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Cause and Consequence of Carbon Nanotube Doping in Water and Aqueous Media

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Abstract: To utilize carbon nanotubes in real-world applications, we have to master their chemistry. At present there is a lack of understanding regarding what happens during basic manipulations, such as doping with acids, forming suspensions by sonication in water with surfactants, or detecting peroxides. We show that sonication of nanotubes in water leads to the in situ formation of molecular oxygen, causing doping, which can be quenched with ethanol. In the presence of the anionic surfactant sodium dodecyl sulfate, oxygen doping is overshadowed by doping due to the sulfate group. Stable suspensions of undoped nanotubes can be created with Triton-X spiked with ethanol. Hydrogen peroxide does not dope, but in high concentrations or in the presence of catalytic iron nanoparticles it decomposes to yield oxygen, which may dope. Hydrochloric acid does not dope, unlike sulfuric acid. Our results clarify the origins of doping while processing carbon nanotubes in water.

1. Introduction

Water is often used as dispersant medium to individualize single-walled carbon nanotubes (SWCNTs) using surfactants[1−3] to achieve stable dispersions or even separate SWCNTs based on chirality using additives such as DNA.[4−6] Certain covalent functionalization schemes are also performed in water, such as the diazonium reaction[7] and hydroxylation of SWCNTs via irradiation with UV light.[8] Bulk synthesis of SWCNTs results in bundles, and the common goal of all these chemical modifications is to enhance the dispersion of the SWCNTs and to decrease their inherent ability to aggregate. Sonication is often employed as an initial step to disperse the SWCNTs in solution. The electronic structure of SWCNTs has been shown to be sensitive to impurities and new species formed during sonication in organic solvents.[9] In the case of water, reactive species are also formed during sonication, such as short-lived hydroxyl and hydrogen radicals.[10] Sonicated SWCNTs are used as starting materials in numerous covalent and non-covalent functionalization schemes[11,12] or in procedures for separation of the different chiral nanotube species.[4,13] Fundamental to all these methods is the use of the inherent electronic properties of the SWCNTs for further modification. However, the impact of preprocessing, such as sonication, on the electronic structure has not been adequately assessed.

Doping of SWCNTs is achieved by intercalation, similar to graphite intercalation compounds, or by replacement of carbon atoms by other atoms such as boron and nitrogen.[14] During wet chemical processing, certain atoms or molecules can be intercalated in the SWCNT network. Electron donors and electron acceptors can be used to tailor the electronic properties of SWCNTs, leading to either n-type[15,16] or p-type doping.[17−19] It should be emphasized that in some cases these added molecules only indirectly "lead to doping", and it is the formation of new species during sonication that causes doping.[9] This doping phenomenon can be characterized by Raman spectroscopy, where an upshift in the higher frequency mode

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Raman features correlates to p-doping,[9,17,20] and by X-ray photoelectron spectroscopy (XPS), where a shift to lower binding energy (BE) of the C 1s core level is also associated with p-doping.[9,17,19]

Here we report the effect of water and additives such as hydrogen peroxide, sodium dodecyl sulfate (SDS), Triton-X-114, and dilute mineral acids on the electronic properties of SWCNTs and determine the nature of the species causing p-type doping, thus altering the electronic properties of the SWCNTs. We also devised a way of avoiding in situ doping during sonication via addition of small amounts of ethanol. Doping was characterized by Raman spectroscopy, titrimetry, and XPS. Our results help to correctly interpret data from a number of literature reports involving processing of SWCNTs in aqueous media.

2. Sample Preparation and Experimental Methods

2.1. Materials. SWCNTs (high-pressure carbon monoxide [HiPco] process, batch no. PO343 [5 wt % total Fe content]) as purchased from Carbon Nanotechnologies Inc. (now Unidym) were annealed at 800 °C for 1 h under vacuum following a very slow ramp at a rate of 1 °C/min to remove any contaminants. Millipore water (18 MΩ·cm) was obtained from a Simplicity UV purification system. Hydrogen peroxide (ACS grade, 30%) and sulfuric acid (reagent grade, 95−98%) were purchased from Caledon. Fe(III) oxide nanoparticles (ACS grade, <50 nm, 99%), SDS (puriss. for ion pair chromatography, ≥99%), Triton X-114 (lab grade), and dodecane (Reagent plus, ≥ 99%) were purchased from Sigma-Aldrich. Sodium sulfate decahydrate (cryst. certified) and hydrochloric acid (trace metal grade, 35%) were purchased from Fisher Scientific. Sodium chloride (reagent grade, ≥99%) was purchased from BioShop. Ethanol (EtOH, anhydrous) was purchased from Comalc. Argon gas (UHP grade, 99.99%) and O_2 gas (U.S.P. medical grade, 99%) were purchased from Vitalaire. The chemicals were used as received unless otherwise stated. A polytetrafluoroethylene (PTFE, 0.2 μm) filter membrane from Pall Life Science was used throughout this study.

2.2. Sample Preparation. All sonication experiments were performed under ambient conditions for 1 h using a Branson 1510 bath sonicator (42 kHz, 70 W). During sonication the temperature of the water bath increases from room temperature to within a range of 32−38 °C over the course of 1 h. An inert atmosphere was maintained inside the sonication vessel by using an inflated balloon containing argon gas. The vessel was consistently positioned in the middle of the bath in the region of highest visible agitation. Stirring was carried out in a flamed-dried round-bottom flask under Ar atmosphere for 1 h using a 0.5-in. PTFE-coated stirring magnet. Some neat solvent samples were presonicated for 1 h under Ar in the absence of SWCNTs. O_2 gas was slowly bubbled into 15 mL of water for 1 h to produce water saturated with oxygen. Argon gas was bubbled through the dispersant medium for 1 h for degassing. A 5 mg sample of SWCNTs was added to the dispersant medium (7.5 mL) and agitated via sonication or stirring under Ar for 1 h. The dispersion was then filtered over 0.2 μm PTFE membrane. Similarly, samples of SWCNTs (5 mg) were independently prepared using solutions (7.5 mL each) of Triton X 114 (1 mM), SDS (32 mM), $Na_2SO_4\cdot10H_2O$ (32 mM), NaCl (32 mM), H_2SO_4 (32 mM), HCl (64 mM), and dodecane. The SWCNT-to-solvent weight/volume ratio is maintained throughout this study, and critical micellar concentration (cmc) of the surfactants was used. Equivalent amounts of anions were maintained, whereas normality was kept constant in the case of HCl. Fe_2O_3 nanopowder is added to the SWCNTs in order to spike the iron content to 10 wt % above its initial value and stirred in purged water.

2.3. Characterization. A Renishaw 2000 Raman microscope was used to acquire spectra over a range of 100−3700 cm^{-1}, with a spectral resolution of 2 cm^{-1}, using a backscattering configuration with a 50× objective excited with an Ar^+ ion laser at 514 nm (2.41 eV). Data were collected on numerous spots on the sample and recorded with a fully focused 1% laser power having a spot size of ~1.2 μm; the latter has a power density of ~10 μW/μm^2 at the sample, which does not damage the sample.[21] All spectra were collected with the optically opaque, filtered bucky-paper sample supported on a PTFE membrane. Recording spectra in the solid state rather than of SWCNTs suspended in solution improved the reproducibility of the data and avoided artifacts due to solvent effects and degree of aggregation (which varies for different treatments and also changes over time within the same sample). The spectra are scaled with respect to the maximum intensity of the D* mode (2500−2800 cm^{-1}) to visually aid the comparison within and among the samples. The D* peaks have been deconvoluted by fitting lorenztian peaks.[22]

A Kratos Axis Ultra spectrometer, with a monochromatic Al Kα X-ray source (15 mA, 1486.6 eV), was used to record photoelectron spectra of the samples. The nanotube samples (thin films and powder) were pressed onto gold for analysis. The BE was measured with respect to the Fermi level. The instrument work function was calibrated to give a BE of 83.96 eV for the Au $4f_{7/2}$ line for metallic gold, and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu $2p_{3/2}$ line of metallic copper. High-resolution (0.1 eV) spectra were obtained using a 20 eV pass energy and an analysis area of ~300 × 700 μm^2.

Hydrogen peroxide was detected iodometrically. The sonicated water sample (20 mL) was added to 100 mL of 1 M sulfuric acid saturated with KI (1 g). Starch was used as an indicator and the solution titrated with 0.005 M sodium thiosulfate.[23]

3. Results and Discussion

3.1. Sonication in Water Leads to Doping. We have investigated the effect of water on the electronic properties of SWCNTs during both sonication and stirring, using an annealed SWCNT sample as reference. Out of the distinct resonantly enhanced features observed in the Raman spectra of SWCNTs, we have focused our attention on the G band (1400−1600 cm^{-1}) and the D* band (2500−2800 cm^{-1}). The Raman spectrum of the reference annealed SWCNTs has a broad shoulder at ca. 1540 cm^{-1} (G band) and D* peaks with maximum intensity at 2657 cm^{-1} when illuminated with a green laser (Figure 1a). A quantitative interpretation of the shape of the G band is only meaningful in the case of individual tubes[24] and therefore not possible in our case. The D* band is the average Raman signal observed for annealed SWCNTs, which can be explained by the curvature effect and π-orbital misalignment of carbon atoms in the SWCNT structure.[25,26] The analogous D* band for either crystalline or disordered graphite has a double-peak feature

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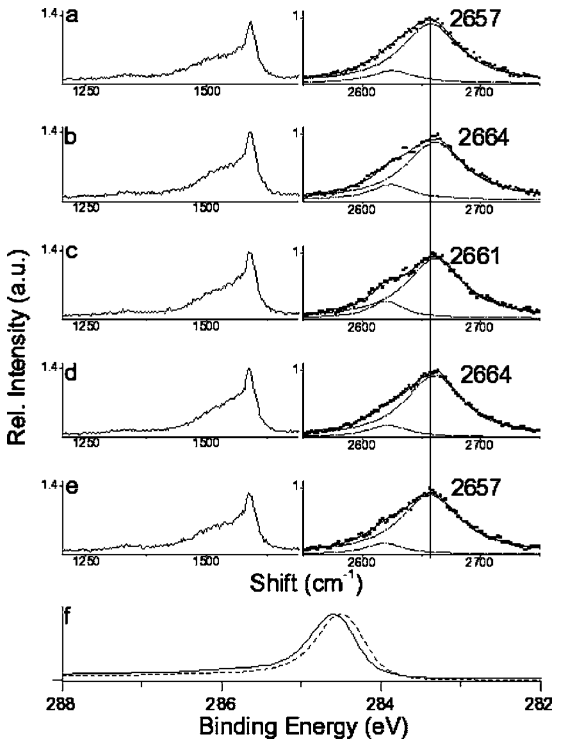

Figure 1. Evidence for doping after sonication and stirring of SWCNTs in water. (a) Raman spectrum of annealed pristine nanotubes. (b) Raman spectrum after sonication in water. (c) Raman spectrum after stirring in water. (d) Raman spectrum after sonication in purged water. (e) Raman spectrum after stirring in purged water. (f) High-resolution XPS spectra comparing the C 1s peak of annealed SWCNTs (solid trace) and SWCNTs sonicated in water (dashed trace).

which is independent of defects.[27,28] Doping not only shifts the D* band but also induces formation of a side peak.[22] The D* peak is used as a gauge for doping, where the observed shift is indicative of charge transfer.[9,17,20] An upshift in the D* peak along with the loss in continuum states (depletion of the shoulder at ca. 1540 cm^{-1}) and enhancement of the G band intensity (ca. 1600 cm^{-1}) is correlated to p-type doping.[9]

For SWCNTs sonicated in water, the intensity of the D peak is unchanged; i.e., no defects are introduced (Figure 1b). However, the shoulder of the G band is depleted, and the D* peak is shifted by 7 cm^{-1}, to 2664 cm^{-1}. SWCNTs stirred in water show a slight depletion in the shoulder of the G band, with a relatively smaller shift (5 cm^{-1}) in the D* peak to 2662 cm^{-1} (Figure 1c). SWCNTs stirred in purged water (degassed with Ar) show no such shifts or changes in the G band (Figure 1e), whereas sonicating the SWCNTs in purged water still leads to p-type doping, where the D* peak shifts to 2664 cm^{-1} (Figure 1d). The dopant is therefore a species generated during the sonication of water.

The amount of oxidants (such as hydrogen peroxide or molecular oxygen) formed after sonication of Millipore water was measured iodotitrimetrically.[23] The titration was carried out in long-necked 250 mL graduated cylinders to avoid air oxidation. A blank sample of unsonicated purged Millipore water was also titrated and showed no change in coloration, thereby no measurable air oxidation occurred. The concentration of oxidants in the sonicated sample was found to be 4 × 10^{-4} M by titration with sodium thiosulfate (5 × 10^{-3} M).

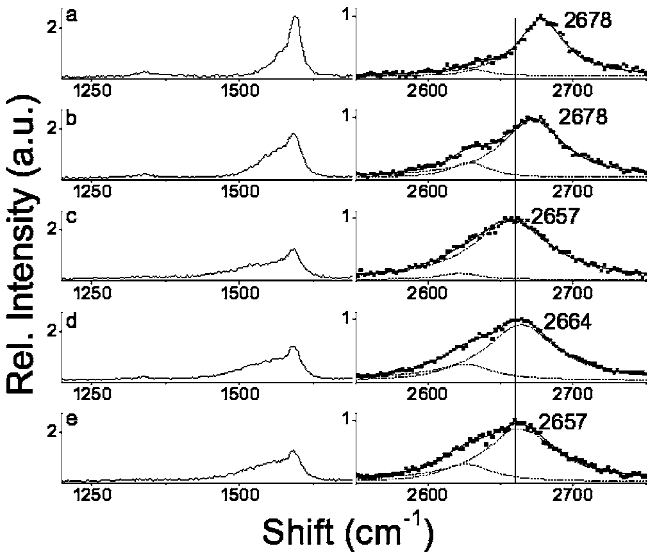

Figure 2. Raman spectra refuting direct interactions between SWCNTs and H_2O_2 as a cause of doping. (a) Sonicated in 30% H_2O_2. (b) Stirred in 30% H_2O_2. (c) Stirred in 1% H_2O_2. (d) Stirred with iron nanoparticles in 1% H_2O_2. (e) Stirred with iron nanoparticles in water.

XPS confirms doping in SWCNTs that were sonicated in water. Since XPS data collected on solids are referenced to the Fermi level, any change in Fermi level causes a change in the observed BE, in this case a shift in the C 1s core-level spectra of SWCNTs after doping.[9,17,19] The high-resolution spectrum of the C 1s peak of SWCNTs sonicated in water (dashed trace in Figure 1f) displays a shift of 0.1 eV to lower BE with respect to that of the annealed sample (solid trace). The Fermi level is lowered toward the valence band edge; hence, the observed shift to lower BE is correlated to p-type doping, corroborating our Raman observations.

3.2. Hydrogen Peroxide Does Not Dope. Sonication of water is known to generate small amounts of hydrogen peroxide,[10] which in turn has been reported to lead to p-doping of SWCNTs.[29−32] Indeed, both sonication and stirring in 30 wt % hydrogen peroxide cause an upshift in the D* peak by up to 21 cm^{-1}, to 2678 cm^{-1} (Figure 2a,b) The shift is also accompanied by a depletion of the shoulder and an enhancement in intensity of the G band peak. An increase in the D peak indicates an increase in defect density due to oxidation of the SWCNTs. Bubble formation was observed at the SWCNT surface prior to agitation, as the peroxide decomposes into water and oxygen. In contrast, Raman spectra of SWCNTs stirred for 1 h in 1 wt % H_2O_2 in purged water (0.3 M) show no shift in the D* peak and the intensity of the G band is not enhanced (Figure 2c). Other dopants, such as tetracyanoquinodimethane (TCNQ), have been shown to alter the spectrum even at very low concentrations (10^{-6} M).[33] It has been previously suggested[32] that 0.005−0.02 wt % H_2O_2 (0.0015−0.006 M) could lead to p-doping of SWCNTs, which therefore could find use as

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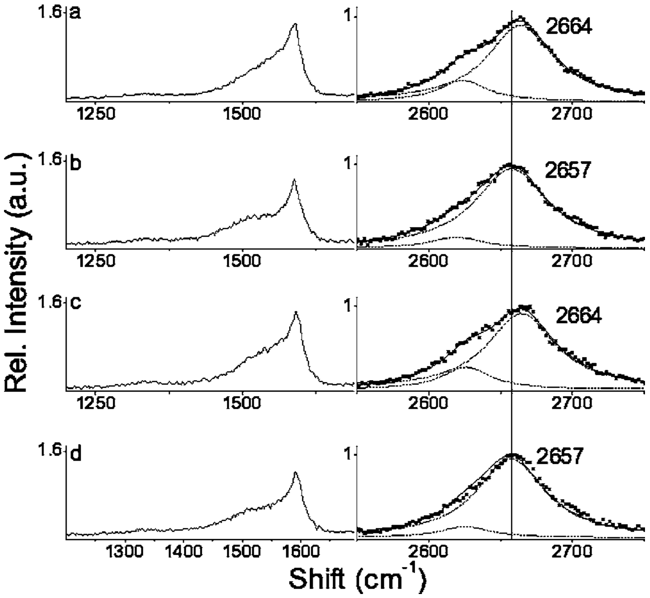

Figure 3. Raman spectra proving that molecular oxygen formed in situ during sonication is the dopant. (a) Stirred in presonicated water. (b) Stirred in presonicated and Ar-purged water. (c) Stirred in O_2-purged water. (d) Sonicated in 1 vol % EtOH in purged H_2O.

biological sensors. The nanotubes used in that study (HiPco batch no. 79 from CNI, Dec 2, 2001)[32] differ from the nanotubes used here in their higher iron content. Iron oxide nanoparticles have been shown to be active sites for the reduction of hydrogen peroxide,[34] which reacts with Fe(II/III) to generate hydroxyl radicals via a Fenton-like reaction.[35] The HiPco SWCNTs used in our study have a 5 wt % Fe content, none of which is accessible.[9,36] Addition of 10 wt % Fe(III) oxide nanoparticles to the SWCNTs sample (already containing 5 wt % Fe) results in a shift in the D* peak upon stirring in the 1 wt % H_2O_2/H_2O mixture (Figure 2d). The shoulder of the G band is depleted and the D peak increases slightly, possibly due to the reaction of the SWCNTs with hydroxyl radicals.[8] No doping is observed when a SWCNT sample is spiked with 10 wt % Fe_2O_3 and stirred in purged water (Figure 2e). Thus, we conclude that hydrogen peroxide itself does not p-dope SWCNTs, even though its decomposition products may do so.

3.3. In Situ Formation of Molecular Oxygen Is the Cause of Doping. To investigate whether the species responsible for doping are long-lived, purged water is presonicated and then stirred with SWCNTs. The Raman spectrum (Figure 3a) indicates p-doping. A shift (7 cm^{-1}) in the D* peak is observed at 2664 cm^{-1} along with the depletion of the shoulder and enhancement in intensity of the G band peak. When the presonicated water is purged with Ar prior to stirring with SWCNTs, no doping effect is observed (Figure 3b). This means that the species formed during sonication is stable but comparatively volatile, such as dissolved oxygen, a known decomposition product of hydrogen peroxide. To replicate this process, O_2 gas was bubbled through purged water for 1 h. The Raman spectrum of SWCNTs stirred in the resulting solution for another hour shows a prominent increase in the G band intensity along with the loss of the shoulder and a blue shift of the D* peak to 2664 cm^{-1}. (Figure 3c) These are features characteristic of p-type doping.

Molecular oxygen has been suggested to cause p-doping in SWCNTs bundles,[18,37,38] as opposed to a report of changes in the work function of the electrodes being at the origin of p-doping in an individual short nanotube.[39] Indeed, it has been shown theoretically[37] and experimentally[38] that charge transfer is favored in bundles of SWCNTs upon oxygen adsorption. Other theoretical work has suggested that oxygen binds strongly to the surface of carbon nanotubes,[40] and Ricca et al.[41] have shown that chemisorption of O_2 is not favorable at room temperature whereas physisorption is weak but stable. This supports our data that no enhancement in the D peak is observed for SWCNTs sonicated in water or SWCNTs exposed to O_2. Due to its higher electronegativity when compared to carbon, oxygen is an electron acceptor and hence a p-dopant.[18,42] Hence, molecular oxygen is the p-doping species formed during SWCNT sonication in water.

Oxygen is formed via the formation and decomposition of hydrogen peroxide during sonication. Sonication breaks down the water molecules, yielding $H^{\bullet}$ and $^{\bullet}OH$ radicals (eq 1).[10]

$$H_2O \rightarrow H^{\bullet} + {}^{\bullet}OH \qquad (1)$$

The radicals can recombine to form water (eq 2) or react further to generate other species, such as molecular oxygen (eqs 3−7).

$$H^{\bullet} + {}^{\bullet}OH \rightarrow H_2O \qquad (2)$$

$$2H^{\bullet} \rightarrow H_2 \qquad (3)$$

$$2{}^{\bullet}OH \rightarrow H_2O_2 \qquad (4)$$

$$2{}^{\bullet}OH \rightarrow O + H_2O \qquad (5)$$

$$2O \rightarrow O_2 \qquad (6)$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (7)$$

Alcohols such as ethanol are known to retard the decomposition of certain organic solvents,[43] and they have also been applied to quench the formation of radical species during sonication.[9,44] SWCNTs sonicated in ethanol (deoxygenated[45] by heating to 50 °C) do not show any sign of doping,[9] and the doping effect observed when SWCNTs are sonicated in water is suppressed when a 1 vol % ethanol in purged water mixture is used (Figure 3d). The shoulder of the G band is unaltered, and the D* peak does

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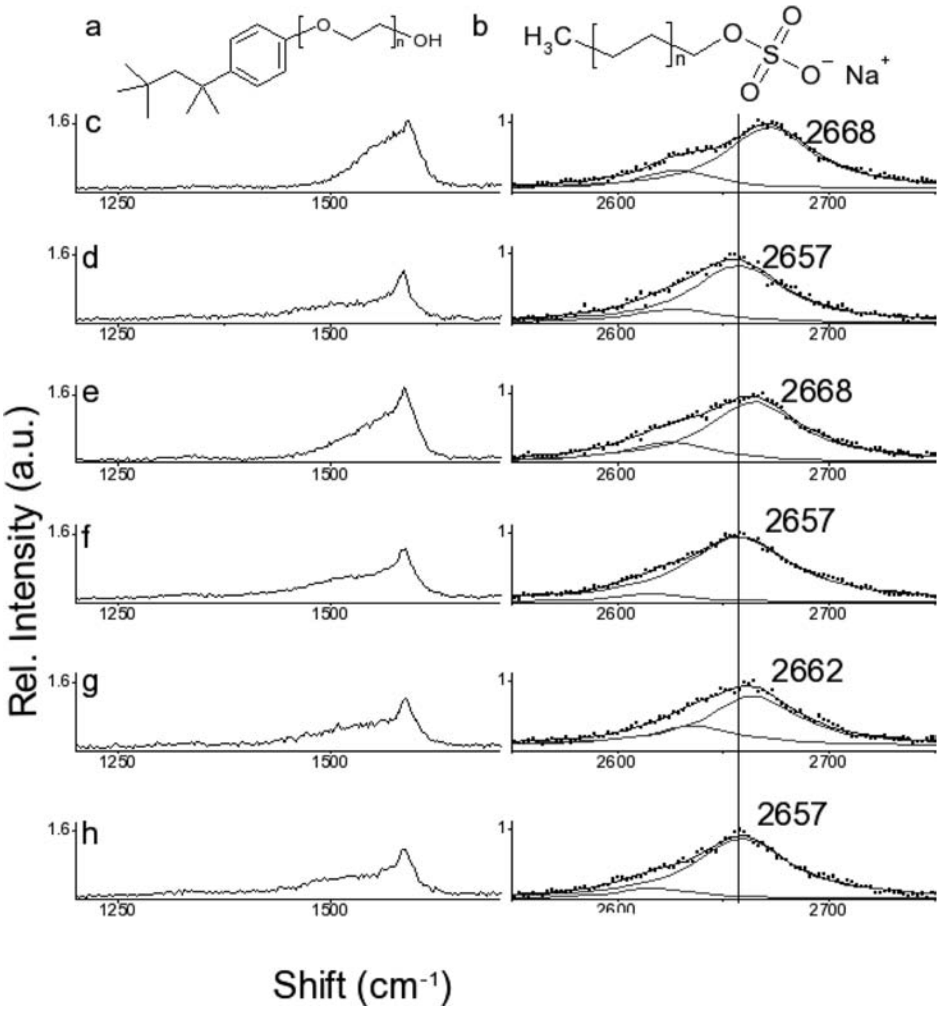

Figure 4. Raman spectra identifying the cause of doping during interaction with surfactants. (a) Structure of Triton-X-114. (b) Structure of SDS. (c) Stirred in 1% SDS. (d) Stirred in dodecane. (e) Stirred in 32 mM sodium sulfate. (f) Stirred in 1 mM Triton-X-114. (g) Sonicated in 1 mM Triton-X-114. (h) Sonicated in 1 mM Triton-X-114, 1% ethanol.

not shift. The formation of molecular oxygen during sonication of water can therefore be quenched by addition of 1 vol % ethanol to purged water.

3.4. Sodium Dodecyl Sulfate Dopes More. Due to their hydrophobicity, water by itself does not readily produce stable dispersions of SWCNTs, and surfactants[1−3] are commonly used to aid their individualization. However, the sonochemical degradation of surfactant molecules has previously been reported.[46] We have therefore studied the impact of both stirring and sonication on SDS (Figure 4a) as an example of an anionic surfactant and Triton-X-114 (Figure 4b) as an example of a nonionic surfactant. The effect of sonicating SWCNTs in a mixture of SDS and water on their electronic structure has been previously studied with optical absorption spectroscopy.[47] We find that the shoulder of the G band in the Raman spectrum is depleted, the intensity of the G band is enhanced, and the D* peak is shifted by 15 cm^{-1}, to 2672 cm^{-1}, both when stirred (Figure 4c) and when sonicated (Supporting Information, Figure S1). These are characteristic features related to p-type doping. Comparing the spectra of SWCNTs stirred in dodecane (Figure 4d) with 32 mM sodium sulfate (Figure 4e) clearly identifies the electron-withdrawing sulfate group as a strong p-dopant, with no measurable contribution of the alkyl chain. Similar observations are made when the SWCNTs are sonicated in dodecane and 32 mM sodium sulfate (Supporting Information, Figure S2). We can confidently identify sulfate as a dopant since stirring of nanotubes in purged water did not lead to doping (Figure 1e) and the maximum observed shift in the D* peak due to dissolved oxygen is smaller than the shift observed due to SDS or sulfate. This strong shift persisted in a sample of SWCNTs sonicated in a mixture of SDS, water, and ethanol (Supporting Information, Figure S1). SWCNTs suspended in water with the help of SDS will therefore always be p-doped.

3.5. Triton-X Does Not Dope. Triton-X is a class of nonionic surfactants shown to aid in the formation of suspensions of SWCNTs in water.[48] Raman spectra of SWCNTs that were stirred in a 1 mM (cmc) aqueous solution of Triton-X-114 do not show any evidence of doping (Figure 4f), in contrast to nanotubes that were sonicated in 1 mM Triton-X-114 in water (Figure 4g). These results are in analogy to findings with purged water (Figure 1, panels e and d, respectively), which was also used to prepare the Triton-X solutions. Triton-X would therefore be a suitable candidate for the preparation of undoped nanotube suspensions if not for the generation of molecular oxygen during

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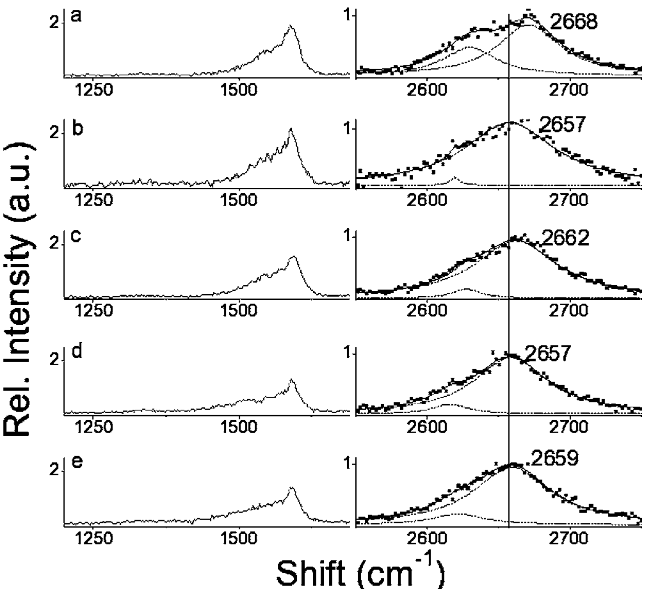

Figure 5. Raman spectra identifying the cause of doping during sonication in aqueous dilute acids. (a) Stirred in 32 mM sulfuric acid. (b) Stirred in 64 mM hydrochloric acid. (c) Sonicated in 64 mM hydrochloric acid. (d) Sonicated in 64 mM hydrochloric acid, 1% ethanol. (e) Sonicated in 64 mM sodium chloride.

sonication. As has previously been shown for pure water, oxygen formation can be quenched by adding small amounts (1 vol %) of ethanol, which was not found to disrupt the surfactant effect of Triton-X in the concentrations used (Figure 4h). All previously known procedures using surfactants and water produce suspensions of p-doped SWCNTs either due to the surfactant itself (e.g., SDS) or at least due to oxygen generated during sonication even if purged water had been used. The possibility of producing aqueous suspensions of undoped nanotubes has now been demonstrated for the first time by sonication in a mixture of 1 mM Triton-X-114 in water with 1 vol % ethanol.

3.6. Hydrochloric Acid Does Not Dope. Aqueous dilute hydrochloric acid has been reported to cause doping in SWCNTs.[19] Since we have now shown that sonication in water by itself can lead to doping, it is worth revisiting the issue of doping by aqueous acids. We have previously shown that HCl gas dissolved in an organic solvent leads to doping only in nanotube samples with accessible iron content,[9] whereas SWCNTs that have undergone further purification (as used in this study; previously titled "new batch" in ref 9) were shown to be doped only in the presence of additional catalytic iron nanoparticles.[9] In the case of SWCNTs stirred in dilute sulfuric acid (32 mM), strong signs of doping are seen in the Raman spectra (Figure 5a), as one would expect, given the previously established doping effect of the sulfate group (Figure 4c,e). The features associated with p-type doping are still observed in the Raman spectra of the SWCNTs sonicated with dilute sulfuric acid (32 mM) and cannot be quenched with ethanol (Supporting Information, Figure S3). The sodium cation is clearly not needed for the doping effect. However, the pH of the acid also is not relevant for doping. Using hydrochloric acid of the same normality (64 mM) and hence the same pH (approximately, since both are strong acids), stirring does not lead to doping in SWCNTs (Figure 5b), whereas sonication does (Figure 5c). All solutions are prepared with purged water, so the origin of doping in the case of hydrochloric acid or NaCl (Supporting Information, Figure S4) lies in the formation of molecular oxygen during sonication, which once again can be quenched by addition of 1 vol % ethanol (Figure 5d). Finally, we confirm that neither Na^+ nor Cl^- in the concentrations used leads to doping of SWCNTs, even during sonication (Figure 5e). Aqueous acids therefore are not generally suitable as dopants for nanotubes, other than the doping effects of certain anions (e.g., SO_4^{2-}, but not Cl^-) and the formation of molecular oxygen from sonication of water.

4. Conclusion

Oxygen has been suggested to be critical[49,50] to enable the protonation of SWCNTs in micelles, and it has been stated that its adsorption on the nanotube is undetectable by Raman scattering, absorption, or fluorescence spectroscopy.[49] Our results can explain the above statement: SDS causes p-type doping that overwhelms the D* peak shift and changes in the G band caused by the oxygen that was generated during sonication. The role of dissolved oxygen has been questioned in literature,[50] as it has been suggested to cause pH-induced bleaching[49] of the optical spectra of the SWCNTs. Our results point to another source of dissolved molecular oxygen during sonication. Water is a common dispersant medium but, when sonicated, leads to the formation of molecular oxygen via a radical pathway. We have shown that SWCNT networks are sensitive to wet-chemical processing and the SWCNTs are p-doped when sonicated in water, even if the water is previously purged of dissolved gases. The dopant, molecular oxygen, causes an upshift of 7 cm^{-1} in the D* peak. Small amounts of ethanol added to water can quench its doping effect. We have also demonstrated that trace amounts of hydrogen peroxide (up to 1 wt %), also generated during sonication, are not the dopant species but are indeed activated by Fe nanoparticles. Hydrochloric acid is also not a dopant. The additive SDS shows significant p-type doping behavior, which we attribute to the sulfate (electron-acceptor) group that overwhelms the doping characteristics of molecular oxygen. Aqueous suspensions of undoped SWCNTs can be achieved by sonication in a mixture of water, ethanol, and Triton-X. To manipulate, position, and use the SWCNTs for potential applications, the effect of preprocessing must be considered. Although sonication provides a great tool to quickly disperse the SWCNTs, it also influences the chemistry of the SWCNTs. Further studies are required to garner a better understanding of the effect of sonication on reactive oxygen species, DNA,[51] and even surfactants[46] in conjunction with SWCNT chemistry. Since it is becoming increasingly clear that all nanotubes that have ever undergone covalent sidewall functionalization in organic or aqueous conditions were prepared in a doped state, one has to wonder whether maybe all covalent functionalization mechanisms require doped nanotubes as starting materials.

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Supporting Information Available: Additional Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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