indicating emulsification. The emulsion was kept for 20 min at room temperature. The product was isolated with a benchtop centrifuge at 12,000 rpm. The sorted SWNTs were localized at the interphase. The upper supernatant was carefully removed. The C/M/W ratio was 1:4:3 (v/v/v).

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