Directing single-walled carbon nanotubes to self-assemble at water/oil interfaces and facilitate electron transfer†

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Both the behavior and the general key factors for assembling flexible SWNT films at the water/oil interface were investigated; the electron transfer, one of the most fundamental chemical processes, at the SWNT-sandwiched water/oil interface was also firstly illustrated using scanning electrochemical microscopy.

Owing to an important prerequisite for various applications of nanotechnology, the hierarchical assembly of nanostructures is highly anticipated.[1] Recently, liquid/liquid (L/L) interfaces have started to gain increasing attention for such assemblies.[2–5] Of key advantage, at L/L interfaces, such as the water/oil (W/O) interface where the interfacial tension is high, the assembly is highly dynamic. It enables defects to be corrected rapidly. This feature is reminiscent of the self-assembly process occurring in nature, usually associated with self-healing, which opens immense possibilities in generating biomimetic nanodevices. Several groups have successfully demonstrated the potential to recruit the L/L interface to assemble (bio)nanoparticles.[2–6] Therefore, it is interesting to extend such an assembly method to other nanostructures.

Carbon nanotubes (CNTs) have shown significant potential applications, but limitations in assembling them still exist.[7] Thus, various methods have been explored such as the template method,[8] layer-by-layer assembly,[9] and the Langmuir–Blodgett (LB) technique.[10] However, investigations on recruiting the W/O interface are few. Wang and Hobbie first reported the W/O interfacial assembly of pristine single-walled CNTs (SWNTs) by an emulsion technique.[11] However, due to strong intertube van der Waals attractions, the SWNTs were heavily entangled at the interface. A similar emulsion technique was also applied to assemble amine-functionalized multi-walled CNTs (MWNTs) into "nanotubesomes" by Pan-huis and Paunov.[12] More recently, Matsui *et al.* reported oxygen-rich MWNTs could assemble into a monolayer at the W/O interface.[13] Research in more depth continues, *e.g.* to develop a more general assembly pathway for applications on demand and to address the key factors involved. Moreover,

due to unique electronic properties, SWNTs might help heterogeneous electron-transfer reactions (one of the most fundamental chemical processes) at the L/L interface. However, up until now such studies have been very few.

We have reported the preparation of multifunctional materials using an ionic liquid (IL) backbone as the platform and the application of this principle in SWNT modification.[14] The work also hints that imidazolium modified SWNTs (SWNTs-Im, Fig. 1a) might self assemble at the W/O interface due to their unique wettability. SWNTs-Im were readily dispersed in water by ultrasonication and were stable for days. Upon adding chloroform, SWNTs-Im remained in the upper layer (gray, Fig. 1b). Then, after ultrasonication for seconds and standing overnight, SWNTs-Im spontaneously transferred onto the W/O interface (Fig. 1c). A film was visible at the interface, which, when the vial was tilted, was observed to stretch without fragmentation (Fig. 1d). The flexibility of these films was illustrated by their ability to heal over damaged cycles (*e.g.* pushing a glass rod through the interfacial film). These films could be transferred onto silicon wafers and indium tin oxide (ITO) glasses using Langmuir techniques.[4] Similar films were also observed at the toluene/water interface (Fig. S1†).

The thickness of SWNT films will delicately affect their applications such as for optoelectronics, high-flux membranes, batteries, *etc.*[15] Here SWNT-Im films with different thicknesses could be obtained by fixing the area of the W/O interface and controlling the concentration of SWNTs-Im aqueous solution. Fig. 2a shows a typical scanning electron microscope (SEM) image of the SWNT-Im thin film, in which
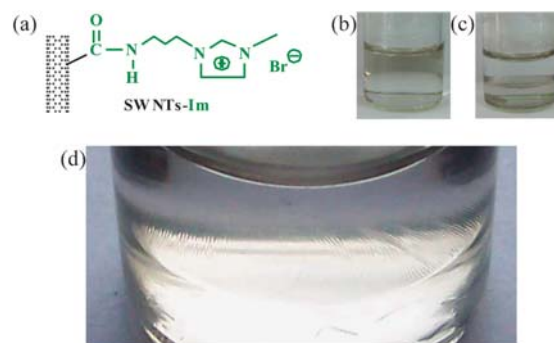

Fig. 1 (a) Structure of SWNTs-Im; (b) chloroform covered with SWNT-Im aqueous solution; (c) SWNTs-Im sandwiched at the water/chloroform interface, and (d) stretching marks formed at the interface in (c) when the vial was tilted.

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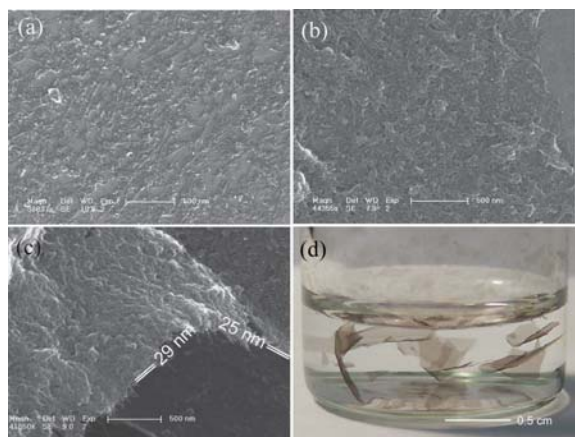
Fig. 2 SEM images of SWNT-Im (a) thin and (b) thick films on ITO, and (c) thick film on a Cu grid transferred from the W/O interface, scale bars are all 500 nm. (d) Free-standing SWNT-Im films isolated in water, scale bar is 0.5 cm.

a low concentration of SWNTs-Im was used. The clear contrast between SWNTs-Im and the ITO substrate indicated only two or three layers formed at the W/O interface. When the concentration was increased by 5 times, a thicker film formed (Fig. 2b and c). The thickness was estimated to be *ca.* 20–30 nm, which corresponded to approximately ten SWNT-Im layers. Moreover, when the organic phase volatilized, the transparent free-standing SWNT-Im multilayer films could be isolated from the interface (Fig. 2d) with the ratio of the width to the thickness up to *ca.* 1.5×10^5.[16]

The orientation of the SWNTs-Im at the W/O interface was also investigated by molecular dynamics (MD) simulation (see details in ESI†). Intermolecular forces such as ionic interactions, hydrogen bonding and London-forces between SWNTs-Im and solvent molecules would play important roles. The $E_{potential}$ values of the system obtained from the MD simulation indicated that the Im part of SWNTs-Im was preferred in the water phase (Fig. S2† and Table 1). This was in agreement with the fact that Im unit with Br^- was hydrophilic. The main contribution to the stability was from the electrostatic interaction.

In contrast, neither pristine SWNTs nor SWNTs-COOH, the starting materials to synthesize SWNTs-Im, formed flexible films at the W/O interface. Interfacial assembly of SWNTs is driven by minimizing the interfacial energy, ΔE. Due to the assembly of SWNTs from the aqueous solution to the W/O interface, ΔE can be given by $-\pi R^2 \gamma_{ow}(1 - \cos\theta)$, where R, γ_{ow} and θ represent the equivalent radius of SWNTs, the tension of the W/O interface and the contact angle of SWNTs with the interface, respectively.[3,17] This indicates that for a

given W/O interface (*i.e.* γ_{ow} was constant), R and θ are two key variables. Because they are microns in length, pristine SWNTs could collect at the W/O interface, but the obtained film was easily cracked under a disturbing force. SWNTs-COOH were also microns in length and dispersible in the aqueous phase, but never collected at the W/O interface. This could be well explained by the contact angle measurements.[4,5] SWNT-Im films exhibited a contact angle of *ca.* 90° (Fig. 3a) with the toluene/water interface (Fig. 3c middle), in which ΔE was the most favorable.[3–5,17] The contact angle of the SWNT-COOH film was *ca.* 70° (Fig. 3b), which indicates SWNTs-COOH have a stronger affinity for water than for oil, and a larger fraction resided in the water phase (Fig. 3c left).

Therefore, to self-assemble flexible SWNTs at the W/O interface, firstly it was necessary to modify SWNTs for better dispersion, which would also enable SWNTs to move at the interface and achieve equilibrium rapidly. Secondly, a proper wettability of the SWNTs was also essential to minimize ΔE. Although the micron size of SWNTs favors minimizing ΔE, the contribution of the wettability would be predominant and be influenced by the aforementioned modification. Thus these two factors should be harmonized with each other. Besides, the functional group on the SWNTs would affect the orientation of the SWNTs at the interface.

Using the W/O interface not only offered an alternative pathway for assembling SWNTs, but also additionally provided a unique SWNT-sandwiched W/O interface, which would have many potential applications. For example, electron transfer (ET) reactions are among the most fundamental and thoroughly studied chemical processes. In particular, ET at the interface between immiscible electrolyte solutions (ITIES, *e.g.* the W/O interface) has been studied extensively.[18,19] One important reason is that ITIES has been suggested as a simple model for biological and artificial membrane.[18] Due to the biomedical purpose of SWNTs across cellular membranes,[20] SWNTs-sandwiched ITIES would provide an ideal biomimetic system to explore the fundamental problems involved, such as homo/heterogeneous ET. Moreover, SWNTs might have potential applications in heterogeneous catalytic reactions as electron mediators. Therefore, the contribution of the SWNTs-Im to ET at the W/O interface was investigated by scanning electrochemical microscopy (SECM, Fig. 4a).

SECM could provide information on the electrochemical interaction of redox species at a tip and the interface under investigation, which was useful to elucidate the ET rate at the interface.[18,19] In the feedback mode, when the normalized distance less than 5, if the initial form of the tip-generated species diffusing to the interface can be regenerated, the current at the tip will be enhanced, and *vice versa*.[18,19] At the W/O interface without SWNTs-Im, the tip current

Table 1 The potential energies ($E_{potential}$) and their component parts from electrostatic ($E_{electro}$) and van der Waals (E_{vdW}) interactions (kcal mol^{-1}) from the MD simulation

Entry	$E_{electro}$	E_{vdW}	$E_{potential}$
a	−21 178.89	3729.30	−8930.52
b	−21 122.08	3719.38	−8884.32

a The Im part of SWNTs-Im in the water phase. *b* The Im part of SWNTs-Im in the oil phase.

Fig. 3 A water droplet covered with toluene resting on (a) a SWNT-Im film transferred from the W/O interface, and on (b) a SWNT-COOH film by spin-coating on a silicon wafer. (c) Schematic position of a SWNT at the W/O interface for a contact angle less than 90° (left), equal to 90° (middle) and greater than 90° (right).
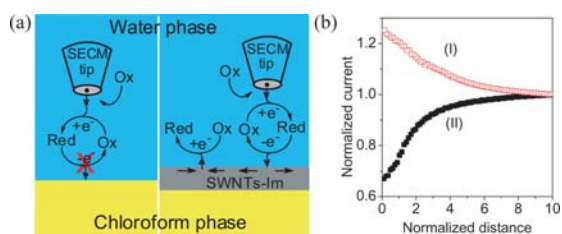
Fig. 4 (a) SECM arrangement (not to scale) for a feedback measurement at the pure (left) and SWNT-Im-sandwiched (right) water/chloroform interface; (b) experimental approach curves (CHI 900) for a tip in aqueous solution approaching the SWNT-Im-sandwiched (I) and pure (II) water/chloroform interface. Currents are normalized to the steady-state diffusion limiting current, $i_{T,\infty}$ and distance to tip radius. The aqueous solution contained 0.5 mM $Ru(NH_3)_6^{3+}$ and 100 mM KCl. The tip (Pt, 10 μm radius, RG = 10) was held at −0.35 V vs. Ag/AgCl (saturated KCl) for $Ru(NH_3)_6^{3+}$ reduction and approached at 1 μm s^{-1}. The counter electrode was Pt wire.

decreased when the tip approached the interface (Fig. 4b, II, negative feedback). It indicated the initial redox species ($Ru(NH_3)_6^{3+}$) in water could not be regenerated and the diffusion of the original redox species ($Ru(NH_3)_6^{3+}$) to the tip was blocked (Fig. 4a, left). However at the SWNT-Im sandwiched interface, the tip current increased when the tip approached the interface (Fig. 4b, I, positive feedback). It indicated that with the aid of SWNTs-Im the initial form of the redox species could be regenerated at the W/O interface (Fig. 4a, right). In the current preliminary work there were no reactions in the oil phase, but the result here indicated the possibility of an enhanced ET at W/O interface between two redox centers which were in the respective phases. Tsionsky et al. reported that the lipid monolayer at the W/O interface decreased the rate of interfacial ET because of its electrochemical inertness.[21] Here, on the contrary, due to unique electronic properties, SWNTs-Im at the W/O interface accelerated the interfacial ET. Positive feedback in SECM measurements of SWNTs has been reported very recently by assembling them on solid substrates,[22] but not previously at ITIES. Our preliminary result indicated that SWNTs hold great potential to accelerate the ET at the W/O interface.

It should be noted that other ''ordinary'' surfactants were also able to guarantee SWNTs a good dispersion and proper wettability. But thanks to its unique properties, the Im group was superior in further delivering other functional counteranions such as complexes[14] and biomolecules[23] onto SWNTs-Im by ion exchange. From another point of view, SWNTs-Im could act as ''hosts'' to introduce ''guests'' to be assembled at the W/O interface, which would greatly enrich related studies.

In summary, by functionalizing SWNTs with the Im group, we reported an approach to self-assemble flexible SWNT films at the W/O interface, and found that the dispersion, the wettability and intermolecular interactions related to SWNTs played critical roles. The functionalization itself was simple and well developed, and the thickness of the SWNTs films was also controllable. Moreover, the electron transfer, one of the most fundamental chemical processes, at unique SWNT-sandwiched ITIES was also firstly investigated by SECM. It will pave the way for both fundamental ET research and other applications. Potential works focused on more detailed ET research of SWNT-sandwiched ITIES, delivering other functional units into the W/O interface by means of SWNTs-Im, and SWNTs-aided heterogeneous catalysis are currently underway.

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