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Studies and comparison of the liquid adsorption behavior and surface properties of single- and multiwall carbon nanotubes by capillary rise method

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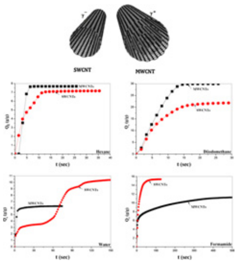
HIGHLIGHTS

- ► SWCNT adsorbed polar liquid greatly, MWCNT adsorbed non-polar liquid greatly.
- ► The surface energy of both SWCNTs and MWCNTs dominated by the LW interactions component.
- ► SWCNT strongly the Lewis base, MWCNT strongly the Lewis acid.

GRAPHICAL ABSTRACT



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ABSTRACT

The liquid adsorption behaviors and surface properties of single- (SWCNT) and multiwall (MWCNT) carbon nanotubes were studied and compared by the capillary rise method. It was found that these CNTs both adsorbed the diiodomethane greatly as compared with other liquids, e.g. water, formamide and hexane, and the reason is due to the total surface free energy of these CNTs both dominated by the Lifshitz–van der Waals interactions component, especially the SWCNTs at about 95%. Comparison further indicated that the SWCNT adsorbed the polar liquid greatly due to stronger in the Lewis base component and the MWCNT adsorbed the non-polar liquid greatly due to stronger in the Lewis acid component. The total surface free energy of SWCNT is about 50 mN/m slight greater than that of the MWCNT.

1. Introduction

Since discovered by Iijima [1–3], the carbon nanotube, CNT, has attracted great interests due to its unique physical and chemical properties. Up to now, CNT has been broadly studied and applied [4–11].

Among various properties studied and reported elsewhere [5–11], the wetting and surface properties of CNTs has been focused by several researchers [6,7]. For example, Dujardin et al. [6,7] have measured the contact angles between several metals and CNTs and found that the application of melt metals with high surface tension, e.g. 130–190 mJ/m^2, can lead a non-wetting change to a partial wetting because CNTs are super-straws. Nuriel et al. [9] have measured the contact angles on multiwall CNT, MWCNT, using some molten polymers as probes and found that the MWCNT has great polar component, e.g. about 60%, of the total surface free energy. However, these probes are unexpected to characterize unknown solids. As has been also known, the contact angle-based the critical surface tension, γ_c, of SWCNT is ranged within 40–80 mJ/m^2 [12]. The contact angle-based total surface free energy, γ_S, of MWCNT is in the range of 25–45 mJ/m^2 [9,13], the dispersion component, γ_S^d, at 20 mJ/m^2, and the polar component, γ_S^p, at 5 mJ/m^2 [13]. In terms of the inverse gas chromatography, IGC, measurement, the γ_S of MWCNT is at about 120 mJ/m^2, 315 K [8,11]. Since the contact angle

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Table 1
Physico-chemical properties of probe liquids [20–22].

Liquids	ρ (g/ml)	η (mPa s)	γ_L (mJ/m^2)	γ_S^{LW}	γ_L^+	γ_L^-
Hexane	0.660	0.3	18.43	18.43	0	0
Diiodomethane	3.323	2.8	50.80	50.80	0	0
Water	0.998	1.0	72.75	21.80	39.66	16.39
Formamide	1.132	4.6	58.20	39.00	3.54	25.49

measurement also presented the γ_S for fullerene at 57.8 mJ/m^2, 312 K [9], for graphite at 279 mJ/m^2, 416 K, and for carbon black, CB, in a range of 174–204 mJ/m^2, 453 K, respectively [11], or at room temperature 25 °C about 20–35 mJ/m^2 [14]. It is considered a comparison of the data of all carbon materials is required and in fact it is also expected [15–17].

The aim of this work is therefore proposed to apply the capillary rise method as recently we reported [14,18] and some typical liquids as probes to study the liquid adsorption behavior and surface properties of both SW- and MWCNTs, then to compare with literature reported values on different carbon materials.

2. Experimental

2.1. Materials

The commercial SWCNT (TNSSC, purity > 90%, length 0.5–2 μm, diameter 1–2 nm, SSA > 380 m^2/g, tap density at 0.14 g/m^3) and MWCNT (TNIMC6, purity > 90%, length 10–30 μm, diameter 20–40 nm, SSA > 110 m^2/g, tap density 0.16 g/m^3) both provided by Timesnano, Sichuan, China and used as received. The detailed introduction of these CNTs can be also seen from the company website [19]. The MWCNT was also used and introduced previously [18,20].

The liquids of hexane, diiodomethane and formamide in analytic level were purchased from local chemical store at Shanghai and used as received [14,18]. The used distilled water was self-made in our laboratory. The surface tension and related components of these liquids are cited from literature [21,22] and summarized in Table 1.

2.2. Capillary rise method

The capillary rise measurement was performed as below. The CNTs were initially charged in a glass tube with an inner diameter of about 4 mm, and for each charging, the packing density was controlled as a constant by controlling the weight of CNTs at 0.014 ± 0.001 g and the packing height at about 8 mm [14,18,23–28]. A surface tension analyzer (Shanghai Fangrui Instrument Co.) was applied to record the liquid amount absorbed by CNTs and the corresponding time.

All these measurements were performed at 25 °C.

3. Results and discussion

Taking CNTs absorbed liquid amount, defined as Q_t, g/g, as Eq. (1) defined as a function of the adsorption time, t, Fig. 1 presented the dynamic liquid adsorption behavior of both SWCNTs and MWCNTs in relation to the probe liquids of water, hexane, formamide and diiodomethane, respectively.

$$Q_t = \frac{W_{ad}}{W_0} \tag{1}$$

where W_{ad} is adsorbed liquid weight of CNTs at varying time, and W_0 is the weight of CNTs initially charged in glass tube.

Observed both the SWCNTs and MWCNTs can adsorb these liquids and the whole adsorption process presented in several stages where the weight offset was caused by the formation of a liquid meniscus around the sample at initial stage [29], and after certain time the adsorption approached to a constant when the main influence was from the gravity [30,31].

A comparison of these four probe liquids found that the diiodomethane was greatly adsorbed and the hexane was small adsorbed by both these CNTs. These suggested that the Lifshitz–van der Waals, LW, interactions might be strongly occurred in these adsorption processes and these might be dominated by the CNTs probably due to CNT with great LW component. Since a comparison of these two kinds of CNTs found that the SWCNTs adsorbed polar liquids greatly and the MWCNTs adsorbed non-polar liquids greatly, this suggests that these CNTs may have different acid–base properties. This is exactly because the water–adsorption curves for SWCNT showed two stages while for MWCNT only in one stage. This multistage adsorption behavior is interested. In fact, a comparison of our recently reported cases further found that this two adsorption stages is also presented for CB after oven drying but without showed for as-received CB [14] and some polymers [18]. Therefore, the multistage adsorption phenomenon is considered may reveal the wetting of layered carbon structure. In other words, this adsorption might be a character of layered carbon materials.

According to Fig. 1 showed adsorbed liquid amount for these two kinds of CNTs, it is furthermore suggested that the liquid adsorption in MWCNTs is mainly influenced by the Lifshitz–van der Waals, LW, interactions while in SWCNTs is mainly influenced by the Lewis acid–base, AB, interactions. This finding is also interested because this different liquid adsorption behavior is not only for understanding the wettability of both SW- and MWCNT, but also a help for understanding the super-straw behavior of CNTs [6,7].

To take Fig. 1 to fit the Langmuir adsorption model as showed in Eq. (2) [32], the related adsorption parameters were quantitatively estimated and summarized in Table 2.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{2}$$

where k_2 is the second order kinetics adsorption rate constant, $1/s$; Q_e is the absorbed liquid amount at equilibrium state, g/g.

According to Table 2, the adsorption rate is the fastest for MWCNTs to adsorb hexane and the lowest for MWCNTs to adsorb diiodomethane, while the adsorbed amount is the greatest for MWCNTs to adsorb diiodomethane and the smallest for SWCNTs to adsorb water. These adsorption kinetics parameters are found in good agreement with Chen et al. reported data [16].

Table 2
Kinetics parameters on liquid adsorption of CNTs.

CNTs	Liquids	k_2 (1/s)	Q_e (g/g)	R
MWCNTs	Hexane	0.165	6.07	0.9387
	Diiodomethane	0.002	44.90	0.9999
	Water	0.156	6.42	0.9458
	Formamide	0.003	11.96	0.9333
SWCNTs	Hexane	0.063	7.71	0.9967
	Diiodomethane	0.011	23.56	0.9983
	Water	0.045	4.22	0.9966
	Formamide	0.010	16.34	0.9963