

Emulsions Stabilized by Carbon Nanotube–Silica Nanohybrids

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Emulsions have been stabilized by carbon nanotube–silica nanohybrids. The as-prepared nanotube–silica particles generate water-in-oil (w/o) emulsions, regardless of the water/oil volume ratio used. The emulsion volume fraction was much higher than that obtained with nanotubes only, and it was found to increase with water/oil ratio due to an increasing amount of water retained in the emulsion droplets. However, beyond a certain water/oil ratio, the emulsion fraction rapidly decreased. This point of collapse is a strong function of the amount of carbon nanotube–silica particles in the system. Oxidation of the nanohybrids by nitric acid can effectively modify the particle surfaces and change the resulting emulsion properties. The treatment in nitric acid increases the density of functional groups on the carbon nanotubes. Depending on the extent of functionalization, the effect of oxidation can vary from increasing the volume of emulsion stabilized to reversing the type of emulsion to oil-in-water (o/w). The emulsions are remarkably stable against coalescence and sedimentation and can be easily separated by filtration or centrifugation, which make them suitable for applications in interfacial catalytic processes in which the catalyst can be easily recovered after reaction.

1. Introduction

Emulsions stabilized by solid particles have been known for more than a century¹ and were named after S. Pickering, who discovered that coalescence of droplets is suppressed when solid particles are adsorbed at the oil–water interface.² It is widely accepted that this suppression in coalescence is a kinetic effect caused by a combination of the formation of a rigid interfacial film and the increase in viscosity of the continuous phase.^{3–9} One of the attractive features of Pickering emulsions is the great easiness for breaking the emulsion and recovering the two phases when needed.^{3,10} Applications of solid-stabilized emulsions in various fields have been described in several articles and patents. For example, emulsifier-free cosmetic preparations have been proposed, in which finely dispersed particles are adsorbed at the interface generating oil-in-water emulsions. Bragg¹¹ has described a method for petroleum recovery by injection of emulsions stabilized by undissolved solid particles, which are partially oleophilic. The resulting particle-stabilized emulsion can be used as a driving fluid for displacing hydrocarbons from the porous formations. Many other types of solid particles have been applied as emulsification agents for obtaining Pickering emulsions.⁹ To segregate to the interface of two liquid phases instead of to one of the phases, particles need to be amphiphilic/amphiphobic, partly

wetted by each of the two phases.¹² Depending on whether the particles are more hydrophilic or more hydrophobic, they tend to stabilize oil-in-water or water-in-oil emulsions, respectively.^{9–13} Particle size,¹⁴ particle concentration,¹⁵ oil/water ratio,^{16,17} pH,¹⁸ salt concentration,¹⁹ and solvent type²⁰ all have been found to be crucial in determining the resulting emulsion properties.¹⁰

In this contribution we describe the behavior of emulsions stabilized by carbon nanotube–silica hybrids. Single-walled carbon nanotubes (SWNT) have unique structural and electronic properties.²¹ Their hydrophobic nature^{22,23} is well recognized, but it is also known that they can be poorly suspended in organic solvents.²⁴ It has been shown that nanotubes can undergo self-assembly at the oil–water interfaces.^{25–27} Specifically, water-in-toluene emulsions can be stabilized by pristine SWNTs²⁸ and single-stranded-DNA-modified SWNT²⁹ in which the emulsion droplet diameters decrease as a function of the SWNT concentration. Ziegler and co-workers³⁰ have used the amphiphobic nature of SWNTs to develop an effective purification method. They

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found that bundles are selectively removed from aqueous dispersions by trapping them at the water/toluene interface, making high-quality gum arabic-suspended SWNTs comparable to those prepared by ultracentrifugation.

Surface wettability and particle size are two important parameters for controlling emulsion properties,⁸ but they are not easily controlled in pristine SWNTs. The SWNT–silica hybrids discussed in this contribution allows us to control these properties. The CoMoCAT synthesis process developed by our group several years ago is capable of consistently producing SWNTs of high quality.^{31,32} Moreover, the process employs sub-micrometer silica particles as a catalyst support. Consequently, the as-produced SWNT/catalyst composite is an interesting combination of hydrophobic/hydrophilic species. We have recently used this nanocomposite as an electrically conductive polymer filler that greatly helps dispersing the nanotubes in polymers.³³ For example, we found that for a given nanotube load it is possible to greatly vary the conductivity of polymer composites by simply varying the type of silica employed. Because a significant portion of the cost of nanotube materials is the purification step, the SWNT–silica nanohybrids offer the added benefit that they do not need to be further purified, since essentially they are the as-produced product of the CoMoCAT process. Therefore, SWNT–silica appears as an interesting system to be used in the stabilization of emulsions.

As mentioned, the amphiphobic nature of pristine SWNTs³⁴ makes them accumulate preferentially at the water/oil interface instead of dispersing in any of the bulk phases.²⁸ At the same time, silica particles have been extensively studied for oil-in-water Pickering emulsions as hydrophilic emulsifiers.^{3,15,16} Therefore, we anticipate that the SWNT–silica combination offers a unique structure that can offer great flexibility in controlling the surface wettability by adjusting the carbon/silica ratio, silica particle size, nanotube length, and surface functionalities, which in turn can be varied by varying reaction conditions and surface treatments. Thus, it is possible to modify the distributions of partitioning coefficients between oil and water.

In this contribution, we report the preparation of water-in-oil and oil-in-water emulsions with variable fractions of emulsion volume by using the carbon nanotube–silica nanohybrids as stabilizers. For a given water/oil ratio, the volume fraction of emulsion obtained with the nanotube–silica nanohybrids is much higher than the fractions obtained under the same conditions with either nanotubes or silica particles alone. The effects of varying the water/oil volume ratios, the concentration of added solids, and the functionalization of the nanotube surface on the type of emulsion formed, emulsion droplet size, and total emulsion volume, have been investigated. Potential applications of these solid emulsifiers as interfacial catalysts and for emulsion polymerization are proposed.

2. Experimental Section

2.1. Materials. Decalin (>98%), cyclohexane (>99%), and toluene (99.9%) were provided by Fluka, Fischer Chemical, and Avocado Research Chemical, LTD, respectively. Water was purified by circulating through two ion exchangers (Cole-Parmer Inc.). SWNTs were obtained via our own CoMoCAT synthesis method. A detailed description of the CoMoCAT method can be

found in previous publications and patents.^{29,32,35,36} In brief, the silica-supported Co–Mo catalyst is synthesized by impregnating appropriate amounts of cobalt nitrate and ammonium heptamolybdate over SiO₂; the silica used in this case was a HiSil 210 (primary particles $d < 50$ nm, BET area 135 m²/g, from PPG). The total metal loading was 2 wt % at a Co/Mo molar ratio of 1:3. After reduction in H₂ at 500 °C, the catalyst is heated in He flow to 750 °C and then exposed to a flow of pure CO for 1 h. The as-produced material was passed through a microfluidizer to achieve an uniform SWNT–silica aggregate size of about 1 μ m. The carbon weight percentage of the products was characterized by a total carbon analyzer and determined to be about 7%. The purified SWNT (SG 65) were provided by SouthWest Nanotechnologies Inc. (SWeNT).

2.2. Characterization Techniques. The SWNT–silica nanohybrids were characterized by Raman spectroscopy, electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The Raman spectra were acquired on a Jovin Yvon-Horiba Lab Ram equipped with a charge-coupled detector and a He–Ne laser (632 nm) as excitation source. The TEM images were obtained on a JEOL JEM-2000FX. The XPS spectra were recorded on a Physical Electronics PHI 5800 ESCA system, equipped with an Al K α X-ray anode operated at 350 W and 15 kV. The base pressure of the main chamber was kept at about 1.0×10^{-8} torr.

2.3. Emulsion Preparation. Before preparation of the emulsions, the SWNT–silica nanohybrids were presonicated in water for 3 h (Fisher Scientific, 600 W, 20 kHz). It was found that this presonication step is important to achieve a high extent of emulsification and small droplet size. The aqueous solutions containing the sonicated SWNT–silica nanohybrids were mixed with different amounts of decalin in a second sonication step, for 15 min. During this step, a homogeneous emulsion is formed, which remains between the water (bottom) and the organic (top) phases. The interfaces between the three phases can be clearly distinguished given that essentially all of the SWNT–silica nanohybrids remain suspended in the emulsion fraction. The characteristics of the prepared emulsions were monitored on an Olympus Mplan microscope immediately after each preparation. The average sizes were estimated based on the images of several emulsion droplets. The volume fraction of the emulsion phase was measured after suspending the homogenized solution for 1 h.

3. Results and Discussion

3.1. Characterization of Dry SWNT–Silica Nanohybrids. Before being used in the stabilization of the emulsions, the SWNT–silica nanohybrids, ultrasonicated in water, were characterized by a combination of techniques. Figure 1a shows a TEM image of an SWNT–silica aggregate. It is seen that the sizes of the primary silica particles are rather uniform, around 50 nm in diameter. The SWNT bundles can be clearly seen, with a bundle diameter around 10 nm, which is typically observed in the product synthesized by the CoMoCAT method at 750 °C.³⁷ Also, it is well-known that this process produces SWNTs of average diameter of 0.8 nm, with the (6,5) chirality as the dominant species.³⁸ Figure 1b shows the Raman spectrum of the nanotubes present in the hybrid after the sonication step. Raman spectroscopy is typically employed to evaluate the purity of the SWNT product and to estimate the presence of defects based on two characteristic bands, an intense band below 1600 cm^{−1}, typical of sp² ordered carbon (G band), and a smaller band around

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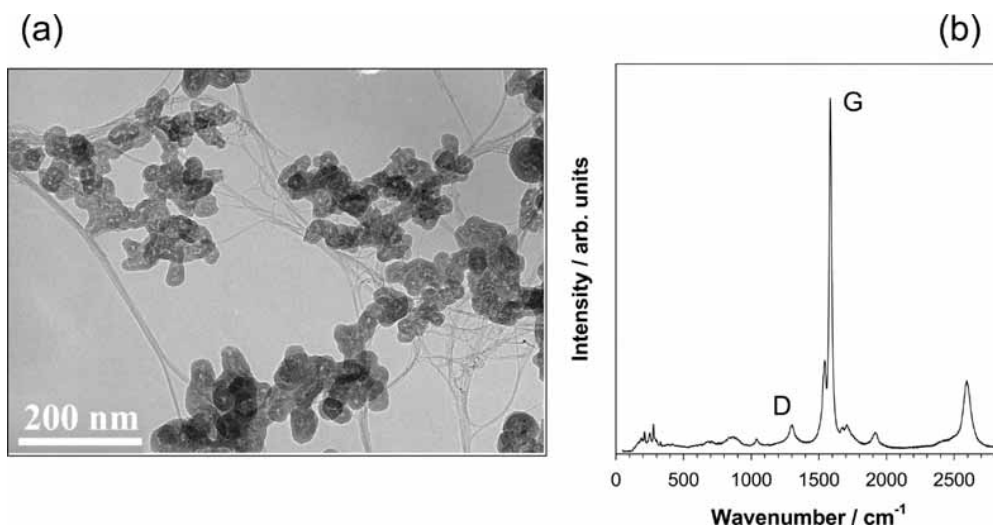


Figure 1. SWNT–silica nanohybrids (containing ~7 wt % SWNTs) used in the study after ultrasonication in water for 3 h (Fisher Scientific horn sonicator, 600 W, 20 kHz). (a) TEM image. (b) Raman spectrum.

Table 1. Surface Concentrations of Different Elements on the SWNT–silica Hybrids Ultrasonicated in Water for 3 h

element (sensitivity factors)	C 1s (0.314)	O 1s (0.733)	Si 2p (0.368)	Co 2p (3.529)	Mo 3d (3.544)
atomic concentration (%)	18.05	58.35	23.60	traces	traces

1300 cm^{-1} , typical of sp^3 carbon associated with defects (D band).³⁸ In this case, the G/D band ratio of the dry SWNT–silica nanohybrids is very high, indicating a low amount of carbon impurities and imperfection in the sonicated SWNT.³⁹ Table 1 summarizes the information obtained by XPS for the sonicated and dried SWNT–silica nanohybrids. The signals corresponding to Co and Mo, used as catalytic species in the synthesis of the SWNT, were practically negligible, indicating that these metals remain under the carbon species. From the relative intensity of the C(1s) signal compared to the other elements, the surface fraction of carbon for the sonicated nanohybrids can be quantified to be around 18.0%, which is significantly higher than the bulk concentration of 7 wt % C, as determined by TGA.

3.2. Water-in-oil Emulsions Stabilized by the SWNT–Silica Nanohybrids. The SWNT–silica nanohybrids characterized above were found to efficiently stabilize emulsions from oil/water mixtures. Figure 2a shows a diagram illustrating the appearance of an emulsion prepared by homogenizing sonicated nanohybrids in equal volumes of water and decalin to get a concentration of 2 g/L, and further sonicating for 15 min. The emulsion phase accounts for ~40% volume fraction of the total liquid. This fraction coexists between the two one-phase fractions, oil and water. The microscopic image taken for the liquid droplets acquired from the emulsion phase shows that the average emulsion droplet sizes appear to be around 3–20 μm , tens of times smaller than those prepared by only SWNT.³⁰ Figure 2b demonstrates that in this case the emulsion is of the w/o type, determined in the dye solubility test by tracing the colors of the emulsion droplets and the continuous phase after adding a green water-soluble dye (fluorescent Na salt) appearing inside the droplets, and a red oil-soluble dye (Sudan III), appearing in the continuous phase.

Figure 2c shows the well-known mechanism by which w/o emulsion droplets are stabilized by particles preferentially hydrophobic, as is the case of the SWNT–silica nanohybrids. The dominant hydrophobicity in the SWNT–silica nanohybrids make the particle surfaces wetted more by the oil phase, hence resulting in a high contact angle of the particles at the oil–water and the formation of the w/o structure. By contrast, as shown

below, one can reverse the emulsion by increasing the hydrophilicity of the nanohybrids.

3.2.1. Effect of Varying the Oil/Water Ratio. We have found that the amount of emulsion stabilized by the nanohybrids and the size of the droplets depend on several factors that include the o/w ratio, concentration of SWNT–silica nanohybrids, sonication time, etc., and can be modified via surface modifications. For example, it is known that changing oil/water volume ratio can affect the emulsion stability and even invert the emulsion type.^{14,17,40} However, as shown below, regardless of the water/oil ratio the emulsions stabilized by the as produced SWNT–silica nanohybrids are always w/o. This is in good accordance with the strong hydrophobicity previously reported for the pristine SWNT.²³

Figure 3 summarizes the volume fraction of emulsion (left axis) and the droplet size (right axis) obtained at increasing water/decalin volume ratios for the two SWNT–silica particle concentrations (0.2 and 0.075 wt %). The variation in emulsion fraction with the water/oil ratio is remarkable. The emulsion fraction rapidly increases with the water/oil ratio up to a point at which it abruptly forms droplets. Different maximum values are obtained depending on hybrid particle concentration. For the higher particle concentration (0.2 wt %), more than 50% volume fraction of emulsion can be obtained at a water/decalin volume ratio of ~1.2/1. By contrast, at lower particle concentrations, not only the maximum emulsion fraction is significantly lower, but also it occurs at a lower water/oil ratio. That, is the maximum emulsion fraction is about 35%, and it happens at a water/oil ratio around 0.4/1.

The graph on the right panel shows that the emulsion droplet sizes also go through a maximum at intermediate water/decalin volume ratios, and this trend is particularly obvious for the 0.075 wt % case. The initial increase seen in both, emulsion volume and droplet size, with increasing amount of water phase in the mixture, is mostly due to a higher amount of water filling the

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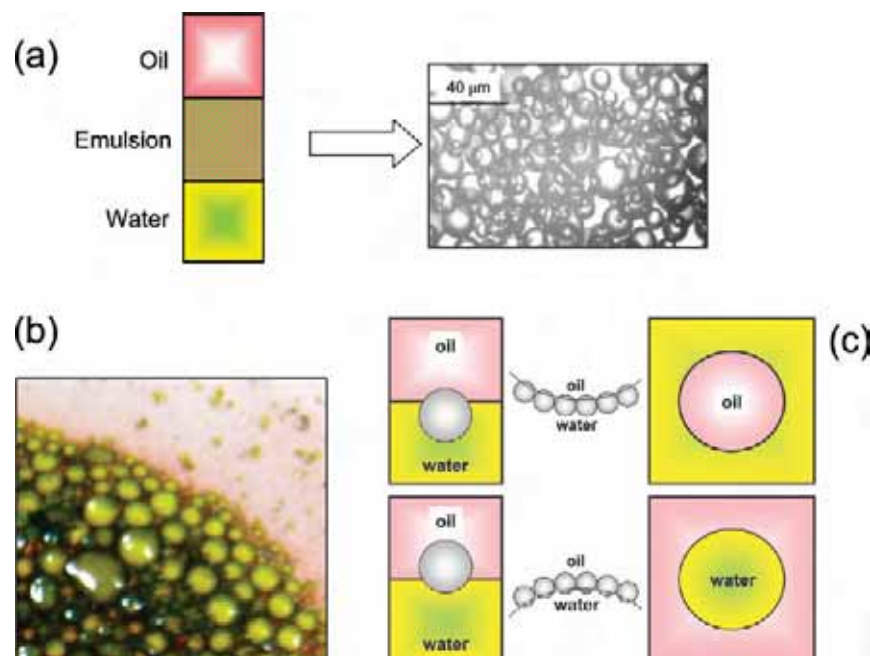


Figure 2. (a) Schematic description of the three fractions observed in a typical emulsion system together with a microscopy image of the emulsion fraction. (b) Color photograph of the emulsion prepared from SWNT–silica hybrids. Water-soluble dye (green color, fluorescent Na salt) and oil soluble dye (red color, Sudan III) were added to identify the water-in-oil type of the emulsion. (c) Schematic description of the stabilization mechanism of the oil-in-water and water-in-oil emulsions.

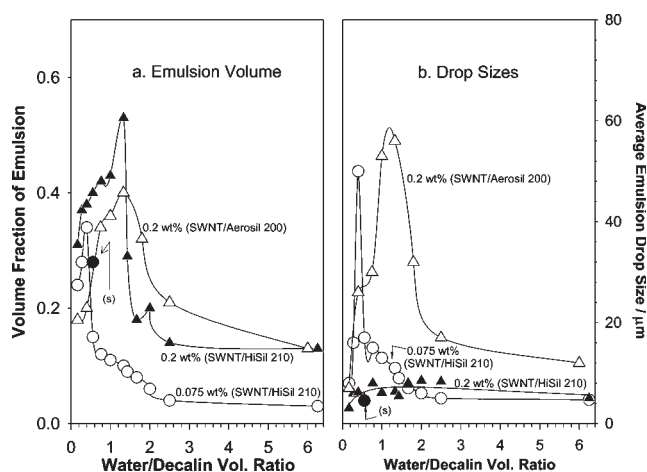


Figure 3. Effect of varying the water/decalin volume ratio on (a) emulsion volume fraction and (b) decalin droplet size. The SWNT–silica particle concentrations were fixed at 0.2 wt % (▲) and 0.075 wt % (○), respectively. Data for emulsions prepared with 0.2 wt % SWNT–silica (Aerosil 200) with small silica particle sizes are indicated with open triangles (△). A single data point obtained with pure SWNT is also shown as a solid circle (●) indicated with the letter (s).

droplets in the emulsion, making them larger in size. This process has a limit, beyond which the SWNT–silica nanohybrids can no longer stabilize the water droplets and the emulsion collapses. That is, the SWNT–silica nanohybrids remain in a higher state of agglomeration within the decalin phase, as clearly observed by optical microscopy (data not shown). These aggregates may increase the viscosity¹⁵ and negatively affect the emulsion formation.^{16,41} It is worth mentioning that the trends reported here are

quite general, and we have also observed similar behavior with a number of other organic solvents and conditions.

It has been previously shown that varying particle size of the emulsifiers can greatly affect the emulsion properties and even invert the emulsion type.¹⁴ To illustrate this effect, we characterized the emulsions prepared by SWNT/silica hybrids synthesized by CoMoCAT using Aerosil 200 silica (primary particles $d \approx 12$ nm, BET area 200 m²/g) as catalyst supports. The amount of SWNT in these hybrids (~ 7 wt %) was close to those using HiSil 210 silica as support, which allowed us to compare only the effect of silica particle size, at constant nanotube content. Overall, the results with the smaller particle silicas showed that the trends observed for the SWNT/silica (HiSil 210) hybrids are still valid for the smaller silica particle hybrids. Likewise, with these hybrids the type of the emulsions prepared was still w/o type, as observed with SWNT/silica (HiSil 210). However, a lower extent of emulsion volume fraction and much larger emulsion droplet sizes were found with smaller silica particles. This difference is in agreement with that observed by Binks and Lumsdon for polystyrene latex particles.¹⁴ The difference in droplet size caused by changes in silica particle size might be due to a lower hydrophile-to-lipophile balance on the smaller particle size silica/SWNT hybrids.¹⁴

Figure 3 also includes one data point obtained with pure SWNT used as emulsifiers instead of the SWNT–silica nanohybrids. Although in this comparison the total amount of solids is the same, the actual amount of nanotubes used when the emulsifier is the nanohybrid is 15 times lower than that required to obtain the same volume fraction of emulsion. That is, although pure nanotubes can also generate w/o emulsion, in agreement with the previous reports,^{29,42} the effectiveness of the hybrids is remarkable.

3.2.2. Effect of Varying Nanohybrid Particle Concentration. In standard Pickering emulsions, particle concentration has

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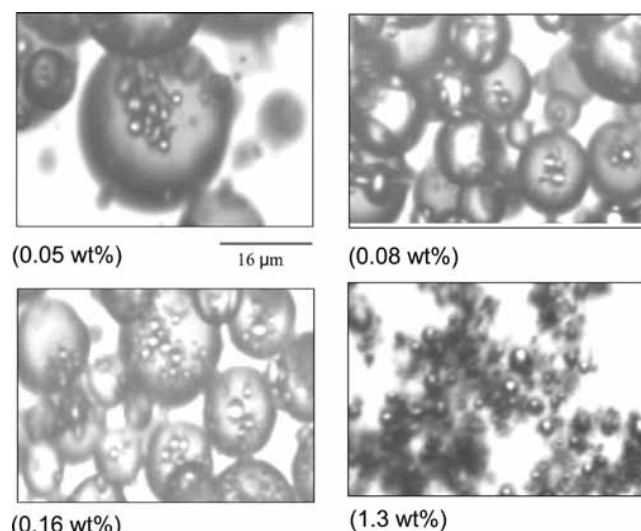


Figure 4. Microscopy images of the emulsions prepared at increasing SWNT-silica nanohybrid concentrations with a water/decalin volume ratio fixed at 0.65/1. The bar length represents 50 μm .

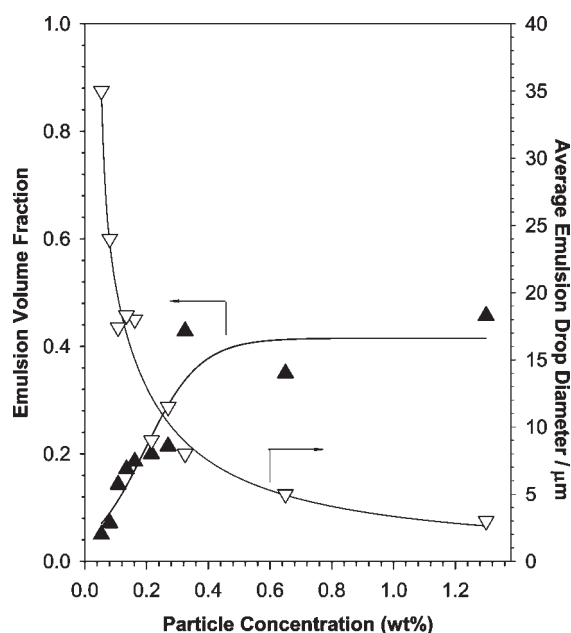


Figure 5. Emulsion volume fraction (solid symbols, left axis) and droplet average diameter (open symbols, right axis) as a function of SWNT-silica hybrid concentration.

been found to substantially affect both the emulsion stability and droplet size.^{14,15} Figure 4 shows microscopy images taken for the emulsions prepared by the SWNT-silica nanohybrids at different particle concentrations, keeping the water/decalin volume ratio at 0.65. Quantification of the observed trends is done in Figure 5, which includes more samples than those illustrated in Figure 4. The droplet size is seen to decrease as a function of particle concentration, a trend previously observed for other emulsion systems.¹⁵ At high particle concentrations a severe particle flocculation, similar to those observed at high water/decalin ratios, was observed; the high viscosity of the continuous phase may again play a role in stabilizing droplets of very small size. Interestingly, the emulsion droplets appear to cluster at all particle concentrations, perhaps as a result of nanotube-nanotube

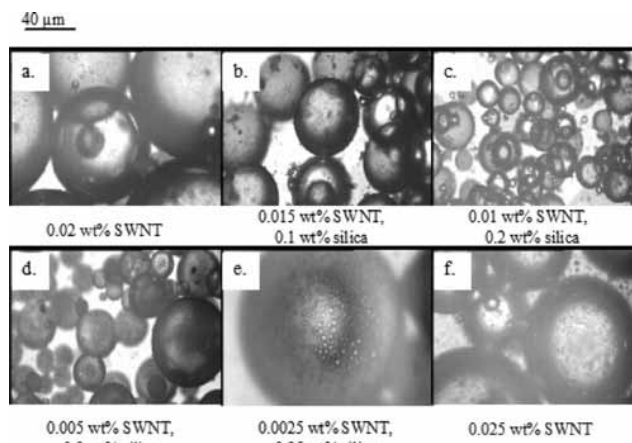


Figure 6. Microscopy images of emulsions prepared by physical mixtures with different amounts of purified SWNTs and silica particles. The water/decalin volume ratio was fixed at 0.4/1. The bar length represents 40 μm .

attraction. Similarly, these attractive forces may be responsible for the observed flocculation of the excess solid particles around the emulsions droplets with formation of a rather open network structure. The emulsion volume fraction and average droplet appear to follow opposite trends. For solid concentrations higher than 0.4 wt %, the addition of the nanohybrids does not increase the emulsion volume, and only result in increasing extent of the formation of the composite flocs as found in the oil phase (Figure 4), and a slight decrease in the average droplet diameter. However, for the values below 0.4 wt %, almost a linear increase as a function of particle concentration can be found, in accordance with the previous reports using other solid particles as emulsifiers.¹⁵ Decreasing solid particle concentration not only leads to larger emulsion droplets but also to a greater heterogeneity of the droplet size, implying a less efficient emulsification under these conditions.

3.2.3. Formation of Multiemulsions. Interestingly, multi-emulsion droplets (o/w/o) can be observed for particle concentration lower than 0.16 wt %, and more than half of the emulsion droplets were found to possess this structure for the lowest particle concentration (0.05 wt %). The inner o/w emulsion droplets are around 1 μm in diameter. For particle-stabilized emulsions, multiemulsion structures have been proposed to form in the presence of both hydrophobic and hydrophilic particles⁴³ or in the case of phase inversion.¹⁵ In this case, it might be expected that some silica particles with low coverage of SWNT may also migrate to the decalin/water interface and form the o/w type of emulsion. The TEM images (Figure 1) and XPS data (Table 1) clearly show that some silica particles are barely covered by carbon nanotubes. It is interesting that this multiemulsion structure can only be observed when decalin is used as organic phase, but not when using toluene, hexane, or cyclohexane. This disparity may be due to the different emulsion stabilities obtained when using decalin as organic phase compared to other organic compounds. Decalin generated the highest amounts of emulsions with the smallest average droplet sizes, which might be related to the significantly higher surface tension of decalin (~ 32 mN/m) compared to that of the other hydrocarbons investigated (~ 18 to 25 mN/m).

The formation of multiemulsions is related to the different hydrophobic properties of the SWNT-silica particles. When we

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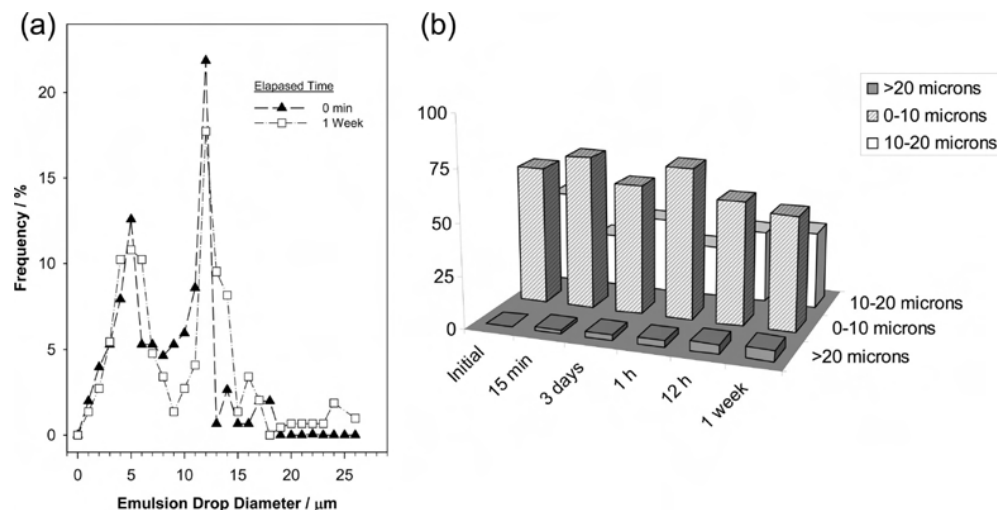


Figure 7. (a) Distribution of droplet diameters for a freshly prepared emulsion (▲) and after one week (□). The water/oil ratio was 0.65/1 and the SWNT–silica hybrids concentration was 0.15 wt %. (b) Bar graph showing the time evolution of the three major droplet diameter fractions for the same emulsion.

compared the emulsions stabilized by SWNT–silica nanohybrids to those stabilized by either purified SWNT or physical mixtures of SWNT and silica particles, interesting differences were observed. Figure 6 shows the microscopy images taken for the emulsion droplets formed after adding physical mixtures containing different amounts of silica (hydrophilic) and purified SWNT (hydrophobic) into decalin/water solutions. All the emulsions were prepared keeping the water/decalin volume ratio fixed at 0.4/1. As seen in the sequence in Figure 6, panels a to e, as the amount of the silica particles added increased and SWNT decreased, the emulsion droplet sizes initially decreased; but further addition of silica particles resulted in an opposite effect. At this point, the decrease in SWNT concentration becomes the dominant factor affecting the droplet diameters. Most importantly, under these conditions multiemulsion droplets can be observed (Figure 6, panels d and e), indicating that low concentration of hydrophobic particles may lead to large droplets and formation of these multiemulsion structures. Figure 6f shows one image taken for the same concentration of SWNT as that in Figure 6e, but without the addition of silica particles. As mentioned above, pure SWNTs produce much less amount of emulsion, the droplets are of smaller size, and no multiemulsion structure can be observed, confirming the role played by the silica particles.

3.2.4. Stability of Emulsions. We have observed that the emulsions prepared with the SWNT–silica nanohybrids exhibit high stability, even when heated as high as 70 °C or when placed in acidic media (i.e., pH < 1). On the other hand, these emulsions can be easily separated by mechanical means. We found that two clean liquid phases are readily obtained after centrifugation or after filtration. Moreover, the filtered nanohybrids can be reused to form a new emulsion.

3.2.5. Droplet Size Distribution. Figure 7 shows the droplet diameter distribution of the different emulsions prepared with a water/oil ratio of 0.65/1 and 0.15 wt % SWNT–silica nanohybrids. It is expected that coalescence, sedimentation, and Ostwald ripening may lead to changes in size distribution. In fact, small changes are observed as a function of time, but they are relatively small. Right after the preparation, the emulsion appears to be bimodal, exhibiting two main diameter distributions centered at around 5 and 12 μm; the elapsed time of even a week does not significantly affect the location of the center and width of the

diameter distributions, evidencing the remarkable stability typical observed for solid-stabilized emulsions. It is worth noting that after three days a few emulsion droplets of diameters larger than 24 μm start being seen, indicative of a small extent of Ostwald ripening. This fraction seems to increase slowly with time.

3.3. Oil-in-water Emulsions Stabilized by the SWNT–Silica Nanohybrids. To gain more control on the type of emulsions that we can obtain, we attempted to modify the hydrophilicity of the SWNT–silica nanohybrids, based on the concept that the emulsions are o/w or w/o depending on the hydrophilic/hydrophobic balance. Accordingly, we attempted to enhance the hydrophilicity of the hydrophobic component (SWNT) and determine whether emulsion inversion can be achieved.

3.3.1. Nitric Acid Modification of SWNT–Silica Nanohybrids. Oxidization by nitric acid has proven to be a convenient way for grafting functional groups (–COOH) on wall defects and particularly at the ends of SWNT, a process that greatly changes the hydrophilicity of SWNTs.^{44–46} Yi et al. have recently found that carbon nanotube capsules can be self-assembled in w/o emulsions when MWNTs are treated with nitric acid.⁴⁷ We have found that the same strategy is highly effective for modifying the emulsification properties of SWNT–silica nanohybrids. By controlling the extent of SWNT functionalization we have been able to manipulate the resulting emulsion properties. To reach varying degrees of functionalization, the SWNT–Silica nanohybrids were first bath sonicated in 8 M nitric acid at different temperatures (25–90 °C) and for different times (1–3 h), then thoroughly washed with water until the pH was neutral. The resulting solids were dried, then horn-ultrasonicated in water for 3 h, and homogenized in different amounts of decalin and water to prepare the emulsions. The extent of functionalization was monitored by following the absolute intensity of the G band, as well as the D/G band ratio in the Raman spectrum.

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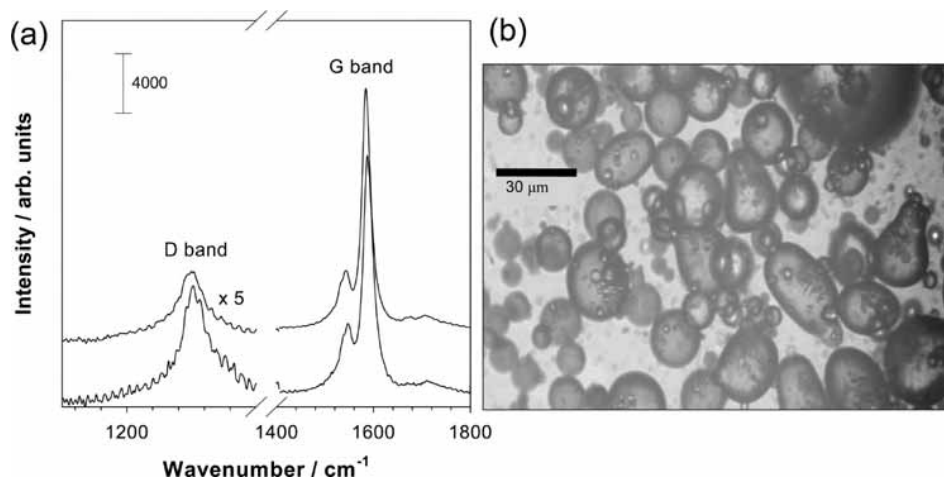


Figure 8. Characterization of the emulsions prepared by the SWNT-silica hybrids oxidized by bath sonication in 8 M HNO₃ for 3 h at 25 °C. (a) Comparison of the Raman spectra acquired for the untreated (upper spectrum) and oxidized (lower spectrum) SWNT-silica hybrids. (b) Microscopy image of the emulsion containing 0.2 wt % oxidized (25 °C) SWNT-silica hybrids (water/decalin volume ratio = 1.8/1).

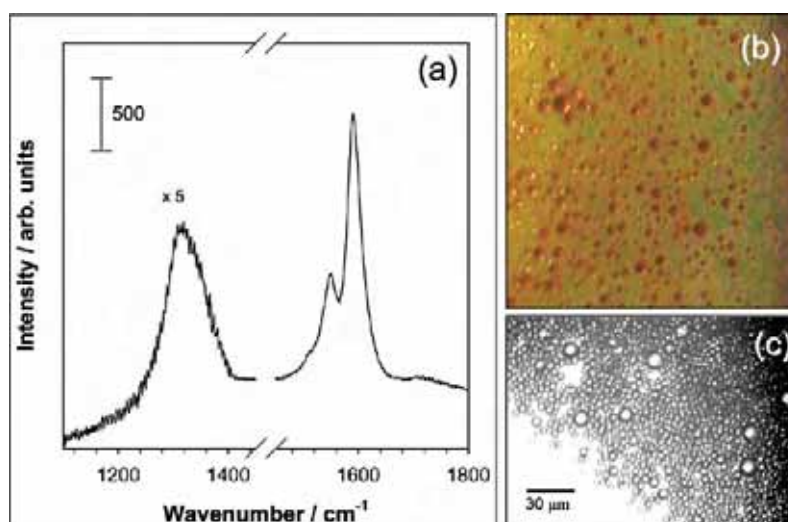


Figure 9. (a) Characterization of the emulsions prepared by the SWNT-silica hybrids heavily oxidized by heating in 8 M HNO₃ at 90 °C for 3 h. (b) Photographs of the emulsion using the dye test, that is, water-soluble green dye and oil-soluble red dye. (c) Microscopy image of the oil-in-water emulsion with heavily oxidized nanohybrid concentration of 0.2 wt % and water/decalin volume ratio of 1/1.

For example, Figure 8a shows the Raman spectrum acquired for the SWNT-silica nanohybrid sample oxidized in nitric acid at room temperature for 3 h. Clearly, compared with the untreated nanohybrids (Figure 1b), the mild oxidation leads to a higher intensity of the D band at $\sim 1300\text{ cm}^{-1}$, indicating the generation of oxidized defects, which increase the hydrophilicity of the SWNT.⁴⁴ Figure 8b shows one microscopic image taken for the emulsion prepared by 0.2 wt % RT oxidized SWNT-silica nanohybrids with a water/decalin volume ratio of 1.8/1. For this mildly oxidized sample, the emulsion type still was w/o. However, an interesting phenomenon starts to occur. Many of the emulsion droplets were not spherical in shape. This clearly indicates that surface modification of nanohybrids dramatically changes the particle hydrophobicity and modifies the interfacial tension of the emulsion droplets.⁴⁸

3.3.2. Emulsion Inversion from w/o to o/w. Emulsion inversion in standard emulsions can be accomplished by simply varying the water/oil ratio. This is not the case on the emulsions stabilized by SWNT-silica particles. As the oxidation

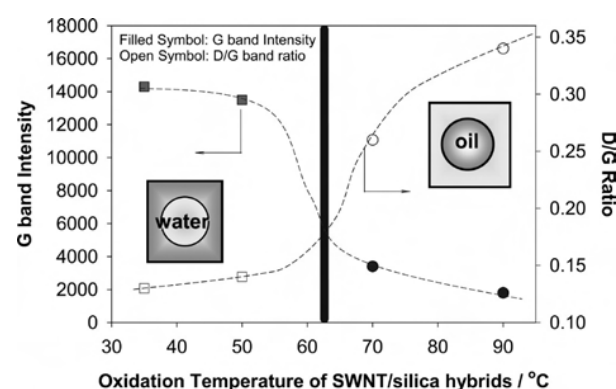


Figure 10. Characterization of SWNT/silica hybrids oxidized at different temperatures by Raman spectroscopy. G band intensity (solid symbols, left axis) and D/G band ratio (open symbols, right axis).

temperature increases beyond 60–70 °C, a more dramatic change in behavior occurs. As illustrated in Figure 9, the now heavily

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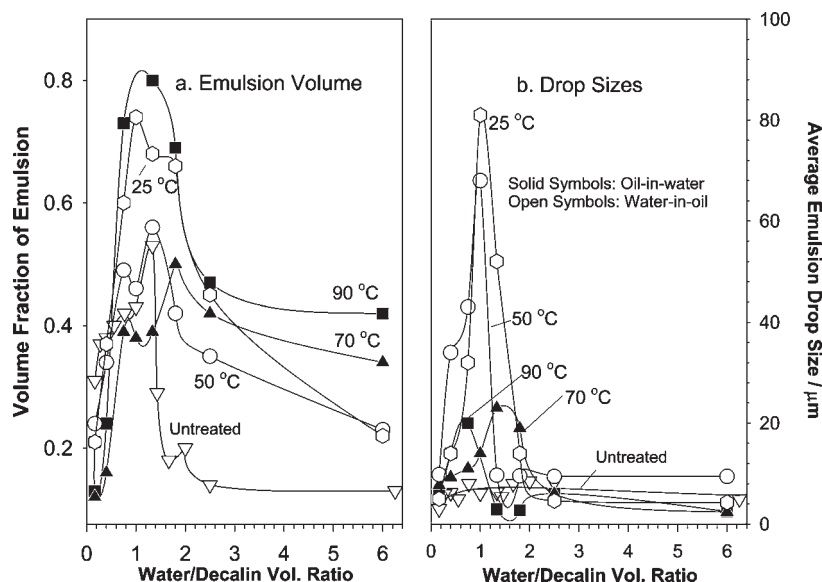


Figure 11. Effect of the oxidizing pretreatment on emulsion characteristics. Emulsion volume fraction (left panel) and emulsion drop diameter (right panel) as a function of water/decalin volume ratio for the SWNT–silica hybrids oxidized at different temperatures with hybrid concentration as 0.2 wt %.

oxidized nanohybrids are able to stabilize o/w emulsions, rather than w/o. The photo taken for the emulsion prepared by nanohybrids oxidized at 90 °C (Figure 9a) clearly shows that the dispersed phase is the oil (red oil-soluble dye added), whereas the continuous phase is water (green water-soluble dye added). In addition, the microscopic images taken for this emulsion (Figure 9b) also exhibit interesting differences compared to those taken for the w/o emulsion stabilized by untreated nanohybrids. In this case, the emulsion droplet sizes are remarkably small and uniform, and the droplets appear to be more closely packed than in the w/o emulsions.

This inversion parallels the greater extent of functionalization obtained at higher oxidation temperatures. Figure 10 shows that when the oxidation temperature exceeds 60–70 °C, the intensity of the G band greatly decreases, the D/G ratio increases, and the emulsion phase inversion occurs. Clearly, the higher extent of oxidation enhances the hydrophilic character of the nanohybrids, so the curvature of the interface changes, forcing the oil phase to the inner part of the droplet.

Figure 11 shows the emulsion volume fraction (left axis) and emulsion droplet sizes (right axis) of emulsions prepared from the oxidized and untreated nanohybrids. Similar trends were observed for all these emulsions regardless of the emulsion types, in terms of maxima in both emulsion volume and droplet sizes reached at intermediate water/decalin volume ratios. However, the emulsions stabilized by the oxidized nanohybrids can retain a larger amount of emulsion at higher water/decalin volume ratio. For example, at a water/decalin volume ratio of 1.6/1, all of the oxidized SWNT–silica nanohybrids can still produce >42% volume fraction of emulsion, whereas the untreated nanohybrids only makes about 13% volume fraction of emulsion. As a result, a much lower extent of particle aggregation is found when using these oxidized nanohybrids. In addition, the average diameters of the emulsion droplets stabilized by the oxidized nanohybrids are strongly dependent on the oxidation temperature used in the nitric acid treatment. The nanohybrids oxidized at 25 °C produce emulsion droplets with an average diameter of 80 μm for a water/decalin volume ratio of 1/1, much larger than those produced by untreated nanohybrids. However, the emulsion

droplet diameters decrease as a function of the oxidation temperature. In particular, a remarkable decrease is seen after the point at which the emulsion phase inversion happens. For example, the sample treated at both 70 and 90 °C stabilize the droplets with diameter of $\sim 2.7 \mu\text{m}$ when water/decalin volume ratio higher than 1.4, even smaller than the values obtained for the untreated nanohybrids. This indicates that the initial w/o type of emulsions might pass through a regime of instability and then invert to stable o/w emulsions as the surface hydrophilicities increase after oxidation treatment at higher temperatures.

It is important to point out that these wide variations in emulsion characteristics are highly reproducible and controllable by relatively simple pretreatments, which make the SWNT–silica nanohybrids as an attractive solid emulsifier. The emulsion volume fractions and droplet sizes can be easily manipulated by adjusting the particle concentrations and water/oil volume ratios. Compared with previously reported emulsions employing purified SWNT,⁴⁹ the ones reported in this contribution not only avoid the complex purification of SWNT but also result in much higher volume fractions of emulsions. Hence, this method appears promising in making a large quantity of stable emulsions given that these types of SWNT–silica nanohybrids are already being produced on commercial scales.

3.3.3. Potential Applications of Emulsions Stabilized by SWNT–Silica Nanohybrids. These solid-stabilized emulsions are particularly suitable for creating catalysts that operate at the water/oil interface in biphasic systems, found in important processes such as bio-oil refining or fine chemical synthesis. After carrying out the interfacial reaction, the SWNT–silica nanohybrids can be easily separated by filtration or centrifugation. Without the solids, which can be reused in subsequent reactions, the emulsion is broken and the two liquid phases are readily separated. An interesting application that we are currently investigating is using either fraction of the nanohybrid (i.e., nanotube side or the silica side) as a support for heterogeneous catalyst on which reactions can selectively take place at either the

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aqueous or oil phase. As shown here, we can modify the type of emulsion from w/o to o/w, so different types of liquid biphasic reactions can be carried out. We envision depositing different catalysts on either side of the interface and selectively convert functional groups of molecules that are water-soluble or oil-soluble at the same time in a selective manner. For example, this “phase selectivity” might allow us to work with complex mixtures and selectively hydrogenate water-soluble molecules in the aqueous phase in the presence of oil-soluble molecules that we do not want to hydrogenate. Working with emulsions, one can have the added benefit of catalytically converting at the interface molecules that are soluble in one phase so they become insoluble products in that phase and migrate to the other phase for easy separation.

Another important application of these emulsions is the preparation of nanotube-based composites via emulsion polymerization. In-situ emulsion polymerization has been reported for Pickering emulsions stabilized by Janus particles.⁵⁰ In previous studies, we have used surfactant-stabilized emulsions to generate a dispersed medium for polymerization, after which the resulting composite had a good dispersion of the nanotubes.⁵¹ Using the solid emulsifiers reported in this contribution, particularly those stabilizing o/w emulsions, we plan to expand the studies to

produce SWNT–silica–polymer composites, which already have shown promise to enhance electrical and mechanical properties.³³

4. Conclusions

We have shown that particle-stabilized w/o and o/w emulsions can be prepared by SWNT–silica nanohybrids. Water/oil volume ratio, particle concentration, and nitric acid oxidation pretreatment greatly affect the emulsion type, emulsion volume fractions, and average droplet diameters, in a reproducible and controllable way. The resulting emulsions exhibit good resistance to coalescence and sedimentation. This novel way to prepare emulsions by supported SWNT shows great advantage in achieving high emulsion volume compared with using only SWNT, and might open new opportunities for utilizing these materials as supports for heterogeneous catalysis to be used in biphasic systems. These catalyst/emulsifiers would be easily removed from the reaction system, breaking the emulsion, and obtaining the two liquid phases containing products. Also, the solid-stabilized emulsions of the o/w type can be used to conduct in situ polymerization with nanotubes kept in a highly dispersed state at the oil/water interface.

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