Reconfigurable Pickering Emulsions with Functionalized Carbon Nanotubes

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ABSTRACT: Pickering emulsions (PEs) achieve interfacial stabilization by colloidal particle surfactants and are commonly used in food, cosmetics, and pharmaceuticals. Carbon nanotubes (CNTs) have recently been used as stabilizing materials to create dynamic single emulsions. In this study, we used the formation of Meisenheimer complexes on functionalized CNTs to fabricate complex biphasic emulsions containing hydrocarbons (HCs) and fluorocarbons (FCs). The reversible nature of Meisenheimer complex formation creates a tunable droplet-water interface. The strong affinity of fluorofluorescent perylene bisimide (F-PBI) to the CNTs was used to enhance that assembly of CNTs to the FC-water interface. The combination of the functionalized CNTs and different concentrations of the perylene additive enable predictable complex emulsion morphologies. Our results show that the interfacial properties of functionalized CNTs have considerable utility in the fabrication of complex dynamic emulsions.

INTRODUCTION

Pickering emulsions (PEs) are widely used in food,[1] cosmetics,[2] and pharmaceutical[3] formulations. The wide utilization stems from the fact that PEs achieve high stability as a result of the stronger adsorption of the particles at the interface as compared to small molecule surfactants.[4,5] However, the stability of PEs generally leads to static systems that don't respond to small environmental changes with limited utility in biosensing,[6,7,8] and dynamic optics.[9] Another drawback of many PEs is a lack of interfacial chemical tunability. PEs are generally prepared from functionalized particles, and additional post-emulsification functionalization of the colloidal particles is challenging. This aspect severely limits the addition of additional functional groups that can enable more complex sensing conditions such as biosensing.[6,7,10] As a result, colloidal particles with functional groups that display dynamic covalent functionalization are desired as a way to create emulsion interfaces with dynamic/expanded functionality.

Carbon nanotubes (CNTs) have previously been used as stabilizing colloidal particles in PEs.[11,12,13] CNTs are in general very hydrophobic and require modification to be more hydrophilic in order to stabilize the oil-water interface. Non-covalent functionalization has been investigated, but has limited stability when the functional groups can easily desorb from CNTs.[14,15] This approach can also produce inconsistent results as a result of the dynamic degree of CNT functionalizations that vary with conditions, organizations, and concentrations. Covalent sidewall functionalization of CNTs by oxidative methods to introduce hydroxyls or carboxylates has also been investigated,[16,17,12]; however, these methods are highly nonspecific in terms of the structures formed.

To address these limitations, we have developed functional CNTs that display dynamic covalent equilibria to produce responsive and tunable complex PEs. Specifically, we have functionalized the CNT surfaces with 2,5-dinitrophenyl groups that form Meisenheimer complexes (MCs) with primary amines.[18] MCs display reversible equilibria such that the interfacial characteristics of an as formed PE can be dynamically changed *in situ*.[18,19] The net effect is that the CNT's interfacial properties can be modified to simultaneously stabilize multiple interfaces within complex droplets.

RESULTS AND DISCUSSION

Functionalized Carbon Nanotubes

Functionalization of the SWCNTs is accomplished by reaction with 3,5-dinitrobenzenediazonium salt, which reacts via a phenyl radical reductively generated *in situ*. The resulting 3,5-dinitrophenyl functionalized SWCNTs (DNB-CNTs) react with primary amines to form Meisenheimer complex functionalized SWCNTs (MC-CNTs) (Figure 1A).[18] Figure 1B shows Raman spectra of pristine-

SWCNTs (p-SWCNTs) and DNB-CNTs. The intensity of the D-band is a measure of sp^3 hybridization defects that result from the covalent functionalization of the graphene walls.[20] Using the starting p-SWCNTs as reference (A_D/A_G = 0.058), our DNB-CNTs show a large increase in the intensity of D-band (A_D/A_G = 0.47), thereby suggesting extensive functionalization. Quantification of the functionalization was accomplished using XPS. From Figure 1C, we can see that our DNB-CNTs contained F, O, and N with N and O at a much higher concentration than p-SWCNTs. Fluorine, present at an extremely small amount (less than 0.5 at%) and is introduced from the BF_4^- counterion. The high-resolution XPS scan of N1s reveals two distinct binding energy peaks that are assigned to N-C and N-O bonds associated with the nitro groups (Figure S1).[21] Based on the atomic percentages obtained from XPS (Table S1) the number of functional groups per 100 carbons is 2.5.

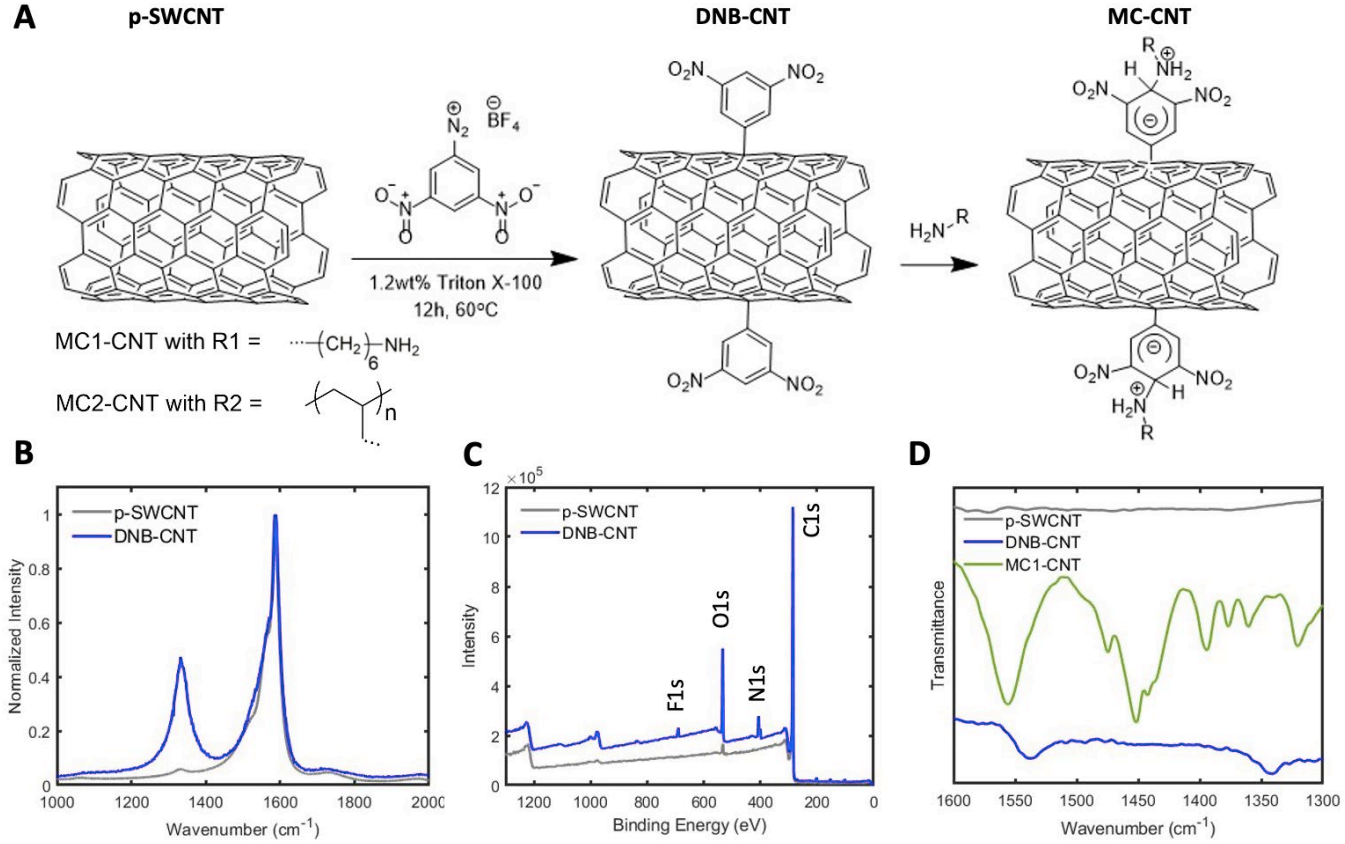

Figure 1. (A) Synthetic strategy of MC-CNTs. MC1-CNT is a functionalized SWCNT that has formed an MC with HMDA and MC2-CNT is functionalized SWCNTs in an MC with poly(allylamine). (B) Raman spectra of the functionalized SWCNT, (C) XPS spectra of the functionalized SWCNT, and (D) ATR-FTIR spectra of p-SWCNT, DNB-CNT, and MC1-CNT.

To further confirm the chemical identity of the covalent functional groups and the MC formation, ATR-FTIR was performed (Figure 1D). The DNB-CNTs show the expected distinct nitro stretching bands at 1537 and 1344 cm^{-1}. These nitro stretches are shifted to 1473 and 1321 cm^{-1}, respectively, when MCs are formed.[18] The shift to the lower energy of the nitro stretching bands is consistent with the negative charge that is distributed within the dinitrophenyl system in the MC.[18] There are other signals detected from the MC1-CNT that confirm the presence of the small molecule amine associated with the MCs (Figure S4). Upon extended washing the MC1-CNTs with water, the nitro stretches shift back to 1537 and 1344 cm^{-1} confirming the reversibility of the MC formation with HMDA. Polymeric amines, such as poly(allylamine), were used to form MCs with DNB-CNTs (ATR-FITR shown in Figure S6). The MC nitro stretching bands at 1484 and 1306 cm^{-1} of the MC2-CNTs do not change after washing with water, indicating that the multivalent nature of the polymeric amines prevents dissociation.[22]

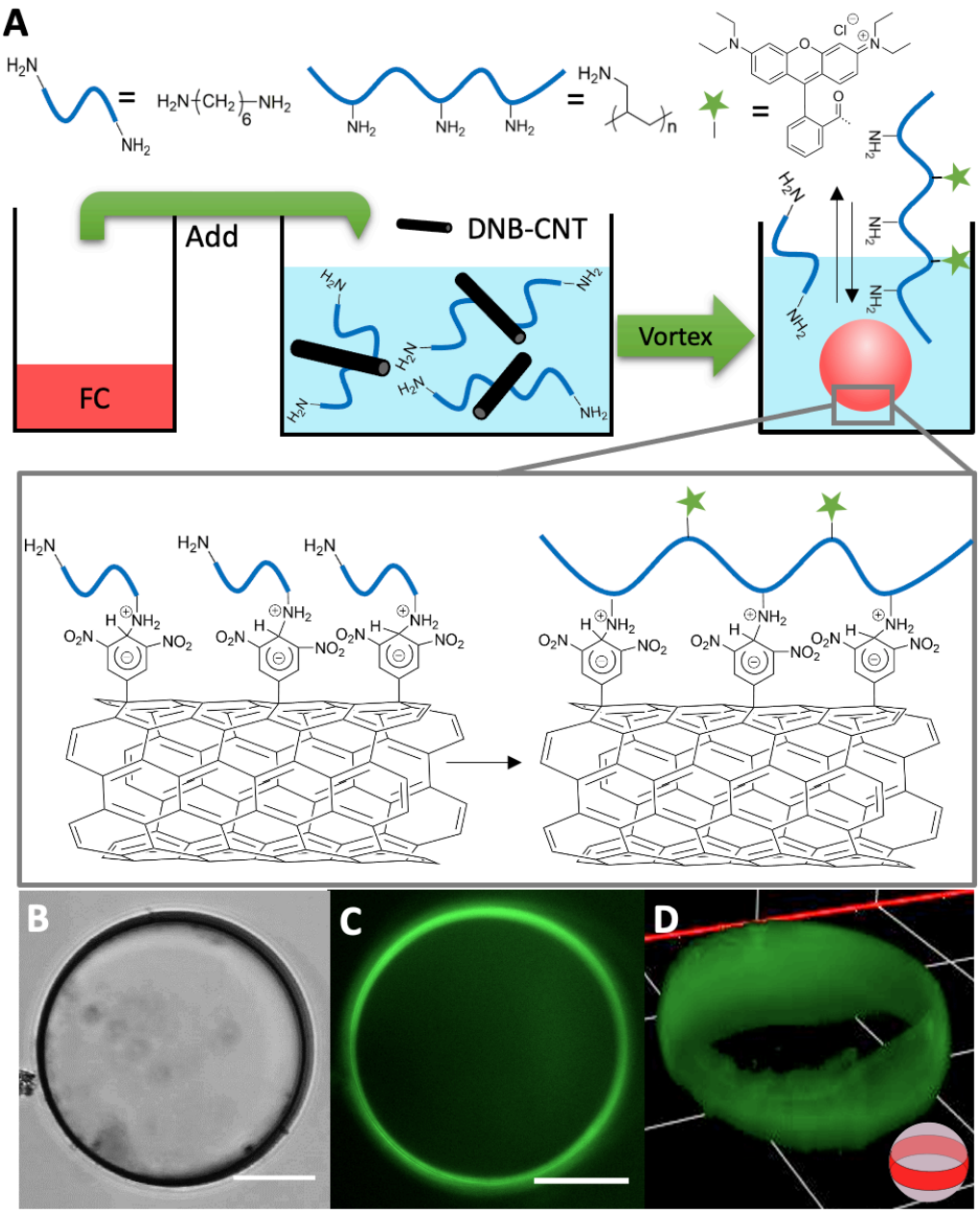

Figure 2. (A) Fabrication scheme for the formation of FC single emulsions with MC1-CNT and amine exchange occurring when the HMDA solution is replaced with PAA-RB solution. (B) Optical image of an oil-in-water droplet stabilized by MC2-CNT. (C) Top view fluorescence image of the droplets. (D) Z-stack image showing the localization of the emission at the droplet's oil-water interface. Scale bar = 50 μm.

Meisenheimer Complex Formation at the Oil-Water Interface

We began with an evaluation of the potential of MC functionalized CNTs to stabilize single oil-in-water emulsions and find that MC1-CNTs consistently produced uniform droplets. MC2-CNTs stabilized droplets were fabricated by leveraging the reversibility of MC formation through an *in situ* modification of the MC1-CNTs stabilized droplets. Figure 2A shows this process wherein exchanging the aqueous amine solution MC1 transforms to MC2 at the interface of the droplets. Figure 2B shows an optical microscope image of HFE7500 droplets stabilized with MC2-CNT. Upon washing the droplets with pure amine-free water, the MC1-CNT stabilized droplets quickly aggregate without coalescing, while MC2-CNT stabilized droplets remain stable without aggregation (Figure S10). The washing the MC1-CNT droplets with pure water removes the HMDA and lowers the effectiveness of the CNT surfactants. In contrast, the poly(allylamine) in MC2-CNT stabilized droplets is irreversibly connected to the functional-CNTs, and maintains a barrier for the inter-droplet association. In the absence of the MCs the strong interaction between CNTs causes the droplets to stick to each other, which eventually leads to coalescence.[23] To confirm that the poly(allylamine) is located at the interface of the droplets, a Rhodamine B fluorescent label, PAA-RB, was used in MC2-CNT. Figure 2C shows a fluorescent image of HFE7500 droplets stabilized with MC2-CNTs,

and a confocal Z-scan reveals that Rhodamine B is localized to the droplet surface and is not distributed to the inside the droplet (Figure 2D).

Double Emulsions

Pickering double emulsions were fabricated with MC1-CNTs, wherein each droplet contains a 1:1 ratio of hydrocarbon (HC) and fluorocarbon (FC) oils. We used diethylbenzene and HFE7500 as HC and FC oils, respectively. The immiscibility of fluorocarbons with hydrocarbons translates to their surface characteristics, and additional functionality is needed to create a thermodynamic driving force to competitively localize functional CNTs to the FC-W interface in the presence of an HC-W interface. We hypothesized that molecules with strong interactions with CNTs such as a perylene[24,25,26,27,28] with fluorous character could be used for CNT assembly at the FC-W interface. In this context, the fluorocarbon soluble perylene, F-PBI,[29] was added to FC oil for the controlled formation of HC-FC double emulsions.

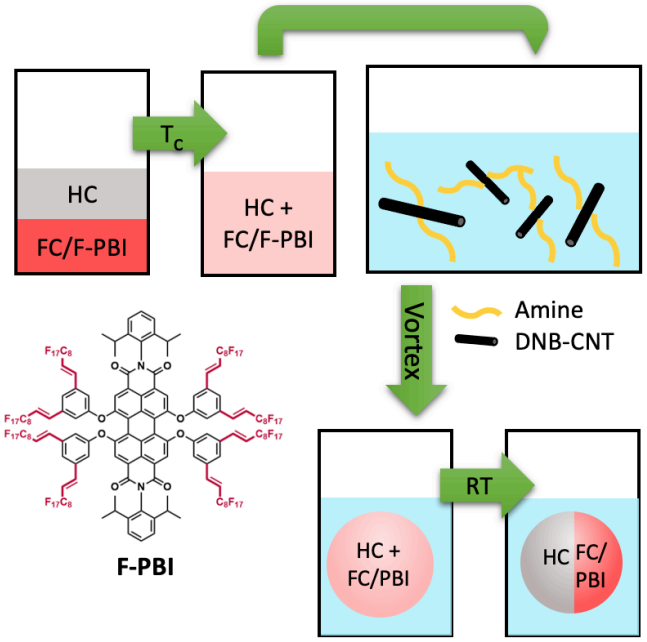

Figure 3. Fabrication scheme for Pickering double emulsions.

The morphologies of the double emulsion droplets were investigated as a function of concentrations of CNTs and F-PBI. At a fixed F-PBI concentration of 10 mg/mL in the FC phase and varying concentrations of CNTs from 10 to 20 mg/L in the continuous water phase (Figure 4A), the morphologies of droplets display a symmetric Janus structure. This structure indicates that the interfacial tension at the FC-W and HC-W interfaces are approximately equal.[30] The average size of the droplets shows a significant decrease as CNT concentration increases (Figure S8), which is to be expected with a higher surfactant to oil ratio.[11] At higher CNT concentrations (60 mg/L), we generated droplets that contain multiple HC domains as smaller domains within the FC phase (mHC-FC/W) (Figure 4B). We hypothesized that high CNT concentrations give a densely rigid interfacial network, which prevents the coalescence of HC domains upon phase separation when the temperature is reduced below the T_c. Figure 4B shows this structure and similar morphologies are often transiently observed during the phase separation of the oil phases of the droplets upon cooling (Figure S11). However, with small molecule surfactants these droplets quickly convert to more thermodynamically stable Janus structures. With the higher concentration of CNTs the temperature-triggered phase separation process produces kinetically trapped multi-droplet morphologies.

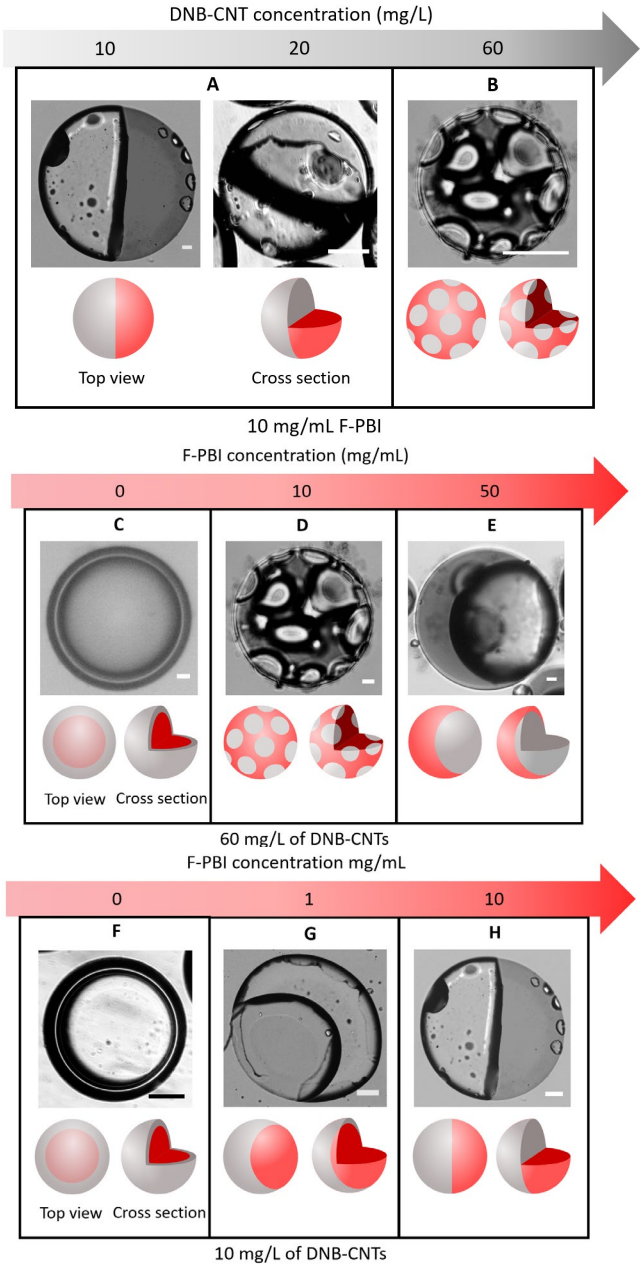

Figure 4. (A-B) Morphology of the complex fluorocarbon/hydrocarbon droplets at increasing concentration of MC1-CNTs (10-60 mg/L) with constant F-PBI concentration of 10 mg/mL. Scale bar = 50 µm. (C-E) Morphologies of the droplets as a function of increasing F-PBI concentration (0-50 g/L) with constant MC1-CNTs concentration of 60 mg/L. Scale bar = 10 µm. (FC-HC) Morphologies of the droplets as a function of increasing F-PBI

concentration (0-50 mg/mL) with a lower constant MC1-CNTs concentration of 10 mg/L. Scale bar = 100 μm.

In another series of experiments, the CNTs concentration was fixed at 60 mg/L, and the F-PBI concentration was varied. In the absence of F-PBI in the FC oil, an FC-in-HC-in-W (FC/HC/W) double emulsion morphology is generated (Figure 4C), which indicates that CNTs prefer to assemble at the HC-W interface over the FC-W interface.[10] When the F-PBI concentration is increased from 10 to 50 mg/mL, the morphology changes from an mHC-FC/W toward an HC-in-FC-in-W (HC/FC/W) morphology (Figure 4D-E). We observed that the FC-W interfacial area increases significantly when F-PBI's concentration increases from 0 to 10 mg/mL. The strong interactions of F-PBI with CNTs directs assembly at the FC-W interface. These interfaces behave as barriers against phase separation, and the droplet's interface kinetically traps the HC in smaller domains. When the concentration of F-PBI is increased to 50 mg/mL, more CNTs are adsorbed onto the FC-W interface. In addition, molecules with a similar structure to our F-PBI have been shown to reduce the interfacial tensions between the HC-FC phases,[30] and hence this additive can also stabilize the multidomain structure by stabilizing the expanded HC-FC interfacial area.

We performed similar experiments with a fixed concentration of MC1-CNTs at a reduced concentration of 10 mg/L and varying F-PBI concentrations. As expected, in the absence of F-PBI, the droplets display the FC/HC/W morphology (Figure 4F). As the F-PBI concentration increases from 1 g/L to 10 g/L, the morphology gradually changes from a partial Janus (Figure 4G) to a symmetric Janus morphology (Figure 4H). Similar to the other experiments, a higher concentration of F-PBI facilitates more adsorption of CNTs to the FC-W interface and increases its area. However, the mHC-FC/W morphology is not observed at higher F-PBI concentrations (≥ 10 mg/mL), as shown in Figure 4D. Apparently, the CNT concentration is insufficient to form the static interfacial structures that kinetically trap this phase

Dynamic Double Emulsions

After obtaining the complex double emulsions stabilized solely by MC-CNTs, we endeavored to see if the droplet morphologies can be dynamically modified by the addition of other surfactants. In these studies, we made use of Zonyl FS-300 (Zonyl), a water-soluble surfactant for the FC phase, and Tween 20 (Tween), a water-soluble surfactant for the HC phase. For droplets stabilized by 60 mg/L of MC1-CNTs or MC2-CNTs in the continuous water phase, but lacking F-PBI, the morphology changed from FC/HC/W to a Janus structure upon adjusting the Zonyl concentration in the water to be 1 wt % (Figure 5A). This change in morphology could be reversed when the aqueous phase concentration of Tween is 1 wt %. The power of the MC-CNT surfactants is revealed by the fact that even with a large excess of Zonyl (1 wt %), the Janus structure persists. In the case of molecular surfactants, large Zonyl concentrations can displace the organic phase surfactants and generate a HC/FC/W morphology.[10] To visualize where CNTs were located before and after the morphology change, we used the fluorescent PAA-RB labeled MC2-CNTs to stabilize FC/HC/W droplets. The fluorescence images in Figure 5A reveal that CNTs covered the entire droplet surface. After switching the continuous aqueous phase to contain 1 wt % Zonyl, only the HC hemisphere is covered with CNTs. Even at higher concentrations of Zonyl, we are unable to produce HC/FC/W droplets because CNTs are tightly bound to the HC-W interface and act as a barrier against further morphology change.

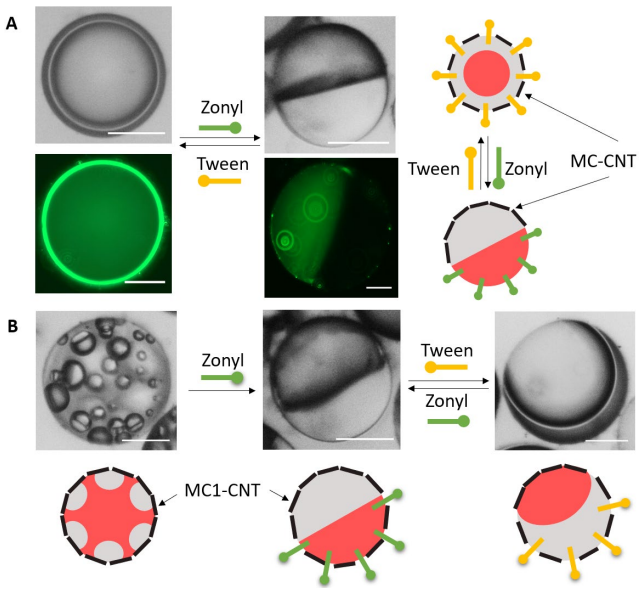

Figure 5. (A) Droplets made with 60 mg/L of MC2-CNTs. The morphology changed reversibly upon the addition of Tween or Zonyl. Fluorescence images confirm that the MC2-CNT surfactants are located at the water interface. (B) Droplets made with 60 mg/L of MC1-CNTs and 1 mg/mL of F-PBI and images showing how the morphology changes upon adding Zonyl and Tween. Scale bar = 50 μm.

When F-PBI is present in the FC phase, other dynamic behavior is observed. Images of droplets made with 60 mg/L of MC1-CNTs in the water phase and 1 mg/mL of F-PBI in the FC phase are shown in Figure 5B. The mHC-FC/W morphology changes to a Janus structure when the aqueous phase is adjusted to 1 wt % of Zonyl. Subsequent addition of Tween (1 wt % in water) changes the morphology to where the HC almost encapsulates the FC phase. The last two morphologies are reversible by adding Zonyl (1 wt %) or Tween (1 wt %). The addition of organic surfactant speeds up the phase separation process of the FC and HC oils and releases the droplets from kinetically trapped thermodynamically unstable polydomain morphology to a more stable morphology. In these systems that contain F-PBI in the FC phase, the systems could not be driven to the states wherein one oil is encapsulated by the other. This is because CNTs are strongly and irreversibly bound to both the FC-W and HC-W interfaces.

The amount of CNTs adsorbed at the interface controls the droplets' morphology when excess organic

surfactants are added. In Figure 6A, double emulsion droplets made with 10 mg/mL of F-PBI are exposed to excess of Zonyl (>1 wt %. As the concentration of CNTs increases, Θ_F increases, which reflects an increasing surface area of the HC-W interface. This is the result of more CNTs assembling at the HC-W interface. In Figure 6B, double emulsions droplets made with 60 mg/L of CNTs are exposed to excess Tween (>1 wt %). Similar to Figure 6A, as the concentration of F-PBI increases, so does the Θ_H as a consequence of a larger FC-W interfacial area. Here again, the F-PBI causes CNTs to assemble at the W-FC interface.

CONCLUSION

In summary, using MC functionalized CNTs, we have demonstrated a one-step process method to fabricate complex Pickering emulsions. The dynamic MC chemistry at the interface allows for the interfacial reactions with the amines in the aqueous solution. The nature of the amine molecules/polymers controlled the stability of the droplets, with the multivalent polymeric amines displaying superior MC stability. Methods that predictably produced different morphologies for double emulsions by varying the CNT and F-PBI concentrations were developed. Increasing the CNTs and F-PBI concentrations led to a gradual change in morphology ranging from kinetically stable morphology (Janus or FC/HX/W) to kinetically trapped and unstable (mHC-FC/W) multidomain morphologies. In the latter case, the rigid network of high concentration CNTs acted as the barrier for the consolidation of the phases within a given droplet. F-PBI facilitated the adsorption of CNTs to the W-FC interface. Higher concentrations of F-PBI resulted in a higher amount of CNTs adsorbing to the interface, which led to a larger FC-W interfacial area. The CNTs stabilized complex emulsions displayed a dynamic morphological response to small-molecule surfactants. Some morphologies were reversible with the addition of Zonyl and Tween. However, CNTs bound to the droplet interfaces showed strong resistance to morphology changes even with the addition of excess Tween and Zonyl. This was explained by the strong adsorption of CNTs at the interface to form a rigid network. We foresee our MC-CNTs stabilized complex droplets to have utility in sensing and coating methods.

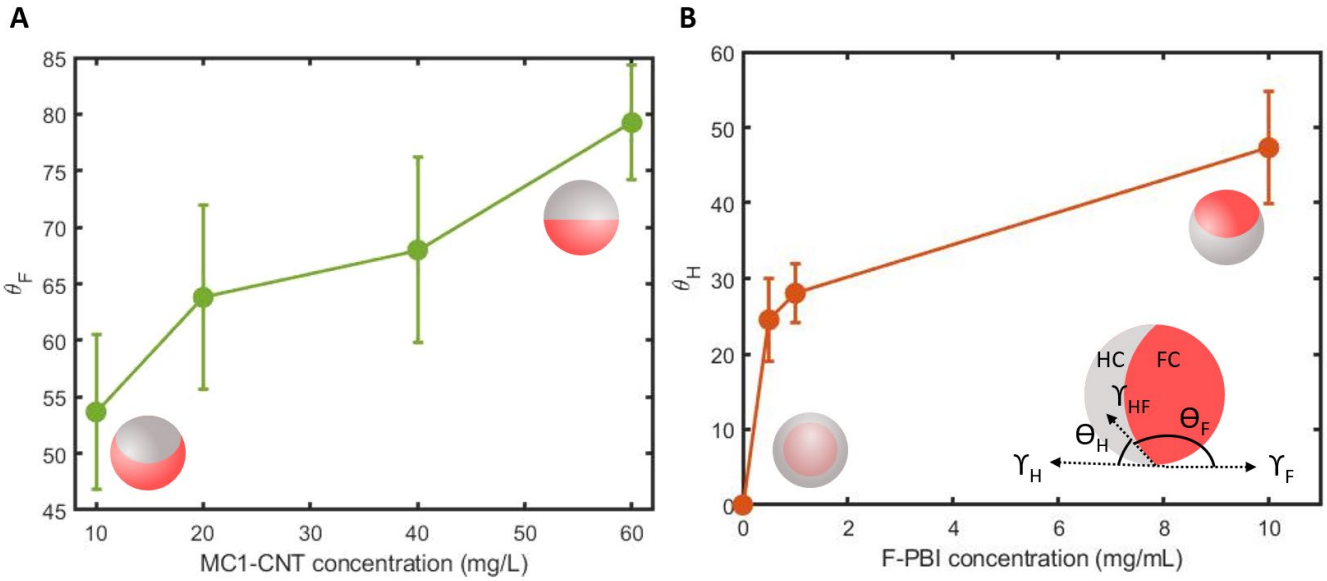

Figure 6. (A) Plot of contact angles Θ_F between the FC–W and FC–HC interfaces versus MC1-CNTs concentration, with a constant Zonyl concentration of 1 wt % and F-PBI concentration of 10 mg/mL. (B) Plot of contact angles Θ_H between the HC–W and FC–H interfaces versus F-PBI concentration with a constant concentration of Tween at 1 wt % and a MC1-CNTs concentration of 60 mg/L.

ASSOCIATED CONTENT

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

Supplementary Figures; Experimental Methods; Materials and Characterization Techniques; Droplets Micrographs and Characterizations.

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