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ANALYTICAL POSSIBILITIES OF CARBON NANOTUBE BUCKYPAPERS DOPED BY GOETHITE

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Abstract

The evaporation of liquids from porous films is a very complex phenomenon, which can be followed by simultaneous weight monitoring, electric resistance measurement, infrared imaging and contact angel measurement. The appropriate evaluation of these measurement results can carry both quantitative and qualitative analytical information. The aim of our recent work is to demonstrate this opportunity through the example of the evaporation of simple solvents from porous buckypapers prepared from non-functionalized carbon nanotubes (*nf*-CNT) doped by goethite.

Introduction

Recent developments in nanotechnology have highlighted the importance of the classical topics of wetting, droplet spreading and evaporation due to their pronounced effect in technological applications (*e.g.*, air/fuel premixing, micro-fluidics, oil recovery, etc.) [1,2]. Multiple phenomena take place simultaneously when a liquid droplet contacts a porous surface: wetting, spreading, capillary filling, gravity induced convective flow, adsorption, evaporation from the surface, evaporation from the pores, etc. The evaporation of a sessile droplet can be studied by several experimental methods: transmission electron microscopy, environmental scanning electron microscopy, contact angle measurement, high speed camera recordings, thermal imaging, just to name a few. The evaporation of sessile droplets can be followed by an equipment assembled at the Department of Applied and Environmental Chemistry, University of Szeged: this equipment can guide simultaneous weight monitoring, electric resistance measurement and infrared imaging at a controlled temperature (typically at 50 °C). There are several experimental results characteristic for the evaporation process, the most important ones being the total evaporation time, time of evaporation only from the surface, full width at half maximum of the time-dependent mass and resistance curves, evaporation rate, initial area of the droplet, and the wetted area at the moment of total evaporation from the surface, etc. [3-5]. The main goal of this work was to demonstrate the analytical possibilities of the mass and resistivity measurements and IR videos through the example of sessile droplet evaporation (acetone, methanol, ethanol, water) from porous buckypapers (BP) prepared from *nf*-CNT and doped by goethite.

Experimental

Materials: The multiwall **carbon nanotubes** were synthesized by 2 h of catalytic chemical vapor deposition from a C_2H_4:N_2 (30:300 cm^3/min) gas mixture at 650 °C over Fe,Co/Al_2O_3 catalyst (metal loading: 2.5-2.5 m/m%). The synthesized materials were purified by repeating 4 h of refluxing in 10 mol/dm^3 aqueous NaOH, then 4 h in cc. HCl solution four times. The **goethite** nanomaterials were prepared by oxidation-precipitation method from water based solution of $FeCl_2$, precipitated by NaOH solution and oxidized by $NaNO_3$. The synthesis was performed at room temperature and under normal atmosphere. The yellow product was purified by centrifugation. The *nf*-CNTs and goethite were converted into **buckypaper** (BP) by filtering 70 cm^3 of their 0.1 g/dm^3 suspensions through a 0.45 μm nominal pore diameter Whatmann nylon membrane filter. The *nf*-CNTs (6.3 mg) and goethite (0.7 mg) were suspended by 40 min ultrasonication in N,N-dimethylformamide [3,4]. The schematic of the BP synthesis is presented in Fig. 1.

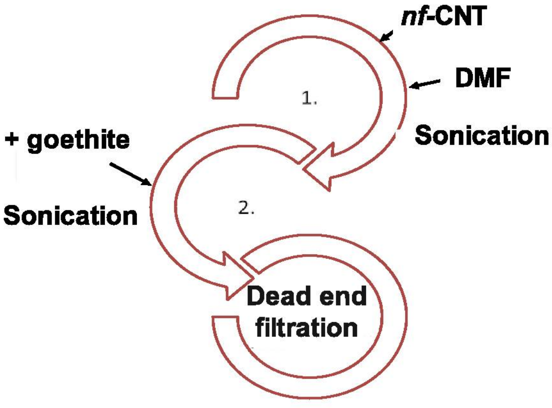

Figure 1. Schematic of the buckypaper synthesis.

Methods:

Electrophoretic mobilities of the CNTs and goethite nanomaterials were measured in a Nano ZS (Malvern) apparatus with a 4 mW He–Ne laser source (λ = 633 nm) using disposable zeta cells (DTS 1070) at 25 ± 0.1 °C. The zeta-standard of Malvern (−55 ± 5 mV) was used for calibration and the samples were diluted to give an optimal intensity. To get comparable data, the dispersions were homogenized in an ultrasonic bath for 10 s, after which 2 min relaxation was allowed. The effect of pH variation were studied at 10 mM NaCl. The Smoluchowski equation was applied to convert electrophoretic mobilities to electrokinetic potential values. The accuracy of the measurements was ±5 mV.

Liquid droplet evaporation (acetone, methanol, ethanol, water) was studied from the buckypaper film. The droplets (5 µL, 50 °C) were instilled with an Eppendorf Xplorer electronic pipette on the surface of the porous films. The temperature, the electric resistance and weight variations could be simultaneously monitored by the equipment assembled at the Department of Applied and Environmental Chemistry, University of Szeged. Buckypaper was placed onto a purpose-built sample holder and kept in place by a top piece that had a 1.4 cm diameter circular opening in it for placing the liquid droplet. The setup included a type K thermocouple in contact with the non-wetted part of the BP. The distance between the porous film and the heater was 1 cm. Data from the thermocouple was fed back to the temperature controller that maintained a base BP temperature of 50 ± 0.5 °C by continuously adjusting the heater power using fuzzy logic control. The sample holder was placed on a Sartorius Cubis microbalance with 0.01 mg readability and the weigh variation during droplet evaporation was recorded. For thermal imaging a FLIR A655sc infrared (IR) camera was used. This unit has a thermal sensitivity of 30 mK, an accuracy of ±2 °C for temperatures up to 650 °C at 640x480 resolution. Its uncooled microbolometer detector has a spectral range of 7.5-14.0 µm. The IR camera is equipped with a 2.9x (50 µm) IR close-up lens, with 32x24 mm field of view and 50 µm spatial resolution. The recorded images are transferred to a PC with FLIR ResearchIR Max software. Sessile droplet evaporation movies were acquired at maximum resolution with 50 Hz frame rate. Each CNT film's emissivity ($\varepsilon_{\text{film}}$) was determined by calibration at the initial film temperature (25 °C) with a black electrical tape ($\varepsilon = 0.95$). During liquid surface evaporation the temperature was determined by taking into account the emissivity of the liquid ($\varepsilon_L = 0.95$); after surface evaporation, the emissivity of the wetted film was calculated as the average between the emissivities of the studied liquid and the porous film. The sample holder plastic plate with the 0.7 cm radius gap in the center was equipped with two copper electrical connections at the opposite edges of the gap on the bottom of the sheet. The BP was fixed to the bottom of the plastic section with magnetic clips. The copper electrodes were contacted to the source meter by 0.3 mm diameter copper wires. The rigidity of these wires did not affect the balance because of the large inertia of the whole assembly mounted on the balance plate. This was confirmed by independent experiments before the evaporation profile (electrical resistance variation as a function of time) measurements. The computer recorded the electrical resistance of the buckypaper as measured by a Keithley 2612A Source Meter. Before the measurements, the BP film was mounted in the assembly and heating at initial temperature was applied until the electrical resistance and the sample weight both stabilized. Then all three recordings (resistivity, IR imaging and sample weight) were started a few seconds before dropping. The evaporation was studied by dropping a single droplet of a selected solvent to the center of the BP film and simultaneously recording the IR video, the mass and electrical resistance until they returned to their original values. The schematic of the equipment is presented in Fig. 2. The ambient air temperature and the relative humidity of the ambient atmosphere were kept constant (at 25 °C and 55 RH%, respectively) [3-5].

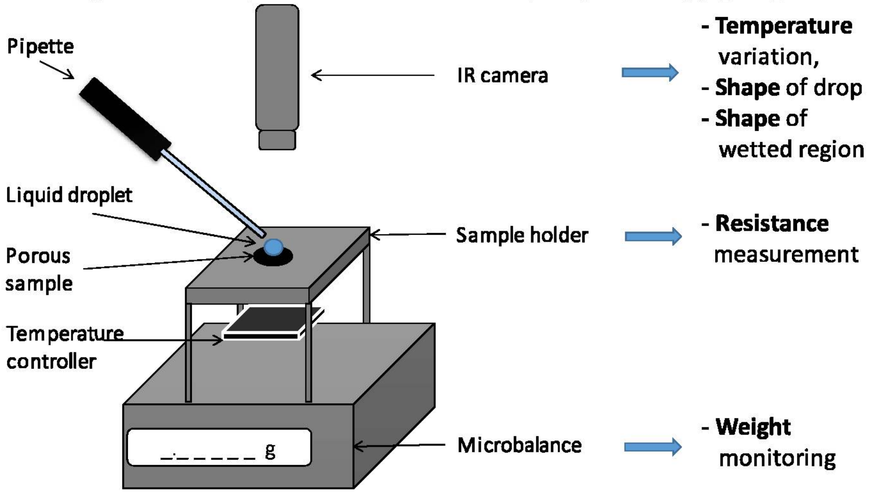

Figure 2. Evaporation monitoring equipment schematic.

Results and discussion

The zeta potential of *nf*-CNTs and goethite nanomaterilas are plotted as a function of pH in Fig. 3. The isoelectric point (IEP, at which the net charge of CNT is zero) is at pH~3 for *nf*-CNT and at pH~4.5 for goethite. The values of zeta potential shift to more negative region with the increasing pH.

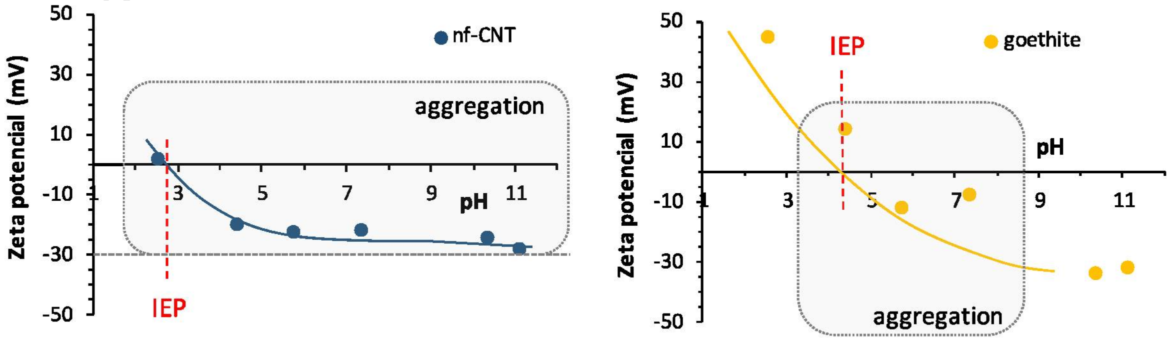

Figure 3. The pH dependent zeta potential of *nf*-CNT and goethite (10 mM NaCl, 25°C).

In general at the moment we drop the liquid on the buckypaper film (t_0), the liquid starts to diffuse immediately into the pores of the BP, but a part of it remains spread on the surface of the film. The evaporation of this liquid from the surface takes place together with the diffusion. Once all liquid evaporates from the surface, namely the primary surface evaporation is complete (t_S), liquid is left only in the pores. The solvent gradually evaporates from the pores as well. The complete evaporation of the solvent (t_t) was confirmed by the fact that the mass and the resistivity of the buckypaper returned to the baseline.

One typical mass variation is illustrated in Fig. 4. where t_0 marks the time when the drop was instilled. The mass of the BP increased as soon as the solvent was dropped to the film and this is followed by a quasi-linear weight decrease. Once the primary surface evaporation is complete (t_s), the mass of the buckypaper decreases as linear (within experimental error) functions of time due to the continuous evaporation of the solvent. The total evaporation time (t_t) was at the moment when the mass of the BP returned to the baseline. At the linear weight decreasing ranges, the rate of evaporation (-dm/dt) is constant. The change of -dm/dt value suggests the change of the dominant evaporation process, *e.g.*, evaporation of the droplet sitting on the surface of the BP, evaporation of the condensed water from the porous system or the evaporation of the adsorbed water from the microscopical surface of the porous system (see the linear ranges in Fig. 4.). From this measurement, the typical experimentally determined data are the shape of the curve: m_{max}, area, FWHM; t_s and t_t, evaporation rate -dm/dt and its change. These are characteristic for the measured system and can be used to identify them [3-6].

The weight variation during the evaporation of acetone, methanol, ethanol and water from the surface of *nf*-CNT doped by goethite can be seen in Fig. 5. It is clear that the more volatile solvents evaporate faster than water.

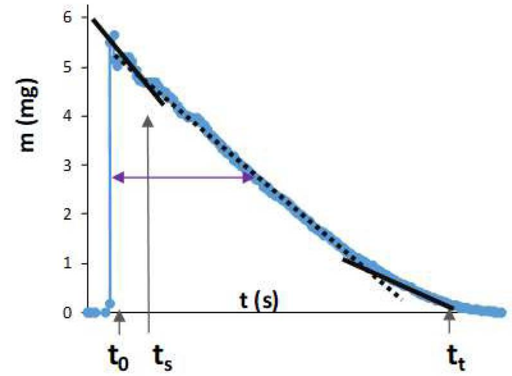

Figure 4. Weight variation of a BP as a functions of time during the evaporation process.

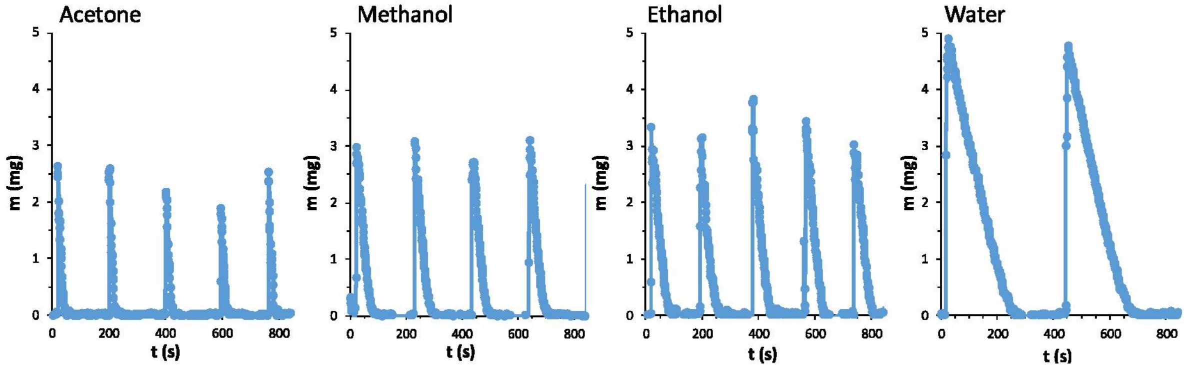

Figure 5. Evaporation of acetone, methanol, ethanol and water from *nf*-CNT buckypaper doped by goethite (5 µL, 50°C).

The IR videos were evaluated at selected representative moments, such a typical series of images is shown in Fig. 6. It is possible to determine the spot area and average temperature of the drop (S_d, T_d) and of the wetted region (S_w, T_w) as a function of time. Some data extracted from weight and resistivity variation and from infrared videos are characteristic for the evaporation of the selected liquid/solid system: surface evaporation time (t_s), total evaporation time (t_t), evaporation rate (-dm/dt) and its change, FWHM values of the curves, initial area of the drops ($S_{d(t0)}$), area of the wetted region at t_s ($S_{w(ts)}$), etc. Some of these data are collected in Table 1.

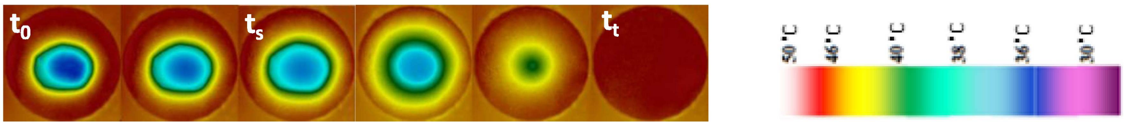

Figure 6. Images exported pro rata from the IR video correspond to t_0, t_s, t_t and several representative intermediate times (*nf*-CNT doped by goethite, 5 µL EtOH, 50°C).

Table 1. Some data extracted from m and R variation and from IR videos recorded during the evaporation of different solvents from the surface of *nf*-CNT doped by goethite (5 µL, 50°C).

	$t_{t(m,R)}$	$t_{s(R)}$	$FWHM_{(m)}$	$FWHM_{(R)}$	$S_{d(t0)}$	$S_{w(ts)}$
acetone	29 s	6 s	7 s	15 s	-	-
methanol	66 s	9 s	24 s	37 s	-	-
ethanol	83 s	5 s	29 s	47 s	3.3 mm^2	63.4 mm^2
water	227 s	18 s	89 s	87 s	5.4 mm^2	72.2 mm^2

Conclusion

The weight monitoring of the evaporation of liquids from porous films can provide information about the mechanism of wetting and vaporization which is a significant area of the basic researches. Furthermore, it can be proved by using appropriate statistical methods (*e.g.,* matrix of Pearson correlation coefficients, hierarchical cluster analysis, functional analysis, etc.), that the experimentally determined characteristic values are specific for the physical properties of the solvents, and they are also dependent on the quality of the solid materials, therefore, they can be used for qualitative chemical analysis via the estimation of physical properties. The results allow us to presume the possibility of this experimental setup and theoretical approach for a potential future application in the field of analytics.

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