

Unusual interfacial phenomena at a surface of fullerite and carbon nanotubes



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ABSTRACT

Interactions of water, methane, HCl, C₆H₆, F₃CCOOD, and hyaluronic acid with fullerite C₆₀/C₇₀ and multi-walled carbon nanotubes (MWCNT) were studied in various media using ¹H NMR spectroscopy. The materials were characterized using microscopy, differential scanning calorimetry, Raman spectroscopy, and quantum chemical methods. Water with weakly (WAW) and strongly (SAW) associated molecules bound to fullerite demonstrates unusual downfield shifts $\delta_{\text{H}} < 18$ ppm. WAW in contrast to SAW cannot dissolve acids. Water bound to MWCNT demonstrates the downfield shift smaller than that observed for fullerite. Fullerite possesses low porosity due dense packing of fullerenes in molecular crystals. Therefore, noticeable adsorption is observed only for compounds, which are capable for intercalation (benzene, toluene, water), but nitrogen cannot be adsorbed by fullerite. For MWCNT with much looser structure than that of fullerite, pre-adsorbed water weakly affects methane adsorption. An increase in pre-adsorption of water results in decrease in adsorption of methane onto MWCNT.

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1. Introduction

Carbon nanotubes (CNT) caps and fullerenes have similar structures composed of pentagonal and hexagonal rings, in which no two pentagons share an edge because of strong destabilizing effect [1,2]. A cylindrical part of CNT with no defects is composed of only hexagonal rings [2]. A small value of the radius of curvature of such fullerenes as C₆₀ and C₇₀ and a much larger value of the radius of curvature of multi-walled CNT (MWCNT) at $d > 10$ nm in diameter and a very large length/diameter ratio lead to a significant difference in structure of π -electron clouds at a surface of these nanostructured carbons. Additionally, a simpler spherical shape of fullerenes than that of CNT causes a significant difference in such secondary structures as fullerites (aggregated molecular crystals) and agglomerated CNT (buckypaper) [1–10]. The molecular crystal structure of fullerite C₆₀ corresponds to a face centered cubic (FCC) lattice with $Fm\bar{3}m$ space group. The lattice spacing in the C₆₀ fullerite is 1.417 nm, and the nearest C₆₀ neighbors distance (from their centers) is equal 1.018 nm, and a distance between rings of

neighboring buckyballs corresponds to a typical van der Waals (vdW) distance for carbons (~ 0.34 nm). This molecular crystal structure of fullerite provides only very narrow voids (pores), in which small molecules (as intercalants) can be adsorbed through the intercalation mechanism (i.e. the adsorbates increase the inter-fullerene distances). Note that fullerenes can have different shapes, e.g. C₆₀ is of a spherical shape, but C₇₀ has a rugby-ball shape. Therefore, fullerites with a mixture of C₆₀ and C₇₀ (studied in the present work) can have the properties different from those of fullerites composed of individual fullerenes C₆₀ or C₇₀.

In contrast to fullerite as a molecular crystal, CNT buckypaper has a disordered structure similar to cotton wool with much larger voids between neighboring tubes than that between fullerene molecules in fullerite. Thus, despite CNT and fullerite belong to the same fullerene family with similar local structures including pentagonal and hexagonal carbon rings, they have different electronic structures and very different textural and morphological characteristics [1–10]. However, buckypaper can have a relatively close-packed arrangement of carbon nanotubes that are supported solely by tube-tube surface interactions due to vdW interactions [2]. In other words, a part of voids in the buckypaper can be in the range of nanopores at half-width (radius) $R < 1$ nm. This can

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affect adsorption features of small molecules, e.g., characterized by upfield shifts in the ^1H NMR spectra [15]. Thus, the degree of overlap and geometric arrangement of the CNT in aggregates can define the adsorption and other properties of the material. The mentioned similarity and differences in the primary and secondary particles of CNT and fullerite can lead to different interfacial and temperature behaviors of polar and nonpolar adsorbates, especially during their competitive adsorption onto fullerite and MWCNT (that will be analyzed in the present paper).

Note that fullerenes are poorly soluble even in organic solvents, e.g. about 4×10^{-4} M C_{60} in toluene and carbon bisulfide and 0.0097 M C_{60} in 1-chloronaphthalene [11]. Van der Waals interactions of fullerenes with solvents do not provide great solvation energy in comparison to intermolecular fullerene–fullerene interactions in fullerite. However, intercalation of some adsorbates (e.g. benzene, toluene, etc.) into inter-fullerene space in crystalline fullerite is possible. Slow evaporation of solvents with dissolved fullerene C_{60} leads to the formation of a molecular crystal (fullerite) with the FCC lattice. Such small molecules as benzene, toluene and other intercalants can penetrate into increased voids in the lattice [12–14] to form stable complexes, which can be decomposed upon heating to 400–500 K. Clearly, nonpolar aromatic molecules (benzene, toluene) can be more strongly adsorbed to fullerite than water molecules, i.e. water cannot displace organics from pores but organics can displace bound water [15]. Therefore, pretreatment (washing in organic solvents, heating) of carbons can play an important role in the adsorption of various compounds.

Low-temperature ^1H NMR spectroscopy applied to static samples to avoid contributions of immobile structures (solids, polymers, ice) allows one to study the interfacial and temperature behaviors of mobile liquid adsorbates at temperatures lower than their freezing points T_f [15]. These adsorbates can be unfrozen at temperatures lower than T_f due to depression of the freezing point

for liquids confined in pores. The freezing point depression and the radius of pores, where liquid adsorbate is located, are linked by the Gibbs–Thomson relation [16–18]. The freezing point depression values allow one to estimate changes in the Gibbs free energy of bound liquids, e.g. water, at $T < T_f$. Waters frozen at $T < 260$ K and at $260 \text{ K} < T < 273$ K can be attributed to strongly bound water (SBW) and weakly bound water (WBW), respectively [15]. The values of the chemical shift of proton resonance (δ_{H}) can be used to differentiate bound water into strongly associated water (SAW) at $\delta_{\text{H}} > 3$ ppm and weakly associated water (WAW) at $\delta_{\text{H}} = 1\text{--}2$ ppm [15,19]. The interfacial and temperature behaviors of bound water depend strongly not only on the textural and chemical characteristics of adsorbents but also on the types of media and co-adsorbates, their concentrations and equilibrium time.

The aim of this work was to compare the interfacial behavior of water affected by nonpolar, weakly polar and polar co-adsorbates (at various amounts of them) at a surface of fullerite C_{60} (85%)/ C_{70} (15%) and MWCNT at temperatures higher and lower than the freezing point for deeper insight into the adsorption mechanism for these carbon materials belonging the same family, but having very different morphologies. These aspects are of importance for practical applications of these materials because water can be adsorbed from air onto any materials that can affect their properties.

2. Experimental and computational methods

2.1. Fullerite

Fullerite $\text{C}_{60}/\text{C}_{70}$ (weight ratio 0.85:0.15) was synthesized using electric arc (200 A, 24 V) method (Frantsevich Institute for

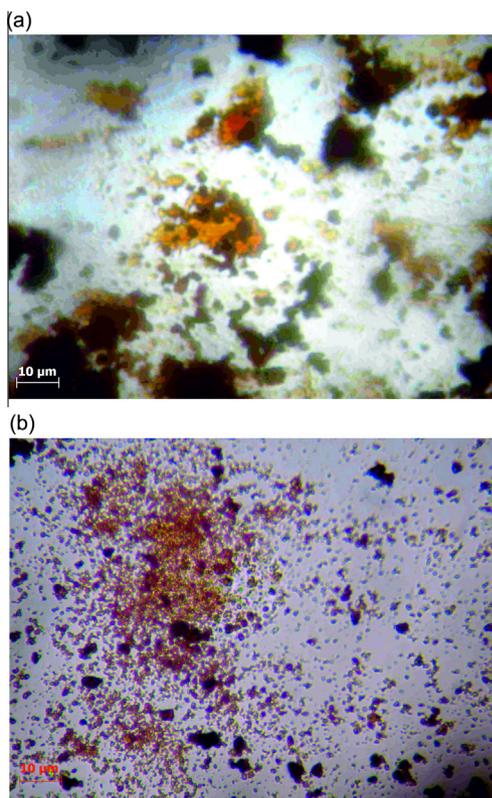


Fig. 1. Microphotos of fullerite in (a) air and (b) n-decane (scale bar 10 μm).

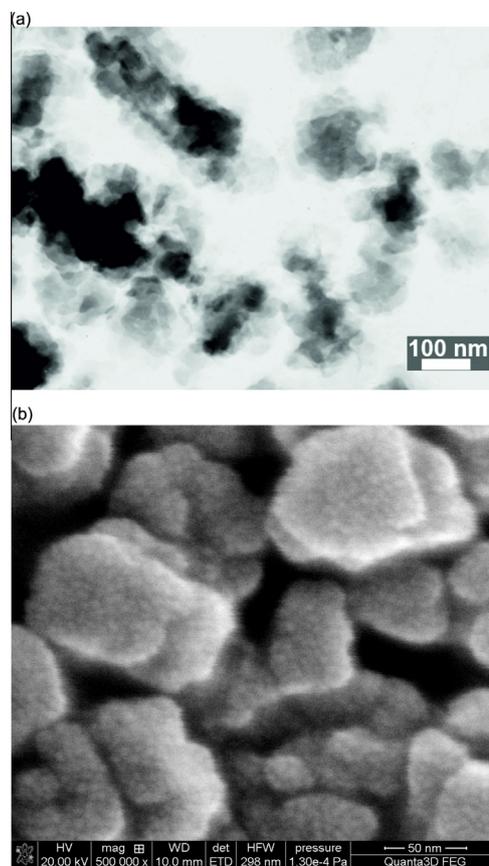


Fig. 2. (a) TEM and (b) SEM images of fullerite aggregate (scale bar 100 nm and 50 nm, respectively).

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