Wetting of carbon nanotube functionalised nylon and its usage as flexible electrode in electrowetting on dielectric

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The nylons functionalised with single walled carbon nanotubes (SWCNTs) at pH 2.5 and 3.5 display the time dependence of the water droplet contact angle, which is attributed to the adsorption of water molecules onto the nylon–water contact surface and the consequent increase in surface free energy. The contact angle of nylons functionalised at pH 4.5, 6.5 and 8.0 varies marginally with contact time, presumably owing to the presence of a large amount of SWCNTs on the nylon surface. Using the obtained nylon as a flexible electrode, an electrowetting on a dielectric system is designed. The contact angle decreases with the increase of the applied voltage and the electrowetting response is sensitive to the surface free energy of the water droplet. A low surface free energy is preferable for actuating the movement of the water droplet at a low-driving voltage.

1. Introduction: At microscale dimensions, the surface area to volume ratio becomes increasingly large, resulting in the dominance of surface forces over body forces. This makes it extremely difficult to move and manipulate small volumes of fluid in miniaturised fluidic devices. Electrowetting on dielectric (EWOD) has been demonstrated to be an attractive technology for the rapid manipulation of liquids on a micrometre scale [1], for instance, droplet actuation [2] and microfluidic operations such as the formation, mixing and splitting of droplets [3, 4]. Currently, the commonly used electrode materials are metals (gold [5], copper [6], stainless steel [7] and so on), semiconductor (silicon) [8] and ceramics (ITO) [9]. These materials are rigid, even brittle in some cases, and thus not suitable for flexible microfluidics and portable electronics. Undoubtedly, the development of a flexible electrode will enrich the applications of electrowetting.

Owing to their excellent conductivity and current carrying capacity, carbon nanotubes (CNTs) have been used to functionalise fabrics to make light-weight, flexible and conductive fabrics. By using the melt spinning process, Devaux *et al.* [10] fabricated electrical conductive polylactide multifilament yarns. By flexographic printing, Fischer *et al.* [11] fabricated conductive polyester and polyamide microfilaments. CNTs could also be imparted into cotton and cotton/polyester by screen printing [12]. By a dip-drying process, conductive cotton, wool and their blends have been prepared [13, 14]. The resultant fabrics demonstrated good conductivity and foldability and may be employed as a flexible electrode. For instance, Hu *et al.* [15] used CNT functionalised cellulose as the porous electrode and prepared a wearable capacitor with high areal capacitance, which is interpreted in terms of the excellent ion access in the porous structure.

In this study, elastic, tough and abrasion-resistant nylon was functionalised with CNTs by a simple dip-drying process and then the time-dependence behaviour of these obtained nylons was examined. By using the resultant nylon as a flexible electrode, an EWOD system was eventually designed and its electrowetting performance is reported for the first time. This study may enrich the application family of EWOD in microfluid manipulation.

2. Experimental

2.1. Functionalisation of nylon with CNTs: The detailed preparation and characterisation of single walled CNT (SWCNT) functionalised nylons can be found in our previous communication [16].

2.2. Sessile droplet method: A droplet of deionised water (2 μl) was placed on the surface of SWCNT functionalised nylon, and a microphotograph of the horizontal view of the water droplet was taken within 2 s. The droplet shape was monitored and recorded till 86 s at intervals of 6 s. The contact angle of each sample was measured using the microphotographs.

The surface free energy of nylon and functionalised nylon, γ_n (mN m^{-1}), can be calculated by using contact angle data in accordance with (1) [17].

$$\cos \theta = 2\phi\left(\gamma_n/\gamma_w\right)^{1/2} - 1 \qquad (1)$$

where θ is the contact angle, Φ is the interaction parameter and γ_w is the surface free energy of water. Substituting ϕ with 0.6 [18] and γ_w with 71.96 mN m^{-1}, nylon surface free energy was calculated by using (2):

$$\gamma_n = 50(\cos \theta + 1)^2 \qquad (2)$$

2.3. Electrowetting experiments: Electrowetting experiments were set up on a drop analysis system (SL200B, Shanghai Solon Information Technology Co. Ltd, China) and performed with 2 μl deionised water drops, as diagrammatically shown in Fig. 1*a*. A stainless steel microrod (diameter 140 μm) was inserted into the droplet to establish electrical contact, whereas the SWCNTs functionalised nylon was used as another electrode. A Teflon layer with a thickness of 17.8 μm was placed on top of the functionalised nylon and used as the dielectric. DC voltage was supplied by a function generator (RXN-303D, Shenzhen Zaoxin Electronic Instrument and Equipment Factory, China) and amplified, if necessary, with amplifier (model HA-800, Pintek Electronics Co. Ltd, Taiwan). The measurements of the contact angle were made via a camera coupled with an imaging system. All the measurements were conducted at room temperature (20 ± 2°C) with a relative humidity of 45 ± 5%.
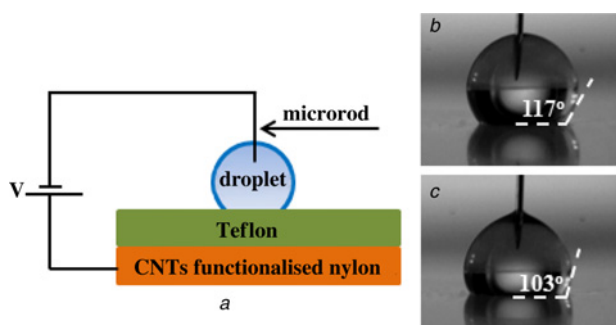
Figure 1 *Schematic of electrowetting experiments (Fig. 1a), contact angle measurements of droplet of deionised water (2 μl) with 2.41 × 10⁻⁴ mol l⁻¹ Tween 20: in absence of applied voltage indicating contact angle of 117° (Fig. 1b), and on application of voltage of 400 V indicating a contact angle of 103° (Fig. 1c)*

3. Results and discussion

3.1. Time dependence of the contact angle: Fig. 2 diagrammatically illustrates the variation of the contact angle with contact time for original nylon and nylons functionalised with SWCNTs at different pH. For original nylon, the contact angle drops from 114.6° to 54.0° after the droplet was placed for 86 s. In the case of nylon functionalised at pH 3.5, the decrease in contact angle becomes less pronounced, that is, from 116.5° to 80.7°. As far as the nylon functionalised at pH 4.5 is concerned, no significant decrease in contact angle is observed.

Fig. 3a shows the detailed variation in the contact angle of the water droplet on nylon and functionalised nylon with prolonged contact time. Clearly, nylon and nylons functionalised at different pH exhibit different time-dependence behaviours. For nylons functionalised at 4.5, 6.5 and 8.0, the contact angles are constant (ca. 120°) over the time period investigated (up to 86 s). In the case of original nylon and nylons functionalised at a pH of 2.5 and 3.5, the contact angle decreases considerably with contact time. Fig. 3b plots the surface free energy of nylon and functionalised nylon against contact time. For nylons functionalised at pH 4.5, 6.5 and 8.0, the surface free energy varies marginally, < 7 mN m⁻¹. As far as the nylons functionalised at a pH of 2.5 and 3.5 are concerned, the surface free energy increases substantially against contact time with the variations being 49 and 25 mN m⁻¹, respectively. This variation trend is even more pronounced for the original nylon, reaching 110 mN m⁻¹.

These differences in the change of contact angle and surface free energy with contact time can be interpreted in terms of the quantity of SWCNTs present on the nylon surface. For nylons functionalised at pH 4.5, 6.5 and 8.0, a large amount of SWCNTs are adsorbed on the nylon surface and the nylon surface is highly loaded with SWCNTs. A three-dimensional conductive network is developed, leading to low resistance, as illustrated in the inset of Fig. 3a. As a result, the functionalised nylon surface exhibits constant hydrophobicity. With the decrease of pH to 2.5 and 3.5, less SWCNTs are adsorbed on the nylon surface because of the increase of ionic strength and a high fraction of the nylon surface is free of SWCNTs, resulting in high resistance [16]. Although the surface free energy of water is higher than that of nylons, that is, 71.96 mN m⁻¹ against < 20 mN m⁻¹, the nylon surface can adsorb water because of the uncompleted coverage of SWCNTs and the presence of hydrophilic groups such as –C=O and –NH–. The adsorption of water to the low-energy hydrophobic organic surface can increase the net surface free energy of the nylon and weaken the water repellency. Accordingly, the reduction of the contact angle with contact time here can be explained as a result of the adsorption of water molecules onto the nylon–water contact surface and the consequent increase in surface free energy. It is worth noting that, in contrast to the SWCNT functionalised nylon, the original nylon surface is completely free of SWCNTs and a larger amount of water can be adsorbed, giving rise to a more precipitous variation of contact angle and surface
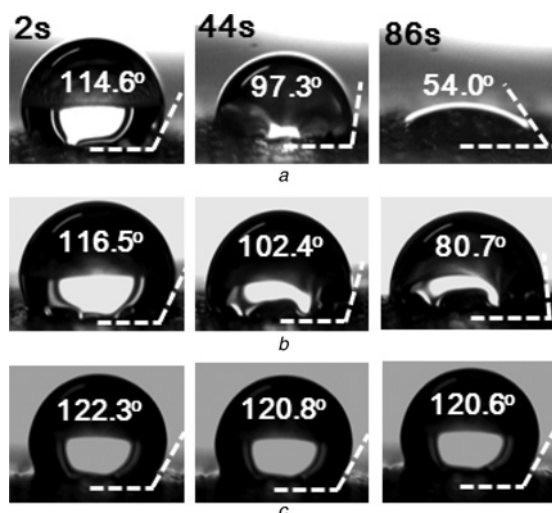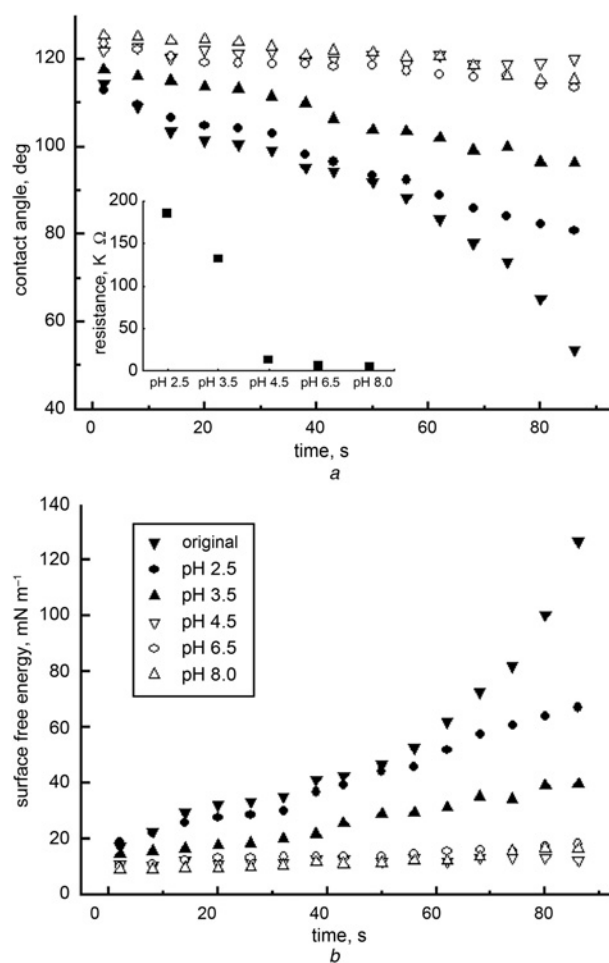

Figure 2 *Photos of water droplet on original nylon (Fig. 2a), and nylon functionalised at pH 3.5 (Fig. 2b) and pH 4.5 at contact time of 2, 44 and 86 s (Fig. 2c)*

Figure 3 *Contact angle and surface free energy against water–nylon contact time for original nylon and SWCNTs functionalised nylons*
a Contact angle
b Surface free energy
Inset a: Resistance of SWCNT functionalised nylon at length of 1 cm

free energy with contact time. The above results indicate that the interactions between the water droplet and the nylon surface can be tuned by functionalising nylon with SWCNTs at different pH.

It is also notable that after the functionalisation with SWCNTs at pH 4.5, the initial water droplet contact angle on nylon increases by about 8°, see Fig. 2. This is because the attachment of CNTs increases the surface roughness of nylon and reduces the fraction of the surface coming into contact with the water droplet. For the nylon functionalised at pH 3.5, this phenomenon is not pronounced, which is as expected in that only a very limited amount of SWCNTs have been attached onto the nylon surface in this case.

3.2. Effect of surface free energy on electrowetting response: To investigate the behaviour of the water droplet containing surfactants under electrical actuation, a specific EDOW-based system using the SWCNT functionalised as one electrode has been designed, see Fig. 1a. As discussed previously, the nylons functionalised at pH 4.5, 6.5 and 8.0 have a larger amount of SWCNTs being adsorbed on their surface and exhibit good electrical conductance. Thus, the nylon functionalised at pH 4.5 was used as the electrode in the electrowetting experiments. In this work, the surfactants Tween 20 and Tween 80 were chosen for two reasons. These surfactants are biocompatible for genomic application and often used in lab-on chip. In addition, they are non-ionic and can minimise the possible electrokinetic effects that

may take place during electrowetting [19, 20]. To examine the effect of surface free energy on the electrowetting response, a water droplet with different surfactant concentrations has been investigated. The critical micelle concentrations (CMCs) of Tween 20 and Tween 80 are 8.0×10^{-5} and 1.0×10^{-5} mol l^{-1}, respectively [19]. As such, two concentrations, namely one-third CMC and three CMC, for each surfactant have been used.

It was observed that the water contact angle decreases with the increase of the external voltage, as demonstrated in Figs. 1b and c, and this trend is true for all the water droplets containing diverse surfactant concentrations. Figs. 4a and b show the details of the variation of contact angle (θ) with the applied voltage squared (V^2). Apparently, the variation of contact angle ($\Delta\cos\theta$) increases linearly with V^2, where θ is the contact angle upon a given applied voltage and θ_0 is the initial droplet contact angle with no applied voltage. It is also notable that the water droplet containing surfactant micelles displays a good electrowetting response as well. A plausible explanation for this phenomenon is that the driving force for actuating the movement of the liquid mainly occurs at the surface of the droplet, instead of the bulk of the droplet. As such, the presence of surfactant micelles in the water droplet does not impair the electrowetting behaviour.

The initial contact angles of the droplet with different surfactants and concentrations, more precisely different surface free energies, are plotted in the inset of Fig. 5. Apparently, in the absence of applied voltage, the contact angle increases with the increasing surface free energy. This is not surprising. The molecules exposed at the droplet surface do not have neighbouring molecules in all directions to provide a balanced net force; instead, they are pulled inward by the neighbouring molecules. The higher the surface free energy, the stronger is the inward pressure, indicating a higher value of the contact angle. To have a close look at the effect of surface free energy on the electrowetting, the slopes of the fitting lines in Fig. 4 are plotted in Fig. 5 against the corresponding surface free energy of the water droplet. Regardless of which surfactant is involved, the slope increases with the decrease of surface free energy; this means a lower voltage is required to generate the same change in the contact angle. From the viewpoint of practical application, a low voltage implies less energy intensity and cost efficiency.

The classical electrowetting equation can be expressed as (3), where θ is the contact angle on the application of DC voltage V, θ_0 is the contact angle in the absence of the applied voltage, ε_0 is the dielectric permittivity of vacuum, ε is the relative dielectric permittivity, γ is the liquid–air interfacial free energy and d is the
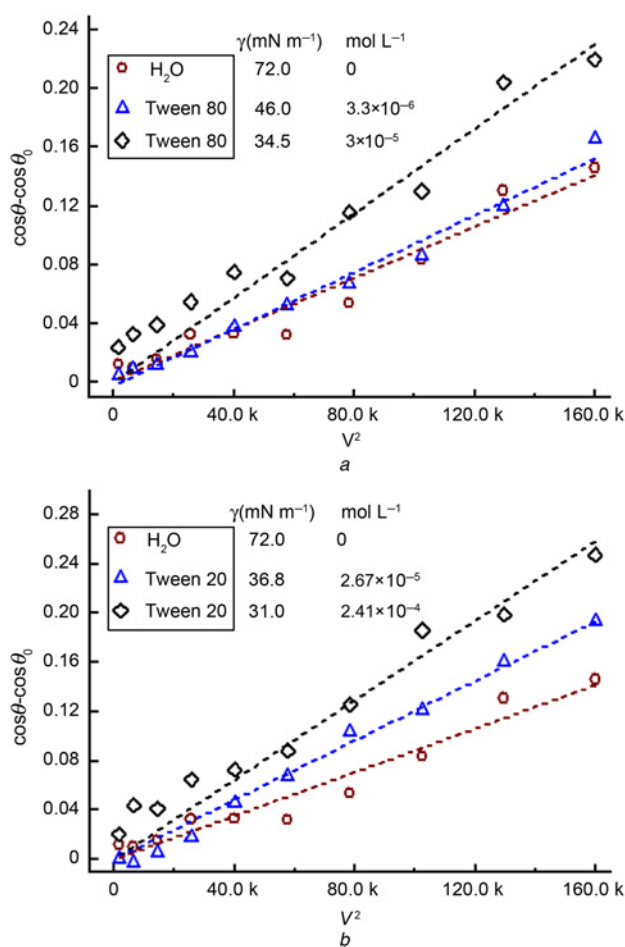

Figure 4 *Water contact angle against applied voltage for different surfactant concentrations*
a Tween 80
b Tween 20
Points correspond to experimental data and dashed lines are linear fitting lines. Surface tensions of various water formulations indicated in Figure
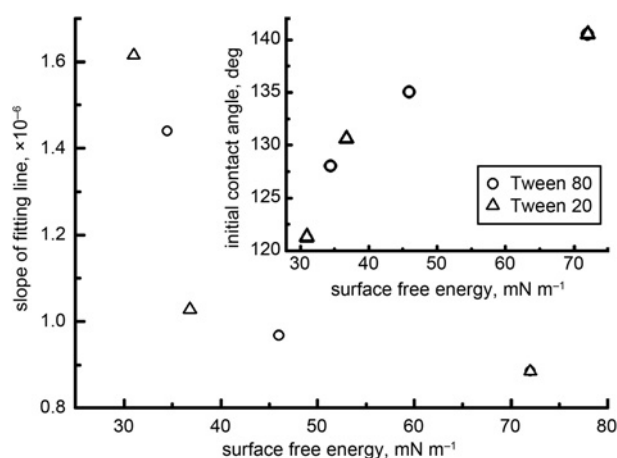

Figure 5 *Slope of fitting line for electrowetting response of water droplet against surface free energy*
Inset: Variation of initial contact angle of water droplet with surface free energy

thickness of the insulating layer.

$$\Delta \cos\theta = \cos\theta - \cos\theta_0 = \frac{\varepsilon_0 \varepsilon}{2\gamma d} V^2 = kV^2 \qquad (3)$$

The thickness of the Teflon involved here is 17.8 μm. ε_0 and ε are assigned the values of 8.85×10^{-12} F m^{-1} and 2.0, respectively. After substituting γ with the corresponding value, the k for the water droplet containing different surfactants with different concentrations can be calculated. All the magnitudes of k fall in the order of 10^{-5}, whereas our experimental results indicate that the k values are on the magnitude order of 10^{-6}, see Fig. 5. This deviation from the theoretical model may be ascribed to the formation of microcapacitors. SWCNTs functionalised nylon was used as the electrode in EDOW here. For individual nylon fibres, the SWCNTs are randomly attached onto the fibre surface with localised discontinuity. Owing to the difference of electrical potential, microcapacitors may form among these scattered CNTs/CNT bundles. These capacitors can function as capacitive dividers on the application of external voltage. This means that the virtual voltage applied on the water droplet–Teflon interface in EWOD is actually much lower than the nominal value. This reduction in the effective electrical field across the Teflon–water interface induces a reduction in the charge density at the solid–liquid interface and consequently the electrowetting force.

4. Conclusions: The adsorption of water to nylon surfaces can increase the net surface free energy of the nylon and weaken the water repellency. It is for this reason that the contact angle of water on nylon and nylons functionalised at pH 2.5 and 3.5 decreases with contact time. Owing to the presence of large amounts of SWCNTs on the nylon surface, the contact angle of water on nylons functionalised at a pH of 4.5, 6.5 and 8.0 varies marginally with contact time. The EDOW system based on the flexible SWCNTs functionalised nylon demonstrates clear electrowetting response and the sensitivity is highly dependent on the surface free energy of the water droplet. A lower surface free energy means a higher sensitivity and thereby a smaller driven voltage to achieve the same variation in contact angle.

6 References

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