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Understanding the Dispersive Action of Nanocellulose for Carbon **Nanomaterials**

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Supporting Information

ABSTRACT: This work aims at understanding the excellent ability of nanocelluloses to disperse carbon nanomaterials (CNs) in aqueous media to form long-term stable colloidal dispersions without the need for chemical functionalization of the CNs or the use of surfactant. These dispersions are useful for composites with high CN content when seeking waterbased, efficient, and green pathways for their preparation. To establish a comprehensive understanding of such dispersion mechanism, colloidal characterization of the dispersions has



been combined with surface adhesion measurements using colloidal probe atomic force microscopy (AFM) in aqueous media. AFM results based on model surfaces of graphene and nanocellulose further suggest that there is an association between the nanocellulose and the CN. This association is caused by fluctuations of the counterions on the surface of the nanocellulose inducing dipoles in the sp² carbon lattice surface of the CNs. Furthermore, the charges on the nanocellulose will induce an electrostatic stabilization of the nanocellulose-CN complexes that prevents aggregation. On the basis of this understanding, nanocelluloses with high surface charge density were used to disperse and stabilize carbon nanotubes (CNTs) and reduced graphene oxide particles in water, so that further increases in the dispersion limit of CNTs could be obtained. The dispersion limit reached the value of 75 wt % CNTs and resulted in high electrical conductivity (515 S/cm) and high modulus (14 GPa) of the CNT composite nanopapers.

KEYWORDS: Nanocellulose, carbon nanotubes, graphene, interaction, surface charge, conductivity, counterions

N anocelluloses are naturally occurring, highly anisotropic, rod-shaped particles of glucan polymers with a high degree of crystalline ordering.¹ They can be extracted from the fibers of different green and abundant plant sources.² They are usually categorized into three main groups: (i) cellulose nanofibrils (CNFs), (ii) cellulose nanocrystals (CNCs), and (iii) bacterial cellulose (BC).³ Because of their high aspect ratio (CNFs have an average length of around 1 μ m and an average diameter of 2-5 nm), chemically modifiable surface, high Young's modulus (100 GPa in the axial crystalline regions),⁴ and relatively inexpensive production methods, nanocellulose has a great potential as a sustainable nanomaterial for the fabrication of many functional structures.⁶⁻⁹ Some of the research applications where nanocellulose is currently being used include nanoscale reinforcements in polymer composites,¹⁰ multilayer functional surfaces,¹¹ gas barriers,¹² electro-conductive composites,¹³ solar cells,¹⁴ and electronics.¹⁵ In electronic devices, nanocelluloses are being used due to their optical transparency and chemical durability combined with their strength and flexibility.^{16,17} One of the most important characteristics of the nanocellulose is that they can be colloidally stable in aqueous solution for a wide range of salt concentration and pH.18 Moreover, they can assemble with

other nanoparticles in a colloidal suspension that can then be transformed into a gel that is utilized to create multifunctional composites.^{19,20}

Carbon nanomaterials (fullerenes, carbon nanotubes, and graphene)²¹ are suitable candidates in numerous applications including nanocomposites, electronics, and optical devices.^{22,23} Unmodified carbon nanomaterials, however, aggregate in aqueous solutions due to their hydrophobic surface.²⁴ Carbon nanotubes (CNTs) form bundles and individualization of the nanotubes is necessary to exploit their full potential in a composite.²⁵ The main routes toward CNT dispersion are chemical functionalization, addition of surfactants, or polymer wrapping.^{26,27} These dispersion routes have different drawbacks: surfactants will induce a lower adhesion with the polymers in composites due to weak interfacial layers, and chemical functionalization disrupts the electronic structure of the pristine nanotubes, which reduces the conductivity of CNT composites.²⁸ The addition of a surfactant or polymer, which

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Table 1. Dispersion Limit of the Nanocelluloses with Different	Charge Densities as the Result of the Addition of Salt and the
Change in ξ -Potential (ξ) with the Addition of CNTs in Water	r

material	dispersion limit (CNTs wt %) in water	dispersion limit (CNTs wt %) in 1 mM NaCl	ζ (mV) at 0 wt % CNT	ζ (mV) at dispersion limit	ζ (mV) at dispersion limit in 1 mM NaCl	
CNF290:CNT	10	0 ^{<i>a</i>}	-40	-30	-40 ^b	
CNF490:CNT	30	7	-55	-46	-53	
CNF1400:CNT	60	33	-67	-60	-58	
CNC1400:CNT	75	51	-61	-57	-53	
^{<i>a</i>} Very close to zero. ^{<i>b</i>} CNF290 at 1 mM has almost zero CNT content, so ζ is the same as pure CNF290 in solution.						

causes a surface coverage of the CNTs,²⁹ perturbs the CNT– CNT contact for electron hopping.³⁰ We have previously shown that CNFs can be used to disperse and purify asprepared single-walled carbon nanotubes (SWNTs) in aqueous medium, resulting in dispersions with excellent colloidal stability that could be further utilized for making functional composites with high electrical conductivity and strength.³¹ It has also been shown that CNCs are able to disperse high amounts of CNTs (both single and multiwalled) in water, and this mixture can further be used in layer-by-layer assembly of hybrid films.^{32,33} This discovery allows CNT dispersion without the need for chemical functionalization, addition of surfactants, or use of water-soluble polymers.³⁴

The mechanism behind the dispersive ability of nanocellulose has yet to be elucidated. The understanding of such dispersive action of nanocellulose helps us to better design composites³⁵ where nanocellulose acts as the stabilizing agent for other nanomaterials in water, and the structural elements for functional materials (e.g., smart aerogels^{36,37} and nanopapers^{38,39}).

In this study, we show several results that together suggest that the dispersive action of nanocellulose is caused by a fluctuation of the counterions on the surface of the nanocellulose, which in turn induces a delocalization of the electrons in the sp² carbon lattice of CNTs, that is, dipoles, and leads to an attractive interaction between the CNTs and the nanocellullose. The CNT and nanocellullose form associated structures that are electrostatically stabilized through the charges of the nanocellullose. We support this hypothesis by using theoretical electrostatic modeling combined with adhesion measurements using colloidal probe atomic force microscopy (AFM) in aqueous media.⁴⁰ Through a better understanding of the molecular interactions between the nanocellulose and CNTs, we were able to further increase the dispersion limit of the CNTs by increasing the surface charge density of the nanocellulose. The increase in dispersion limit resulted in a high electrical conductivity of the CNT nanocomposites (515 S/cm).

The central theme of this work is to find out the mechanism behind the dispersive action of charged nanoparticles with high aspect ratio in the form of nanocellulose and uncharged nanoparticles with high aspect ratio in the form of carbon nanotubes in water. For nanocellulose, we used TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated, oxidized CNFs with three different charge densities (290, 490, and 1400 μ equiv·g⁻¹), prepared as described in detail in a previous report.⁴¹ These different species of CNF are denoted by CNF290, CNF490, and CNF1400, respectively. We then acid hydrolyzed CNF1400 with sulfuric acid to obtain cellulose nanocrystals (CNC1400) based on previous reports with the same charge density but a much lower aspect ratio.⁴² We used SWNTs produced by electric arc discharge (by Carbon Solutions, Inc.) for the preparation of colloidal dispersions. We dispersed the nanotubes by adding them as powders to the CNFs and used ultrasonication followed by centrifugation (see Supporting Information). Among all carbon nanomaterials, we chose to study and model the dispersion of SWNTs with CNFs in aqueous solutions, because they are both anisotropic rods with similar dimensions.

To study the effect of the surface charge density of CNFs on their dispersion capability, we prepared different CNC/ CNF:SWNTs dispersions using the same type of SWNTs with CNFs having different charge. Exploiting that CNTs absorb visible light while CNFs and CNCs are essentially transparent, we used ultraviolet-visible spectroscopy (UV-vis) absorption to estimate the dispersion limit of the CNC/ CNF:SWNT (see Supporting Information and Figure S1). Table 1 shows that the dispersion limit increased with an increasing CNF charge, and reached a maximum dispersion limit of 60 wt % for the CNF1400:SWNTs. This dispersion limit could further be increased to 75 wt % by using highly charged CNCs (CNC1400:75 wt % SWNT).

Table 1 shows the ζ -potentials of different CNC/ CNF:SWNTs dispersions at their dispersion limit measured with dynamic light scattering (DLS). There is a small drop in ζ potential of the CNF:SWNT dispersion compared to the ζ potential of the pure nanocellulose in water. This small decrease can be expected inasmuch as when the CNFs are associated with the SWNTs there should be a change in the shearing surface of the water outside the CNFs. This decrease is however still small and the negative potential is enough to keep the dispersion colloidally stable even above 50 wt % SWNTs. We also observe that the dispersion limit decreased in 1 mM NaCl compared to pure water (Table 1 and Figure 1). Table 2 shows the apparent hydrodynamic diameter of the CNC/ CNF:SWNTs, extracted from DLS. The general trend is that the hydrodynamic size of the nanocellulose and the CNC/ CNF:SWNTs dispersion at the dispersion limit both increase with decreasing charge density of the nanocellulose. Thus,



Figure 1. Optical image of the dispersions: (1) CNF290, (2) CNF490:7 wt % CNT, (3) CNF490:10 wt % CNT-1 mM NaCl, (4) CNF490:30 wt % CNT, (5) CNF1400:33 wt % CNT-1 mM NaCl, (6) CNC1400:51 wt % CNT-1 mM NaCl, (7) CNF1400:60 wt % CNT, and (8) CNC1400:75 wt % CNT, all having the same particle concentration (0.04 g/L).

Table 2. DLS Data Showing Apparent Hydrodynamic Diameter of the Different Nanocelluloses and the Hybrids in Water

dispersion	apparent hydrodynamic diameter (nm)
CNC1400:75 wt % CNT	200 ± 1.8
CNF1400:60 wt % CNT	240 ± 1.4
CNF490:30 wt % CNT	225 ± 1.7
CNF290:10 wt % CNT	320 ± 2.8
CNC1400	90 ± 0.8
CNF1400	115 ± 1.8
CNF490	130 ± 0.9
CNF290	225 ± 1.2

higher-charged nanocellulose can disperse more nanotubes and apparently with more efficient separation of the nanotubes from their bundles. All the DLS curves, that is, the autocorrelation data, display relatively high intercept values and a sharp drop with time, which indicate a freely moving-particle system and a monomodal distribution (Figure S2).

Figure 2 shows AFM images of the CNC:SWNTs. Because the length of SWNTs and CNCs are different, the detailed assembly between the two particles is more distinguishable than for the CNFs and SWNTs, which have similar lengths (see Figure S3). In Figure 2, the particles with approximately 1 μ m length are certainly the SWNTs, because CNCs have the average length of 200 nm (Figure 2a). The blue arrows in Figure 2b,c point to the uncovered parts of the individual SWNTs. Height measurements of these parts show height values below 2 nm which indicate that we indeed have single SWNTs. We can also see a part along the same nanotubes (red arrows, nr 3, 5, and 8) with an increased height (Figure 2d,e). This increase in height is around 3–4 nm, and the length of this associated section is 100-200 nm, which indicates the attachment of the short rodlike CNC particle. Figure 2 indeed suggests that the CNCs and CNFs are attached to or associated with the CNTs in the dispersion.

We estimate the number of nanocellulose particles associated with each SWNT theoretically and link this theoretically obtained number density ratio to the experimentally determined dispersion limits using hydrodynamic theory. As a first approximation, we consider both the CNFs/CNCs and the SWNTs as cylindrical rods having diameter *d* and length *L*. Using Perrin theory,⁴³ we approximate the hydrodynamic properties of the rods with that of a prolate spheroid of aspect ratio L/d. The hydrodynamic radius R_h of such a spheroid, as measured with DLS, is then

$$R_{\rm h}(L, d) = \left(\frac{6}{\pi}\right)^{1/3} \frac{L}{S(L, d)}, \text{ where } S(L, d) = 2 \frac{\operatorname{arctanh} \sqrt{1 - \frac{d^2}{L^2}}}{\sqrt{1 - \frac{d^2}{L^2}}}$$
(1)

Here, S(L, d) is the Perrin S-factor. Individual CNFs and CNCs have a typical diameter of 3–4 nm according to the literature.¹⁸ On the basis of this value, we set the average diameter of the CNCs and CNFs to 3.5 nm. Under this assumption and the measured $R_{\rm h}$ (from DLS in Table 2), we can compute the length of the CNFs and the CNCs by numerically solving eq 1 for *L*. We assume that the CNFs/CNCs are one-chain, triclinic crystal structure cellulose with a density of 1.58 g/cm^{3.44} We also assume that individual SWNTs have an average diameter of 1.55 nm, a length of 1 μ m, and a density of 1.56 g/cm^{3.45} In an aqueous suspension, we define the number concentration (number of particles per unit



Figure 2. AFM height images of (a) CNC1400 coated via dipping layer-by-layer assembly of the 0.1 g/L PEI and 0.06 g/L of the CNC dispersion; CNC1400:75 wt % SWNTs dispersion (b) casted from the 0.01 g/L dispersion on silicon wafer, height values of the pointing arrows 1, 2, and 3 are 1.5, 1.7, and 3.9 nm, respectively; (c) one bilayer coated via dipping layer-by-layer assembly of the 0.1 g/L PEI and 0.05 g/L dispersion, height values of the pointing arrows 4, 5, 6, 7, and 8 are 1.4, 5, 1.2, 1.2, and 4.5 nm, respectively. Scale bars show 300 nm. Height section values of pointed areas of (d) 1 and 3 separately compared to the substrate (0 nm height surface) and (e) 4 and 5 as single line section alongside the individual nanotube and the CNC attached to it. Schematic drawing shows how the assembly of CNCs (short green rods) and SWNTs (long black hollow rods) looks like in the area of (f) point 3 and (g) points 4 and 5. (The close-up shows the assembly of a CNC and a SWNT.)

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Figure 3. (a) Schematic drawing (not to scale) of the spherical probe covered with one bilayer of PEI and CNF on top and the flat SLG surface used for AFM force measurements in aqueous solutions in a liquid cell, (b) SEM image of the SiO₂ spherical probe attached to the cantilever (left) with the diameter of 10 μ m. AFM height image from the probe prepared from CNF1400 using LbL (one bilayer consists of PEI on the SiO₂ sphere and then CNF on top layer) (right); scale bar shows 600 nm. Force/radius (*F*/*R*) versus distance graphs between the two surfaces of SLG and spherical probe coated with CNF290 (blue), CNF490 (red), and CNF1400 (green) in water upon (c) approach and (d) retraction of the two surfaces in water. (e) Adhesion *W*_A as a function of the ionic strength *I* for CNF1400 (green), CNF490 (red), CNF290 (blue) and covered probes against SLG and CNF1400 probe against gold (purple) and silicon wafer (gray).

volume of the medium) of SWNTs (n_{SWNT}) and CNFs (n_{CNF}) respectively by

$$\mu_{\rm SWNT} = \frac{4C_{\rm SWNT}}{\pi d_{\rm SWNT}^2 L_{\rm SWNT} \rho_{\rm SWNT}}, \ n_{\rm CNF} = \frac{4C_{\rm CNF}}{\pi d_{\rm CNF}^2 L_{\rm CNF} \rho_{\rm CNF}}$$
(2)

where C_{SWNT} and C_{CNF} are the weight concentration of SWNT and CNF, *d* is the diameter, *L* is the length, and ρ is the density of the particles. The SWNT to CNF/CNC number ratio *r* can then be defined as

$$r = \frac{n_{\rm SWNT}}{n_{\rm CNF}} = N \frac{f}{1-f}, \ N = \frac{d_{\rm CNF}^2 L_{\rm CNF} \rho_{\rm CNF}}{d_{\rm SWNT}^2 L_{\rm SWNT} \rho_{\rm SWNT}}$$
(3)

Here, *r* represents the number of SWNTs associated with one nanocellulose (CNF or CNC) particle, *f* is the weight fraction of SWNTs, and *N* is a nondimensional prefactor which depends on the physical properties of the SWNTs and the nanocellulose. Using average parameters of the particles described earlier, we calculated that $r_{\text{CNF290}} = 0.16$, $r_{\text{CNF490}} = 0.33$, $r_{\text{CNF1400}} = 1.00$, and $r_{\text{CNC1400}} = 1.5$ for the respective dispersion limits. These numbers imply that only a fraction of CNF290 and CNF490 in the dispersion are associated with a SWNT, whereas all CNF1400s are associated with more than one

SWNT in the dispersion. These values are in good agreement with the dispersion limit values of the CNFs/CNCs:SWNTs is shown in Table 1. As a deduction, the surface charge on the nanocellulose plays a crucial role to disperse and stabilize a larger fraction of the CNTs and in this sense the higher surface charge is more efficient.

To analyze and quantify the interaction between nanocellulose and carbon nanomaterial surfaces, we used colloidal probe AFM. This is a versatile technique to directly access the colloidal forces in aqueous media. It is very challenging to directly assess the interaction force between CNFs and CNTs in experiments due to the nanoscopic scale of the materials. Instead, we considered a model system consisting of a planar sp² carbon lattice surface and a CNF-coated spherical probe in aqueous media. The spherical probe was attached to the AFM cantilever and a flat model surface was approached, contacted, and then retracted away from the probe. By knowing the spring constant of the cantilever and the cantilever deflection, and by applying Hooke's law, the probe-surface interaction force F can be computed as a function of the probe-surface distance x.^{46,47} To avoid artifacts, the flat and spherical surfaces must have a very low surface roughness, so that the probe-surface distance x can be well-resolved, and so that the interaction forces can occur across a perfect contact.⁴⁸ We, therefore, used single-layer graphene (SLG) as the flat nanocarbon surface model and CNFs adsorbed onto the spherical probe. The SLG is a two-dimensional material with a thickness of 0.4 nm, according to the supplier (University Wafer). It has the same sp² carbon lattice surface structure as any of the carbon nanomaterials (CNT, graphene, or fullerenes). We used this model surface because it provides a much smoother surface (almost zero surface roughness, Figure S6) than CNT films on a flat surface. These issues considered, SLG has the closest resemblance to CNTs on the surface.⁴⁹ We used silicon dioxide (SiO₂) particles with a diameter of 10 μ m, as the colloidal probe glued to the cantilever. We coated the SiO₂ particle with CNFs using a layer-by-layer (LbL) deposition of polyethylenimine (PEI):CNFs in a bilayer (Figure 3a). The LbL technique provides good adhesion strength for the CNF and results in an even surface coverage with a roughness in the order of less than 1 nm (see Figure 3b and Supporting Information, Figure S6).⁵⁰ To study the influence of the CNF surface charge density on the sp² carbon lattice in an aqueous medium, we performed force measurements using three different probes that were prepared using CNFs with different charges: 290, 490, and 1400 μ equiv g^{-1} respectively. The adsorption of CNFs with different charges to a cationized SiO₂ surface was measured with the use of quartz crystal microbalance (QCM) in order to clarify whether the two-layered structures of cationic polymer and CNF on the colloidal probe were representative of the CNFs in dispersion. The results (Figure S11) show that the adsorption of the CNF, as expected, is decreased as the charge of the CNF is increased and the adsorbed amount basically scales as the charge of the fibrils. This shows that the most negatively charged fibrils in dispersion will also give the most negatively charged surface on the colloidal probe. The QCM equipment naturally measures both the adsorbed amount of fibrils and the amount of immobilized liquid in the adsorbed layer. Because control measurements with deuterium oxide (D₂O) showed that the amount of immobilized liquid was not changed, we can indeed conclude that the adsorbed CNFs on the probe are representative of the CNFs in solution.

Figure 3c,d shows the force-distance relations between the CNF-covered probe and SLG upon approach and retraction in Milli-Q water. These forces depend on the contact geometry and hence their values are normalized by the radius $R = 5 \,\mu \text{m}$ of the spherical probe and shown as force over radius, F/R. Figure 3c shows three representative plots of the approach force versus distance for the three samples with different charge densities. The approach of CNF1400 probe (green) shows an essentially constant force between the probe and the surface, while there is a repulsive force at just a few nanometers for CNF490 probe (red). This repulsion has a slightly longer distance between SLG and CNF290 (blue). This trend suggests that the CNFs with higher charge show more attraction toward the sp² carbon lattice when the two surfaces are pushed together. Figure 3d shows the typical retraction of the three probes from SLG surface in water. The force required to separate CNF1400 from SLG is higher than for CNF490 and CNF290, respectively. With an additional assumption that the surface coverage of the different CNFs is essentially the same, this trend shows that the higher-charged surfaces adhere more strongly to the sp² carbon lattice in water. To study the effect of reducing the surface charge from the CNF surface on the sp² carbon lattice, all the measurements were first performed in Milli-Q (ultrapure) water and then in 10^{-6} , 10^{-5} , and 10^{-4} M NaCl solutions (Figure S7). With the force data from experiments with

spherical probe vs flat surface, the interaction energies between flat surfaces can be expressed using the Derjaguin approximation as

$$V_{\rm t}(x) = -\frac{F_{\rm t}(x)}{2\pi R} \tag{4}$$

$$V_{\rm r}(x) = -\frac{F_{\rm r}(x)}{2\pi R} \tag{5}$$

where $F_t(x)$ is the approaching force, $F_r(x)$ is the retraction force, $V_t(x)$ and $V_r(x)$ are the energy per unit area in approach and retraction, respectively, and *R* is the radius of the sphere. We define the adhesion energy as the pull-off interaction energy.

$$W_{\rm A} = \max_{x} (-V_{\rm r}(x)) \tag{6}$$

Figure 3e shows that the adhesion energy between the CNF probe and the SLG increases with the surface charge density of the CNF and decreases with the salt concentration of the aqueous medium. This figure is also illustrative of the adhesion energy W_A versus ionic strength I and adhesion energy for different CNFs on SLG, gold (Au) and silicon (Si/SiO₂) surfaces. The interaction between CNF and Au was chosen to study as another example of a conductive flat surface. The interaction energy values between CNF and gold or graphene surfaces are in quantitative agreement for the full range of the ionic strength used. To demonstrate that this adhesion energy is mainly governed by the sp² carbon lattice and not the Si/ SiO₂ backing material, we also measured the adhesion energy between the CNF probe and a silicon surface at different salt concentrations. The adhesion to silicon was an order of magnitude higher and it also increased with an increasing salt concentration (e.g., $1 \le I \le 10 \ \mu M$), which is in qualitative disagreement with the adhesion energy between the CNF probe and the SLG surface. We, thereby, conclude that the adhesion energy of SLG is determined by the sp^2 carbon lattice and not by the backing material. Because silicon is a dielectric, we conclude that the attractive force between CNF and dielectrics increases with the salt concentration and it is the metal-like properties of graphene in the in-plane directions that govern CNF-graphene interactions. For a static situation, the metal surface is always an equipotential surface. This suggests that the graphene surface has a uniform potential everywhere in the plane. The results also show that the ability of CNF to associate with CNT is very sensitive to the presence of added salt. Our interpretation is that there is an attractive force between CNT and CNF that decreases with the ionic strength, similarly to the decrease of the CNF-graphene interaction force with ionic strength. This also suggests that it is the conductivity of the CNT that governs the CNF:CNT association.

In summary, carbon nanomaterials show a tendency to associate more strongly onto nanocellulose surfaces with a higher charge. The higher the charge on the CNFs/CNCs surface is, the higher the attraction to the CNT will be. Upon ultrasonication, the created cavitation normally applies sufficient energy to break the aggregates of carbon nanomaterials in water. However, after the sonication is stopped the aggregates quickly reform due to strong van der Waals attraction and lack of polar interactions with water.⁵¹ Nevertheless, in the presence of CNFs/CNCs the CNTs are pushed toward the effective surface charged regions of the nanocellulose and associate with these highly charged materials that prevent reaggregation by means of electrostatic repulsion (Figure S10). This is also in agreement with the increase in the dispersion limit of the CNTs in water using higher-charged CNFs/CNCs. According to the force measurement results, the interaction between CNC/CNF and CNT occurs at a much shorter range than the Debye length (>100 nm in water) of the charged CNFs (Figure 3c and 3d). So, the electrostatic doublelayer around the CNFs could not cause the association with carbon nanomaterials. This also means that the association between the nanocellulose and the CNT well-inside the double-layer regime is most likely caused by an induction force. There might naturally be several molecular causes to the detected interaction between nanocellulose and the CNT, but taking all the experimental results together we propose that fluctuations of counterions on the surface of the nanocellulose induces a polarization of the electrons in the sp² carbon lattice leading to an attractive interaction between the two nanomaterials (Figure 4). These types of interactions have also been



Figure 4. Schematic drawings show a charged nanocellulose (green rod with its surface charge and the counterions) and a SWNT interaction in water (a) before induced interaction (far from the effective distance of the surface counterions) and (b) after induced interaction (inside the effective distance of the surface counterions) causing a dipole formation on SWNT. Polarization of the SWNT in the longitudinal direction is also plausible. The atoms/ions are colorcoded as follows: black for carbon, red for oxygen, white for hydrogen, blue for sodium, and green for chloride.

identified and discussed before^{52–54} but we are still lacking quantitative relationships for calculating the interaction between two dissimilar surfaces.⁵⁵ The high longitudinal polarizability of the CNTs might be underestimated when using SLG as a carbon nanomaterial model surface; the ion fluctuation effect and the induction of dipoles are likely to be stronger in the attraction of two nanorod system of nanocellulose and CNT. As identified by Ninham et al.,⁵³ the magnitude of the interaction depends on the concentration of counterions at the nanocellulose interface, the electrolyte concentration and the polarizability of the solid in contact with the nanocellulose. Because the induction forces are based on the fluctuation of counterions, the sensitivity of the interactions against an increase in electrolyte concentration is also high. It was earlier also suggested³¹ that the entropy gain upon release of water molecules from the surface of the CNF, as the CNT is associated with the CNF, could be an important contribution to the gain in free energy when the CNFs–CNTs are associated. This is naturally still true but this gain in entropy cannot explain the influence of the CNF charge on the dispersion efficiency and neither can it explain the high sensitivity toward added salt.

To show the potential of the highly charged nanocellulose in stabilizing and dispersing not only SWNTs but also other water non-dispersible carbon nanomaterials, we dispersed multiwalled carbon nanotubes (MWNTs),⁵⁶ and reduced graphene oxides (RGOs) with CNF1400 in water. We used MWNTs with average dimensions of 5 μ m in length and 6–9 nm in diameter and with >95% purity. RGOs are two-dimensional carbon nanomaterials that have been used for various applications.^{57–59} We used RGOs prepared by thermal reduction of graphite oxide into RGOs using Hummers' method according to previously described procedures (see Supporting Information).⁶⁰ Figure 5a shows an optical image of the dispersions.

We then used these stable dispersions to fabricate randomin-plane nanopapers (with both high and low density) using 1 g/L dispersions. We fabricated the nanopapers by vacuum filtering the dispersion, to form a wet and stable hydrogel (Figure 5b), followed by hot-pressing the hydrogels. The nanopaper had a relatively high average density of 1.5 g/cm³, and an average thickness of 20 μ m. We also fabricated lowdensity nanopapers, that can be used in various lightweight applications, by solvent exchanging the wet hydrogel formed after the vacuum filtration with ethanol (the hydrogel contains 4-5 wt % solid content).⁶ The solvent exchange keeps the porous structure of the swollen hydrogel as water is exchanged gradually (to prevent shrinkage) with ethanol to form an 'alcogel". Supercritical point drying of the alcogel then formed low-density nanopaper (Figure 5b and also Supporting Information and Experimental Section for more details) and resulted in highly porous nanopapers with the average density of 0.05 g/cm³ and an average thickness of 1 mm. Figure 5c,d shows SEM pictures of the random-in-plane network of the low and high-density nanopapers, respectively. We measured the electrical conductivity of the nanopapers using a 2-point probe method (Table 3). The electrical conductivity of high-density nanopapers reached the value of 339 S/cm in the CNF1400 composite with 60 wt % SWNTs and 515 S/cm in the CNC1400 composite with 75 wt % of SWNTs. These values are the highest electrical conductivity reported for any randomnetwork polymer-carbon nanotubes composite to the best of our knowledge.^{61,62} We also demonstrate in the Supporting Information that the conductivity of the nanopapers relates to the CNT volume fraction by a power law model. This further supports our argument that the full conductive potential of the CNT nanoparticles is exploited with the CNF dispersion protocol. We also report a relatively high Young's modulus $(E_{\text{CNC1400:75 wt \% SWNTs}} = 14 \text{ GPa and } E_{\text{CNF1400:60 wt \% SWNTs}} = 12$ GPa) and high tensile strength ($\sigma_{\rm CNC1400:75~wt~\%~SWNTs}$ = 142 MPa and σ $_{\rm CNF1400:60~wt~\%~SWNTs}$ = 225 MPa) for the composite nanopapers (see Figure S12 and Table S2). The lower tensile strength of the CNC:SWNT nanopapers derives from its brittle



Figure 5. (a) Optical image shows the stable and clear dispersions formed using highly charged CNF1400 to disperse (from left to right) SWNTs, MWNTs and RGOs in water, the left (dark gray) and right (light gray) dispersions of each system show particle concentrations of 1 and 0.1 g/L in water, respectively. (b) Schematic (not to scale) of the hydrogel preparation, using vacuum filtration of the dispersion and then drying the wet hydrogel (optical image of the hydrogel on the right) followed by supercritical or hot-press drying. (c) SEM images of the low-density nanopapers prepared from CNF1400:60 wt % SWNTs (top left), CNC1400:75 wt % SWNTs (top right), CNF1400:50 wt % MWNTs (bottom left), and CNF1400:30 wt % RGOs (bottom right); scale bars show 1 μ m. (d) SEM images of the high-density nanopapers prepared from CNF1400:30 wt % RGOs (bottom right), CNF1400:50 wt % MWNTs (bottom left), and CNF1400:30 wt % RGOs (bottom right), CNF1400:50 wt % MWNTs (bottom left), and CNF1400:30 wt % RGOs (bottom right), cNF1400:50 wt % MWNTs (bottom left), and CNF1400:30 wt % RGOs (bottom right), cNF1400:50 wt % MWNTs (bottom left), and CNF1400:30 wt % RGOs (bottom right), cNF1400:50 wt % MWNTs (bottom left), and CNF1400:30 wt % RGOs (bottom right), cNF1400:50 wt % MWNTs (bottom left), and CNF1400:30 wt % RGOs (bottom right), cNF1400:50 wt % MWNTs (bottom left), and CNF1400:30 wt % RGOs (bottom right), cNF1400:50 wt % MWNTs (bottom left), and CNF1400:30 wt % RGOs (bottom right); scale bars show 1 μ m.

Table 3. Electrical Conductivity of the Low and High Density Nanopapers at Different Weight Ratio of Highly-Charged Nanocellulose:Carbon Nanomaterials

	conductivity (S/cm) of the nanopapers		
composition	$\rho = 0.05 \ (g/cm^3)$	ρ = 1.5 (g/cm ³)	
CNF1400:30 wt % RGOs ^a	0.01 ± 0.00	0.20 ± 0.03	
CNF1400:50 wt % MWNTs ^a	0.11 ± 0.03	44.44 ± 2.08	
CNF1400:60 wt % SWNTs	0.49 ± 0.00	338.62 ± 4.49	
CNC1400:75 wt % SWNTs	0.91 ± 0.05	514.97 ± 5.46	
^a Not the dispersion limit.			

fracture behavior, whereas CNF:SWNT nanopapers display ductile fracture with 5% strain-at-break, making the latter ideal for applications that require a high fracture toughness. The lowdensity nanopapers have orders of magnitude lower conductivity than the high-density nanopapers due to lower percolation in a porous structure. An interesting characteristic of the low-density nanopapers is that by hot pressing the composite, electrical conductivity reaches similar values to the high-density nanopapers. Therefore, it can be used in various applications such as nanocellulose-based sensors.^{63,64} We suggest that the high conductivity, modulus, and strength of the composites could be attributed to the fact that CNT adheres to CNF/CNC and remains dispersed (with small aggregates) through repulsion of like-charged aggregates that is then locked in the gel that thereafter forms the nanopaper. The smaller aggregates permit an even coverage and more contact

points between nonfunctionalized CNTs. The fact that the CNFs:CNTs stay well dispersed when the water is removed during film formation also strongly indicates that the association between the CNFs and CNTs is practically irreversible. However, more details regarding the nature of the interactions, including the influence of, for example, the type of counterion, need to be explored in future investigations but are beyond the scope of the present work.

In conclusion, we have studied the stabilization, debundling, and dispersion of as-prepared carbon nanotubes and reduced graphene oxides with the aid of charged nanocellulose in aqueous solutions. It was shown that upon ultrasonication CNTs and CNFs/CNCs form heterogeneous aggregates of typically just a few particles, which remain electrostatically stabilized owing to the surface charge of the CNFs/CNCs. This precludes the reformation of CNT bundles. We employed dispersion characterization techniques to study the influence of surface charge density of the nanocellulose on quality and quantity of the carbon nanotubes in aqueous media. The interactions between CNF and carbon nanomaterials were also studied in more detail using AFM colloidal probe technique, where single layer graphene was used as a model surface for carbon nanomaterials. This study corroborated our hypothesis that the counterions fluctuations on the nanocellulose surface cause the assembly with CNTs in aqueous media. Because the interaction between the charged nanocellulose and the carbon nanotubes is governed by conductive sp² carbon lattice, these findings could be utilized for dispersion and stabilization of not only carbon nanotubes but also other carbon nanomaterials

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(having sp² carbon lattice structures) and possibly other materials with similar properties, such as silver nanowires, but this has yet to be established. We also fabricated nanopapers from the dispersions to illustrate the potential of such dispersions in applications of flexible structures with very high conductivity (515 S/cm) and high modulus (14 GPa). The CNF:CNT composite nanopaper also displays ductile fracture behavior with a high (5%) strain-at-break. These composites show great potential for electronic devices,⁶⁵ sensors,⁶⁶ or actuators.⁶⁷ Furthermore, because the nanocellulose–carbon nanomaterial dispersions are highly charged, various self-assembly techniques such as layer-by-layer assembly can be used for making functional materials.^{68,69}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.6b04405.

Experimental Section, additional figures and tables include UV-vis absorbance of CNF/CNC:SWNT aqueous dispersions, DLS data showing normalized intensity correlation function versus time of the CNF/ CNCs and their correspondence hybrids, AFM images of the CNF:SWNTs by LbL, AFM images of the CNF:SWNTs by dry-casting. AFM images of the surfaces of the probes and SLG for the colloidal probe force measurements, table of the conductivity of the highdensity nanopapers using different CNF charges, all the force distance average graphs in different aqueous and salt solutions, zoomed-in SEM images of the CNF:MWNTs and CNF:RGOs, electrical conductivity and percolation calculations of the high-density nanopapers, an image of the CNF:SWNTs dispersion, QCM data for LbL film of CNF, stress-strain behavior of highdensity composite nanopapers, and a table listing their mechanical properties (PDF)

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Notes

The authors declare no competing financial interest.

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