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Aggregation Behavior of Multiwalled Carbon Nanotube-Titanium Dioxide Nanohybrids: Probing the Part-Whole Question

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Abstract

Multiwalled carbon nanotube-titanium dioxide (MWNT-TiO₂) nanohybrids (NHs), a promising support for electrocatalysts, have a high likelihood of environmental release. Aggregation of these NHs may or may not be captured by the sum of their component behavior, thus necessitating a systematic evaluation. This study probes the “part-whole question” by systematically evaluating the role of TiO₂ loading (C:Ti molar ratios of 1:0.1, 1:0.05 and 1:0.033) on the aggregation behavior of these NHs. Aggregation kinetics of these in-house synthesized (using a sol–gel method) NHs and the components is investigated with time-resolved dynamic light scattering in the presence of mono- and divalent cations and with and without Suwannee River humic acid. A deviation in the aggregation behavior from classical electrokinetic theory has been observed which indicates that the material complexity has a strong influence in the observed behavior; hence other material attributes (e.g., fractal dimension, surface roughness, charge heterogeneity, etc.) should be carefully considered when studying such materials. The sum of the aggregation behavior of the parts may not capture that of the whole (i.e., of the NHs); aggregation depends on the TiO₂ loading and also on the hybridization process and the background aquatic chemistry.

Graphical Abstract

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Supporting Information

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Material synthesis; TiO₂ and MWNT-ISP preparation method; preparation of aqueous suspensions; summary of the aggregation experiments; summary of SLS experiments; DLVO modeling; AFM sample preparation and roughness measurements; static light scattering (SLS) procedure; coefficient determination for the best-fit line(s) in the reaction limited aggregation regime; Hamaker constants obtained from the DLVO curve fitting; fractal dimension (D_f) values of MWNTs and NHs; experimental setup for NH synthesis; representative HRTEM micrographs of MWNT and TiO₂ nanocrystals; characteristic XPS spectra for C 1s in oxidized MWNT and for Ti 2p in MWNT-TiO₂ NH; characteristic XPS survey spectra for oxidized MWNT and MWNT-ISP; characteristic XPS survey spectra for NH-High, NH-Mid, and NH-Low; XRD spectra for oxidized MWNTs, MWNT-TiO₂ NHs, and TiO₂ components; AFM micrographs; and SLS raw data and estimated fractal dimension values (PDF)

Notes

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INTRODUCTION

Materials science and engineering has evolved from passive nanostructures to multicomponent nanoheterostructures, known as nanohybrids (NHs).¹ These complex NHs aim to meet the increasing demand for multifunctionality in various applications including biomedicine,² biomedical imaging,³ supercapacitors,⁴ optoelectronics,⁵ solar cell technology,⁶ electrochemical fuel cells,⁷ electrocatalysis,⁸ and chemical sensing,⁹ among many others. Such widespread application of NHs will likely be associated with environmental release and exposure. Since these NHs are multicomponent heterostructures, their environmental behavior will be influenced by the material composition. A systematic assessment of environmental health and safety (EHS) of these NHs is necessary to determine if these multicomponent composites' behavior can be captured by that of the sum of their component parts'.^{10–13} In other words, it is necessary to assess whether the NHs function as heterounits and manifest unique behavior or whether their demonstrated behavior mirrors that of the component mixture's.

Commercialized NH-embedded products have entered markets with increasing demands and have resulted in an estimated revenue of \$2.2B in 2014.¹⁴ Carbon nanotube-metal oxide NHs are one of the most used heterostructures, particularly as catalyst supports in electrochemical fuel cells.¹⁵ One such NH, MWNT-TiO₂ is used as anodic materials in microbial fuel cells for performance improvement¹⁶ as well as a support for platinum (Pt), a widely used catalyst in proton exchange membrane fuel cells.¹⁷ The MWNT backbone of the MWNT-TiO₂ NHs provides corrosion resistance and enhanced electrical conductivity,¹⁸ while TiO₂ increases the stability and durability of Pt against diffusion, detachment, and dissolution.^{19–21} The global decrease in the Pt reserve requires extraction and recovery of this metal (employing harsh acid-digestion techniques) at the end of the lifecycle of the fuel cells.²² MWNT-TiO₂ NHs that are incorporated into the fuel cell design to support Pt catalysts in fuel cell industry thus have a high likelihood of release during the end of life recovery process.

The aggregation behavior of MWNT and TiO₂ components has been studied extensively.^{23–27} Carbon nanotubes (CNTs)^{24,28–33} and TiO₂²⁶ follow the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) type behavior. The dominant factors in CNT aggregation are found to be surface oxidation^{25,30} and solution chemistry^{24,28,31} while nanoscale TiO₂ aggregation has been shown to have been influenced by size,²⁶ surface area,²⁶ composition,

²⁶ shape,²⁶ and surface functionality.²⁷ However, when hybridized, these component materials (i.e., CNTs and TiO₂) with uniquely different physicochemical properties will present a complex interface, which will likely lead to unusual EHS behavior that cannot be predicted by its components. A recent study on EHS of NHs, i.e., transport of carboxymethylcellulose (CMC) modified CNT-Fe₃O₄ NH through porous media, has demonstrated increased deposition of the hybrids compared to that of the component CNTs. The authors claimed that the NHs' larger aggregate size compared to that of the CNTs³⁴ controlled the observed behavior. Complexity of the materials and their unusual behavior manifestation are being realized in the literature.^{10,11}

Composite materials bring in complexity and heterogeneity to the surface by virtue of the combination of multiple materials with unique chemical origin. Hybridization can alter the surface potential as well as modulate the van der Waals attraction forces of the component materials.³⁵ For example, when TiO₂ nanocrystals are grown on MWNT surfaces, not only does the composition of the composites become complex, but these nano features also introduce surface roughness and charge heterogeneity. These attributes will influence how the composites will behave in the natural environment. An aggregation study³⁵ of a carbonaceous-metal oxide NH, i.e., reduced graphene oxide-TiO₂ (rGO-TiO₂) presented observational aggregation data and estimated the Hamaker constant value for the NH. However, how the NH behavior compares with that of its parts (or GO and TiO₂ components) was not assessed in this study. A more recent study on heteroaggregation of GO with hematite nanoparticles (HemNPs) reported apparent formation of GO-HemNP NH during the heteroaggregation process.³⁶ It is to be noted that since the GO and HemNP (at high GO:HemNP ratio) physicochemically interacted and possibly attached with each other, the authors' claim that these attached materials are nanohybrids is not substantiated. This study can be considered as an example of a study of mixtures, but not that of composite NHs.^{1,37} The mechanisms underlying the manifested NH behavior are challenging to determine without resolving the relative contributions from each of the components.

This study aims to answer this question by studying the aggregation behavior of MWNT-TiO₂ NHs synthesized with a wide range of Ti loading (i.e., C:Ti molar ratios of 1:0.1, 1:0.05, and 1:0.033) and their components. The C:Ti molar ratio of 1:0.1, one of the most studied MWNT-TiO₂ composition,³⁸ previously showed to have complete coverage of the MWNT surfaces with TiO₂.³⁹ A range of TiO₂ loading on MWNTs varies the complexity of the multicomponent surface and enables interfacial behavior assessment of these materials in a systematic way. A comprehensive characterization with electron microscopy, atomic force microscopy, and X-ray techniques is performed to evaluate morphological characteristics, estimate surface roughness, crystallinity, and chemical composition. Aggregation kinetics of these NHs is studied with time-resolved dynamic light scattering (TRDLS) under a wide range of monovalent (NaCl) salt concentrations. Efficacy of classical electrokinetic theory to capture aggregation behavior has been determined by fitting the experimental work with DLVO theory. Roles of ionic composition and natural organic matter are assessed estimating aggregation rates at mixed electrolyte conditions (i.e., 1 mM CaCl₂ + 7 mM NaCl or 10 mM total ionic strength) with and without Suwanee River humic acid (SRHA).

MATERIALS AND METHODS

Chemicals and Reagents. Pristine MWNTs (O.D. 8–15 nm) were procured from Cheap Tubes Inc. (Brattleboro, VT). Concentrated nitric acid, sulfuric acid, titanium isopropoxide (TTIP), NaCl (5M), and CaCl₂ (1M) solutions were purchased from Sigma-Aldrich (St. Louis, MO). Isopropanol (ISP) was obtained from Fisher Scientific (Pittsburgh, PA), and standard II SRHA (IHSS Catalog Number 2S101H) was obtained from International Humic Substances Society, Denver, CO. Aqueous suspension were prepared in 18.2 mΩ-cm (Milli-Q) water.

Material Synthesis.

The MWNT-TiO₂ NHs were synthesized using a sol–gel method described earlier³⁹ (details in the Supporting Information, [SI](#)); a method typically used to prepare NHs for fuel-cell applications. Following synthesis of the NHs, the component TiO₂ nanocrystals were prepared by complete oxidation of MWNTs from the MWNT-TiO₂ NHs. Moreover, oxidized MWNTs were exposed to the identical experimental conditions used for synthesizing the MWNTTiO₂ NHs. These heat-treated oxidized MWNTs, or MWNT-ISPs, were prepared to assess the effect of heat treatment on MWNT surface functionality and aggregation. Details of the component TiO₂ and MWNT-ISP preparation methods and aqueous suspension preparation protocol for all materials are described in the [SI](#).

Physicochemical Characterization.

The physical morphology of the synthesized NHs and the component materials was characterized with a JEOL 2010F high-resolution transmission electron microscope (HRTEM), equipped with energy dispersive X-ray spectroscopy (EDS). Electron micrographs were obtained at an acceleration voltage of 200 kV. High annular angle dark field scanning TEM (STEM) images produced micrographs showing elemental distribution on the NHs. The details of the HRTEM and EDS are described elsewhere.^{24,37,40–43} For determining the elemental composition of the dry NMs, a Kratos X-ray photoelectron spectroscopy (XPS-Axis Ultra DLD), equipped with a monochromated Al K_α X-ray source was employed. The XPS data analysis was performed by fitting the high-resolution element specific peaks assuming Gaussian–Lorentzian deconvolution and using CasaXPS software (Casa Software, Ltd., Japan). The crystallinity of the NMs was evaluated with a 600 W Rigaku MiniFlex 600I X-ray diffraction (XRD) equipment. Details of the experimental protocol for XPS and XRD analyses are described in earlier studies.^{40,44}

Solution Chemistry.

To assess the effects of monovalent cation on aggregation kinetics, 55–400 mM NaCl was used. Effect of divalent cation and natural organic matter (NOM) was evaluated by determining particle aggregation rate at 10 mM ionic strength (1 mM CaCl₂ + 7 mM NaCl) with and without 2.5 mg TOC/L standard II SRHA (International Humic Substances Society, Denver, CO). All experiments were performed at 25 °C with pH adjusted to 6.9 ± 0.1 with 0.5 M NaOH or 0.5 M HCl.

Electrokinetic Properties.

The electrophoretic mobility (EPM) of the aqueous suspensions of NHs and the component materials was measured using a Malvern Zetasizer (Malvern Instruments Ltd., Worcestershire, U.K.) at 20 °C. For each measurement, 900 μL of the NM suspension was introduced into a disposable capillary cell (DTS 1070, Malvern Instruments Ltd.). The cells were washed with DI water and ethanol between measurements. Measurements were performed in triplicate using a well-established protocol.^{24,37,40–43} To calculate electrostatic interaction (for DLVO modeling), measured EPM values were converted to ζ -potential with the Smoluchowski equation, built into the instrument software. It is to be noted that the MWNT-based NHs with inherent propensity to bend and form clusters^{31,33} do not interact as individual tubes; thus cylinder assumptions for these clustered suspensions are not appropriate.

Aggregation Kinetics.

The aggregation kinetics was measured with an ALV/CGS-3 compact goniometer system (ALV-Laser GmbH, Langen/Hessen, Germany), equipped with a 22 mW HeNe 632.8 nm laser and a high QE APD detector with photomultipliers of 1:25 sensitivity. The experimental details of the aggregation kinetics experiments and data analysis have been described elsewhere^{24,37,40,41,45} and in the SI. The critical coagulation concentration (CCC) parameters are estimated from the intersection of the best-fit lines, fitting the reaction limited aggregation (RLCA) and diffusion limited aggregation (DLCA) regimes. The R^2 values for the best-fit lines in the RLCA regime are reported to indicate relative confidence levels for the reported CCC values of the respective materials (Table S1).

DLVO Modeling.

DLVO modeling of the aggregation experiment results was performed to assess the efficacy of the model to capture the aggregation behavior of these complex NHs and to decipher mechanisms of aggregation. The stability ratios were estimated with this model, based on the Gouy–Chapman theory that employs linearized superposition approximation (LSA) for electrostatic repulsion and pairwise addition for van der Waals attraction.⁴⁶ It is to be noted that Hamaker constant was used as a fitting parameter to obtain the best-fit lines. Details of the DLVO modeling are provided in the SI.

RESULTS AND DISCUSSION

Morphological Properties and Chemical Composition.

A representative TEM (Figure S2a) micrograph of the component MWNTs shows that the tubes are mostly debundled and are free from catalyst metals with an average outside diameter of 21.3 ± 2.6 nm. It is also to be noted that the MWNTs are curved and bent, indicating the flexible nature of these tubes and propensity to form clusters. These observations are consistent with previous literature reports.^{24,28,31,33} TEM micrograph of the component TiO_2 nanocrystals (Figure S2b) shows large aggregates or sintered particles. Such aggregated structure is expected for these TiO_2 nanocrystals, since these are produced as remains upon complete oxidation of the NH-High at 650 °C.

TEM and STEM micrographs of the NHs with elemental distribution (Figure 1) confirm the presence of Ti and O atoms in all the NHs. The TEM micrographs qualitatively show that the TiO₂ nanocrystal loading is the highest in NH-High. Furthermore, TEM micrograph of the NH-Mid shows that the TiO₂ nanocrystals are evenly distributed on the MWNT surface, while that of NH-High show patchy TiO₂ nanocrystal accumulation on the surface of the already coated MWNTs (with TiO₂). Furthermore, a lowering of Ti intensity is observed in the elemental distribution series (from high to low TiO₂ loading) as shown in Figure 1.

Quantitation of the NH and component composition is performed with XPS; Figure S3(a) shows the peak positions of the deconvoluted plot indicating the presence of multiple oxygen containing moieties (i.e., carboxylates, alcohols, and carbonyls) on the MWNT surfaces, which is in agreement with previous reports.⁴⁷ Representative XPS spectrum of the NHs shows Ti peaks at 458.3 and 464.3 eV (Figure S3(b)), which match with the characteristic peaks for Ti_{3/2} and Ti_{1/2} of anatase phase TiO₂;⁴⁸ the only crystalline phase on these crystals.

Table 1 presents the elemental composition of the materials, obtained from XPS. The oxidized MWNTs' oxygen content is $10.9 \pm 0.2\%$, which decreases to 2.23% upon treatment with isopropanol and heat. Heating of the oxidized MWNTs in a nitrogen environment, which causes deoxygenation (Table 1 and Figure S4) and fixes defects on nanotube surfaces, is primarily responsible for such reduction in oxygen content.⁴⁴ Elemental composition also validates the decreasing presence of Ti in NH-High to NH-Low (Table 1 and Figure S5). The excess oxygen content (oxygen, not associated with TiO₂ nanocrystals) also decrease as the C:Ti ratio increases (Table 1). The oxygen-containing functional groups on the MWNT surface is the most likely a source for excess oxygen. These results indicate that, in the case of NH-High, heat treatment was not successful in reducing the surface oxygen groups, which likely were protected by the TiO₂ crystals that are overcoating the MWNT surfaces.

The XRD patterns of the MWNTs, TiO₂ nanocrystals, and the MWNT-TiO₂ NHs are presented in Figure S6. A strong graphitic carbon peak at 25.7° appears, which is in excellent agreement with literature reports.³⁸ XRD peaks for TiO₂ nanocrystals appear at 2θ values of 25° , 37.5° , 48° , 55.5° , 62.8° and 69.5° , corresponding to (101), (004), (200), (211), (204), and (116) crystal plane; these results confirm the crystalline phase to be pure anatase.⁴⁹

Electrokinetic Properties.

All the materials exhibit negative electrophoretic mobility (EPM), with an overall decreasing trend in the absolute EPM value (i.e., less negative) with the increase in NaCl concentration (Figure 2); double layer compression with increased amount of electrolyte is the underlying mechanism in this case.^{1,37,40,41,45} The MWNTs show the highest EPM values among all the materials ($-3.15 \pm 0.09 \times 10^{-8}$ to $-1.87 \pm 0.07 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ S}^{-1}$ at 1 to 100 mM NaCl, respectively), and the values are within the range of previous literature reports (-3.5×10^{-8} to $-2.4 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ S}^{-1}$ with high and low oxygen content, respectively at low ionic strength).²⁵ The highly negative EPM values of the MWNTs likely originate from the ionizable oxygen, attributable to functional groups etched onto MWNT exterior and at the open tube ends during the acid-treatment process.^{25,30,31} Moreover, these ionizable surface

moieties on the MWNTs are exposed to the particle–water interface, which likely have provided the enhanced stability of these particles (and little variation in EPM values) up to nearly 30 mM of NaCl. TiO₂ shows the least negative EPM values among all NMs (ranging from $-1.8 \pm 0.06 \times 10^{-8}$ to $-0.51 \pm 0.12 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ S}^{-1}$ under 1 to 100 mM NaCl, respectively). Similar EPM values have previously been reported for bare TiO₂ nanocrystals in aqueous suspensions.⁵⁰ The trend for the NHs shows a gradual decrease in the magnitude of the EPM values with the decrease in TiO₂ loading (Figure 2). This trend is consistent with that of the percentage of oxygen, attributable to functional groups etched on the MWNTs (which decreased via deoxygenation) discussed earlier (Table 1); i.e., NH-High possessed the largest percentage of oxygen containing moieties and the oxygen content decrease progressively. However, the large amount of TiO₂ presence on the MWNT surfaces for the NH-High likely cause shielding of some of these ionizable moieties, that lead to a gradual lowering of EPM values at low ionic strength conditions (when compared to MWNTs only case with similar percentage of oxygen attributable to functional groups). The overall lowering of the amount of oxygen attributable to the etched functional groups in NH-Mid and NH-Low (compared to NH-High and MWNTs) can thus explain the lowering of the EPM values for these materials.

Aggregation Behavior and Underlying Mechanisms.

The initial average hydrodynamic radii (HDR) of the MWNTs and the NHs lie between $75 \pm 2 \text{ nm}$ to $101 \pm 2 \text{ nm}$ (Figure S7), measured at 25 °C at a pH of 6.9 ± 0.2 . The MWNT-ISP showed larger aggregate size (133 ± 3), likely due to a high degree of deoxygenation during heat treatment, leading to a higher degree of clustering. The HDR of the TiO₂ nanocrystals is $87 \pm 2 \text{ nm}$, which is in a similar size range to that of the NH and MWNT clusters. The TiO₂ cluster size is higher than that shown via TEM, likely due to high aggregation propensity of these materials with no surface coatings and low EPM, resulting in compromised stability in aqueous suspensions.

As shown in Figure 3, component MWNTs appear to be the most stable material (critical coagulation concentration or CCC of 162 mM NaCl; Table 2) while the other component TiO₂ turns out to be the least (CCC of 18 mM NaCl; Table 2). Similar colloidal stability for MWNTs^{25,30,31} and TiO₂⁵¹ has previously been reported. The stability of these component materials follows the electrokinetic trend (Figure 2). It is thus expected that the NHs, which comprise these two components, will exhibit aggregation behavior between these components, resulting from the interplay between van der Waals and electrostatic interactions.

The NH-High displays high aggregation propensity (CCC of 40 mM NaCl; Table 2) and is closer to that of the TiO₂ behavior (Figure 4); though the electrostatic contribution for this NH is one of the strongest as observed from the EPM results and is comparable to those of the MWNTs up to an ionic strength of 10 mM NaCl and the variation is $\sim 0.5 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ S}^{-1}$. Such variation in EPM between these samples may not capture a factor of 4 difference between these samples (Figure 2). Attachment efficiencies of NH-Mid, however, show a significant rightward shift (CCC of 52 mM NaCl; Table 2), indicating a strong gain in stability. The EPM trend for this NH, however, indicates a weaker electrostatic

contribution compared to that of the NH-High. Such observation suggests that contribution of the TiO_2 on the surface (with higher van der Waals attraction) is much stronger for NH-High compared to NH-Mid (with lower TiO_2 loading), causing instability to the NH-High. The aggregation behavior of the NHs gets more complex when the TiO_2 loading lowers even further, as in the case of NH-Low. Lowering the contribution from the TiO_2 (which should enhance stability or reduce aggregation) in this case is balanced out by the lower contribution from electrostatics (Figure 2), resulting in arresting the apparent stabilization of the NHs with lower TiO_2 loading (CCC of 50 mM NaCl; Table 2).

To assess the effect of deoxygenation (via heat treatment during NH synthesis) on stability, aggregation kinetics is also studied for MWNTs, treated in isopropanol and heat (MWNT-ISP), in identical synthesis conditions as the NHs except with no Ti precursor. The MWNT-ISP has shown destabilization (CCC of 25 mM NaCl; Table 2) similar to TiO_2 , and the EPM values when compared (Figure 2) agrees with the observed aggregation behavior. Thus, MWNT-ISP aggregation is electrokinetically controlled.

The observed aggregation behavior of the NHs and component materials appears to be following the classical DLVO theory, which considers attractive van der Waals and repulsive electrostatic double layer interaction to describe particle–particle interaction. However, the fundamental assumptions of DLVO theory, i.e., spherical particle shape, uniform charge distribution, and smooth particle surfaces, are mostly violated by the complex NHs as suggested by the morphological characteristics described earlier. Such particle–water interfacial complexities have previously been reported to influence colloidal aggregation^{52–55} and necessitate assessment of efficacy of the DLVO theory in predicting aggregation of these complex NHs.

Efficacy of DLVO Theory and the Role of Complex Hybrid Morphology.

Figure 4 shows the DLVO fitting of the experimental stability plots (using ζ -potential calculated from the EPM values and HDR of the investigated NMs at respective ionic strength conditions). Hamaker constant (A_H) values that are used as fitting parameters, allowed to generate the best-fit lines. The Hamaker constant values that resulted in best-fit lines are listed in Table S2. The stability plots of the component materials (i.e., MWNTs and TiO_2) and the heat-treated MWNTs (i.e., MWNT-ISP) exhibit the best fit to the classical DLVO model. The DLVO model fit shows deviation for the NH stability plots, with an increasing error in prediction with the increase in TiO_2 loading. Monovariate regression coefficient (R^2) values are calculated to compare the experimental data and theoretical trends (Figure 4).

The deviation of the experimentally observed aggregation behavior from the theoretical DLVO trends can stem from a number of factors. Equations widely used to calculate DLVO interaction energy include perfectly spherical shape of the particles considered and uniform distribution of charge on the particle surfaces. However, MWNTs and MWNT-based NHs that form clusters in aqueous suspensions are also widely modeled with classical DLVO theory to probe the mechanisms of interaction.^{28–32,37} Hence, the experimental stability plots for the complex multicomponent materials tested, are not expected to exactly follow the DLVO trends; a higher deviation is expected for the NHs because of their surface

complexity (i.e., charge heterogeneity) and roughness upon hybridization. Surface roughness may be one of the factors (beyond the asphericity and surface complexity) contributing to such deviation from classical DLVO model. Effect of surface roughness in colloidal interactions has previously been investigated,^{56–58} where interaction between rough latex particles and a flat surface was considered. Results from this study demonstrated that experimental rate of interaction of the rough particles on the smooth flat plate at unfavorable conditions was higher than that predicted by the DLVO theory for interaction of the smooth particles on a smooth flat plate. NH-High also show higher aggregation propensity than DLVO prediction in the unfavorable aggregation regime (Figure 4). Other NHs, however, do not show such behavior for unfavorable conditions. DLVO overpredicts attachment efficiencies for all the NHs in the favorable aggregation regime (Figure 3).

Surface roughness measurements of the NHs with all three TiO₂ loadings were performed using atomic force microscopy (AFM). Details of the measurement technique have been described in the SI. The AFM results demonstrate that the root-mean-square (RMS) roughness (R_q) values of the NHs showed a general increase when the TiO₂ loading was increased. The R_q values were measured to be 4.81 ± 1.39 nm, 4.78 ± 1.37 nm, and 3.24 ± 1.09 nm (Figure S9) for NH-High, NH-Mid, and NH-Low, respectively. An analysis of variance showed that the effect of loading on roughness was significant, $F(2,87) = 14.4$, $p < 0.0001$. Posthoc analysis using the Tukey criterion indicated that the average roughness of the NH-High was not significantly different from that of the NHMid at the 95% confidence level. All other comparisons were significant. These roughness measurement results indicate that surface roughness, particularly that of the NH-High, might have contributed to a larger deviation of the DLVO fit. However, no correlation between the roughness values and the deviation from DLVO theory could be deduced. Further studies need to be performed to establish better correlation between surface roughness and heterogeneity with the efficacy of DLVO theory for hierarchical nanoheterostructures.

Furthermore, the asphericity of the aggregate clusters likely has contributed to causing a deviation of the DLVO fits. Extent of sphericity of the MWNTs and NHs is determined with fractal dimension estimation (Figure S10 and Table S3). The data show that MWNT clusters with the lowest D_f (among the materials tested) are highly aspherical. As the TiO₂ is hybridized onto MWNT surfaces, the asphericity of the clusters decreased. The NH-Mid and NH-Low do not show statistically significant differences (in D_f) between these samples and have the highest value among the materials tested (Figures S10 and Table S3). It is to be noted that these D_f values are indicative of the starting cluster sphericity and are likely to differ significantly as aggregation progressed over time and under different ionic conditions.⁴³ The noted asphericity of these clusters thus has also contributed to the deviation of the DLVO model—a model that is derived for sphere–sphere interaction.

Effects of Divalent Cation and SRHA on Aggregation.

For electrostatically stable colloids, presence of divalent cations is expected to facilitate aggregation by effective compression of the electrical double layer and specific adsorption onto surface groups.³⁷ All NMs, except NH-High demonstrate a higher aggregation rate at 10 mM total ionic strength with divalent Ca²⁺ compared to the same ionic strength

comprised of only monovalent cations (Figure 5). Component MWNTs show the strongest response to divalent cations (Figure 5) as observed earlier.²⁴ A likely mechanism is specific adsorption of Ca^{2+} onto oxygen moieties on the MWNT surfaces.²⁵ Colloidal bridging of particles with surface oxygen groups is also known to have occurred with divalent Ca^{2+} ions.²⁵ Similarly, MWNTISP shows fast aggregation rate (lower than MWNTs and higher than NHs and TiO_2) in the presence of Ca^{2+} (Figure 5); which is possibly caused by decreased specific ion adsorption and Ca^{2+} bridging, and is mediated by low oxygen containing moieties.

The aggregation rate of NH-High in 10 mM ionic strength is similar, with and without the presence of Ca^{2+} (i.e., 0.030 ± 0.003 nm/sec and 0.027 ± 0.004 nm/sec, respectively). As previously discussed, TiO_2 on MWNT surfaces can serve as a “shield” to the oxygen containing groups and prevent specific adsorption of Ca^{2+} ions. TiO_2 nanocrystals also demonstrate similar aggregation rate in 10 mM ionic strength with and without the presence of Ca^{2+} ions (0.184 ± 0.002 nm/sec and 0.201 ± 0.030 nm/sec, respectively). As the TiO_2 content decreases in the NHs, a larger fraction of the oxygen moieties gets exposed to the surface, which allow for enhanced interaction with Ca^{2+} ions. The aggregation rates of the NHMid and NH-Low have increased significantly with the presence of divalent Ca^{2+} .

Presence of only 2.5 mg TOC/L SRHA dominated the aggregation behavior of the NHs with and without the presence of divalent Ca^{2+} (Figure 5). Such SRHA-mediated colloidal stability has previously been reported.^{24,28,37} In presence of SRHA, the MWNT aggregation rate decreases from 0.640 ± 0.090 nm/sec to 0.050 ± 0.020 nm/sec with Ca^{2+} . For the other NMs, the aggregation rates reduce to a negligible level when SRHA is present. Lowering of aggregation rate indicates strong stabilization of all the materials by SRHA, resulting in electrosteric hindrance to aggregation.³⁶ The faster aggregation of the MWNTs than other NMs in the presence of 2.5 mg/L TOC SRHA and Ca^{2+} indicates likely bridging of oxygen-containing functional groups of the oxidized MWNTs, mediated by Ca^{2+} .

ENVIRONMENTAL IMPLICATIONS

Aggregation of the NH is dependent on the TiO_2 loading; however, the trend in aggregation is not directly proportional to the highly aggregating TiO_2 component. Surface complexity (i.e., surface roughness, charge heterogeneity, etc.), arising from such multicomponent hybrids needs to be identified and accounted for in their EHS assessment. Classical DLVO theory failed to capture the aggregation behavior of the NHs, likely due to the asphericity of the clusters formed by flexible MWNT-based NHs and also due to the interfacial complexities (e.g., surface roughness) introduced by the TiO_2 nanocrystals. Composition of the background water can also strongly influence the aggregation behavior. In the presence of monovalent cations, the NHs show a gradual decrease in aggregation propensity with the decrease in TiO_2 loading, the trend is reversed with divalent cations; variation in exposed surface functional groups leads to altered ion adsorption and cation bridging. Thus, in natural waters (with monovalent salts only), NHs will stay suspended longer than TiO_2 nanocrystals but shorter than MWNTs; in the presence of divalent cations, the trend will likely be reversed. In the presence of SRHA, NHs will exhibit increased stability. It can be concluded that the sum of the aggregation behavior of the parts (i.e., component MWNTs or

TiO₂) may not capture that of the whole (i.e., of the NHs). Surface complexity introduced by the heterostructures as well as the composition of the hybrids (i.e., loading of the metal oxides) may strongly influence nano-EHS results. The results of this study indicate that other carbon nanotube-metal oxide NHs may also behave similarly and undergo a larger degree of aggregation compared to the component materials. Introduction of metal oxide components may present stronger van der Waals attraction, while the surface heterogeneity (charge as well as surface roughness) may further influence their environmental behavior. The amount of the metal oxide component on MWNT surfaces may not proportionally alter the EHS behavior of these hybrids and thus the behavior of the “parts” may be unable to capture that of the “whole”.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Representative HRTEM (a–c) and STEM (d–f) micrographs and elemental mapping (g–i); (a, d, g) NH-High, (b, e, h) NH-Mid, and (c, f, i) NH-Low. All images were taken at comparable magnification.

Figure 2.

Electrophoretic mobility of NHs and the component materials at a range of NaCl (1 to 100 mM). Measurements were taken right after adding appropriate NaCl amounts in the aqueous NM suspensions. All experiments were performed at 25 °C at a pH of 6.9 ± 0.2 .

Figure 3.

Stability plots of the NHs and the components. Each point on the stability plots represents attachment efficiency of the respective NMs at specific NaCl concentration. All experiments are performed at 25 °C at a pH of 6.9 ± 0.2 .

Figure 4.

DLVO models for experimental stability plots (a) oxidized MWNTs, (b) NH (1:0.1), (c) NH (1:0.05), (d) NH (1:0.033), (e) MWNTISP, and (f) TiO_2 nanocrystals. The experimental stability plots are fitted by DLVO estimated attachment efficiencies calculated from the stability ration equation using Matlab software.

Figure 5.

Aggregation rates of all materials at 10 mM ionic strength (10 mM NaCl only and 7 mM NaCl + 1 mM CaCl₂) with and without SRHA (2.5 mg/L TOC). All experiments were performed at 25 °C at a pH 6.9 ± 0.2. The bar charts indicate mean aggregation rates, and the error bars represent standard deviation.

Table 1.

XPS Analyses of MWNTs and the NHs

nanomaterials	% O	% Ti	% O in TiO ₂	% O attributed to functional groups on MWNT
MWNT	10.9 ± 0.2	N/A	N/A	10.9 ± 0.2
NH-High (C:Ti molar ratio of 1:0.1)	27.3 ± 1.1	8.6 ± 0.3	17.2 ± 0.6	10.1 ± 1.2
NH-Mid (C:Ti molar ratio of 1:0.05)	17.6 ± 0.4	4.5 ± 0.1	9.0 ± 0.2	8.6 ± 0.4
NH-Low (C:Ti molar ratio of 1:0.033)	10.9 ± 0.4	3.20 ± 0.05	6.4 ± 0.1	4.5 ± 0.4
MWNT-ISP	2.2 ± 0.1	N/A	N/A	2.2 ± 0.1

Table 2.

CCC Values for the Materials

nanomaterials	CCC value (mM NaCl)
MWNT	162
TiO ₂	18
NH-High	40
NH-Mid	52
NH-Low	50
MWNT-ISP	25