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Bioinspired Materials

Bioinspired Superhydrophobic Coatings of Carbon Nanotubes and Linear π Systems Based on the "Bottom-up" Self-Assembly Approach**

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Dedicated to Professor C. N. R. Rao on the occasion of his 75th birthday

Nature inspires scientists through its creation of aesthetic functional systems, in which biology meets materials. One such example is the self-cleaning superhydrophobicity of plant leaves, particularly of the lotus leaf[1]—which is considered as a symbol of purity in Hindu mythology. Lotus leaves accomplish their water-repellent nature through a surface topography that exposes two different length scales to the outside environment: the surface of a lotus leaf is textured with 3–10 micrometer-sized hills and valleys that are decorated with a nanometer-sized coating of a hydrophobic waxlike material. The hills and valleys reduce the surface contact area available to water, while the hydrophobic nanocoating prevents the penetration of water into the valleys, which makes the water droplets roll off the surface.[2] It is well-understood that, in general, a surface with micro- and nanostructured roughness generates superhydrophobicity with a water contact angle (CA) greater than 150°. While the roughness increases the surface area, which geometrically enhances the hydrophobicity according to the Wenzel model, the air trapped on the surface allows water droplets to partially sit on air, as proposed by the Cassie model.[3]

The self-cleaning ability of natural surfaces has inspired scientists to mimic this property with artificial materials.[4] Many approaches, including electrodeposition, generation of aligned polymer nanofibers by template extrusion, polymer-phase separation, and sol-gel methods, have been tried to date to develop hierarchical micro- and nanostructures to obtain superhydrophobic surfaces.[5] However, these methods involve stringent experimental conditions, sophisticated techniques, and tedious fabrication procedures.[6] Recently, several studies have been reported that concern the superhydrophobic nature of different surfaces with different wetting character that satisfy the validity of both the Wenzel and Cassie models of superhydrophobicity.[4b,7] These studies include the deposition of anisotropic nanoparticles and the layer-by-layer self-assembly of polymers and carbon nanotubes (CNTs).[8] Herein we report a simple and novel approach, based on the principle of the "bottom-up" self-assembly of molecules, for the preparation of a superhydrophobic nanocomposite coating comprised of CNTs and oligo(*p*-phenylenevinylene)s (OPVs) that has self-cleaning ability. Strong π interactions between OPVs and CNTs allows the dispersion of the latter in organic solvents. The well-dispersed nanocomposite can be coated on glass, metal, and mica surfaces, thereby resulting in water-repellent self-cleaning surfaces with high water CAs of about 165–170° and a sliding angle (SA) of less than 2°. These coatings have binary surface topography, with a large amount of trapped air and a very small CA hysteresis, which results in the easy rolling of water droplets with a very low SA.

OPVs are short linear π-conjugated molecules that are used extensively in the fabrication of organic electronic devices.[9] The functionalization of the aromatic moieties with long hydrocarbon chains allows their dissolution in nonpolar solvents. The incorporation of hydrogen-bonding end groups drives the molecules to form a variety of self-assembled hierarchical aggregates that lead to the gelation of solvents.[10] The molecules that we have chosen for the present study are **OPV1**–**OPV3** (Figure 1), which have a strong propensity for π stacking. CNTs are quasi-1D materials of high strength and with inherent electronic properties that are useful for a variety of applications.[11,12] However, many of the applications are hampered by processing difficulties, because of the intractable and insoluble nature of CNTs.[13] The chemical functionalization of CNTs with organic molecules improve their dispersion in organic solvents; however, this may have a negative influence upon the electronic properties.[14] Therefore, their physical interaction with aromatic molecules has become the method of choice for the dispersion of CNTs in solvents.[15]

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Molecular models of CNTs and **OPV1** indicate that the surface curvature of the former is appropriate for the latter to adsorb strongly through π interactions. Such an interaction allows the unbundling of CNTs, thereby resulting in their dispersion in a variety of organic solvents. This is evident by the addition of CNTs to a solution of **OPV1** in chloroform (Figure 1b). The interaction of **OPV1** with the CNTs is clear from the UV/Vis/NIR absorption spectrum, which exhibits the characteristic van Hove singularities of isolated CNTs between 500–1600 nm (Figure 1c).[14a,15c] The emission spectrum of **OPV1** (1×10^{-4} M) in chloroform exhibited strong fluorescence bands at 460 and 486 nm. Upon addition of single-walled carbon nanotubes (SWNTs), the intensity of these bands decreased only slightly, thus indicating that the excited state of the **OPV1** is not significantly influenced by the CNTs in the solution state.[16] In the FTIR spectrum, the aromatic C–H bending mode of **OPV1** between 700 and 900 cm^{-1} almost vanishes in the presence of the CNTs.[16] The ^{1}H NMR spectrum of **OPV1** showed significant broadening of the resonance signals at δ 6.82, 7.14, and 7.47 ppm corresponding to the aromatic and vinylic protons. These observations indicate a strong interaction between the π-conjugated backbone of the **OPV1** molecules with the SWNTs.[15a,16] Further evidence for the interaction of the **OPV1** molecules with the CNTs was obtained by X-ray diffraction and thermal analyses.[16]

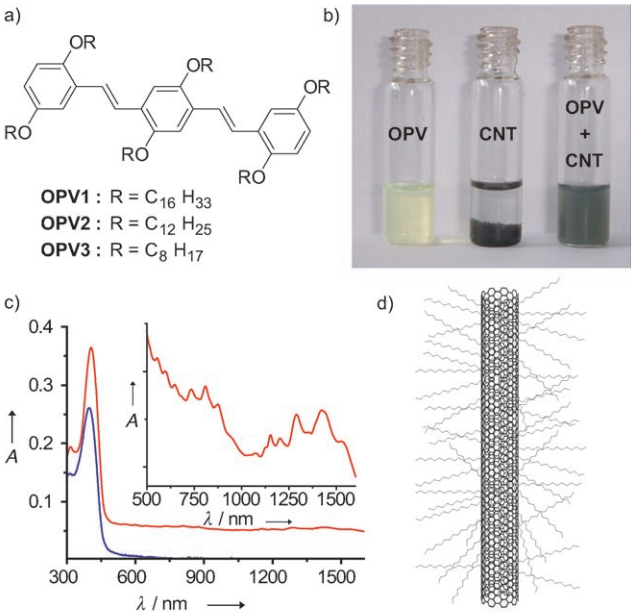

Figure 1. a) Chemical structure of the OPV derivatives. b) Photographs of solutions of **OPV1**, immiscible CNTs, and a dispersion of the **OPV1**–CNT composite in chloroform. c) Absorption spectra of **OPV1** (blue) and **OPV1**–SWNT (red) in chloroform. Inset: enlarged area between 500 and 1600 nm showing the van Hove singularities. d) A schematic representation of OPV molecules adsorbed on a SWNT, showing the hairy alkyl chains projecting outwards.

A nanocomposite was prepared by dispersing multiwalled nanotubes (MWNTs) in solutions of **OPV1**–**OPV3** in chloroform followed by sonication.[16] Figure 2a and b corresponds to the transmission electron microscopy (TEM) images of MWNTs (ca. 100–150 nm in diameter) before the addition of the OPVs, whereas Figure 2c and d is those of MWNTs after the addition of the OPVs. A comparison of the enlarged images of the isolated CNTs shows clear differences in the surface morphology before and after the addition of the OPVs (Figure 2b,d). In the latter case, it is clear that the surface of the CNTs is completely coated with the self-assembled OPVs, thereby generating a nanometer-scale roughness.[16]

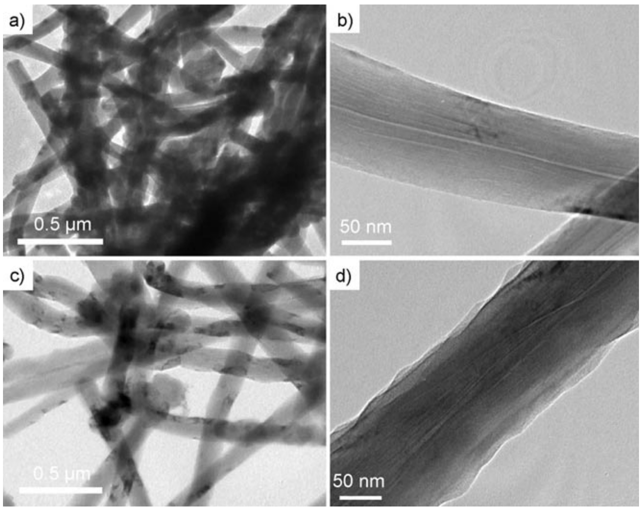

Figure 2. TEM images (unstained) of a), b) MWNTs and c), d) **OPV1**-coated MWNTs at two different magnifications. The sample was drop-cast from a chloroform solution on to carbon-coated TEM grids.

The nanocomposite dispersion could be deposited on glass, mica, or metal surfaces by evaporation of the solvent. Scanning electron microscopy (SEM) images of the MWNT–**OPV1** composite showed individual CNTs, which are randomly distributed to form an uneven surface. The SEM images also revealed that the surface of the CNTs is coated with the self-assembled OPVs, as seen in the TEM images, thereby resulting in a surface with nanoscale roughness (Figure 3a). The atomic force microscopy (AFM) image of the nanocomposite drop-cast on a mica surface is shown in Figure 3b. The 3D view of the surface of the coating shows a hill- and valley-type structure with a roughness of nano- to micrometers. The AFM image of a single CNT coated with **OPV1** is shown in Figure 3c. This image reveals that the nanotube is fully covered with a varying thickness of **OPV1**. Random dispersion of the OPV-coated nanotubes results in a rough surface with height variations ranging from nano- to micrometers (Figure 3b). The long hydrocarbon chains of the OPVs form a hydrophobic coating which can trap a large volume of air. These morphological features of the nanocomposite coating are comparable to that of lotus leaves, except for the fact that the latter has a periodic array of the micro- and nanostructures, whereas the former has a random topography.

The surface topography of the CNT–OPV nanocomposite is expected to have a superhydrophobic character with the property of self-cleaning. Our hypothesis was proved by

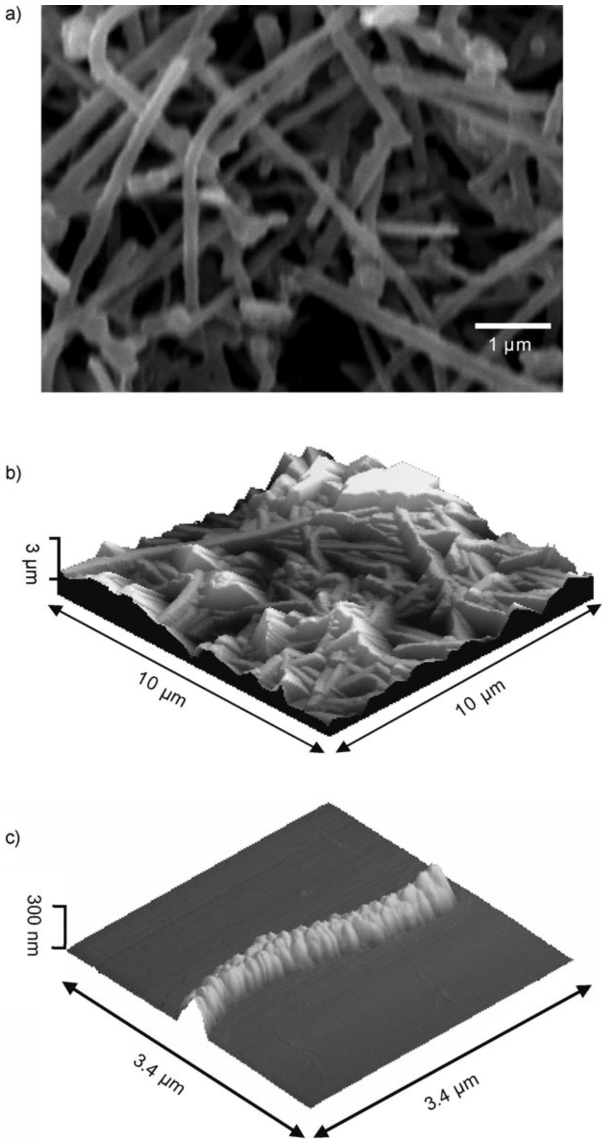

Figure 3. a) SEM image of the superhydrophobic composite surface. The sample was drop-cast from a chloroform solution on to a copper grid. AFM images of the b) **OPV1**–MWNT composite coating and c) a single CNT coated with **OPV1**. Samples were drop-cast from a chloroform solution on to a freshly cleaved mica surface.

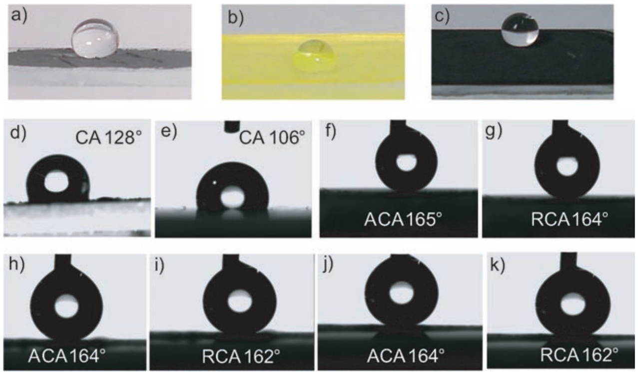

Figure 4. Photographs of a water droplet on a) CNT, b) **OPV1**, and c) **OPV1**–CNT nanocomposite coatings. Images of water droplets and the corresponding contact angles on d) CNT, e) **OPV1**, f), g) **OPV1**–CNT, h), i) **OPV2**–CNT, j), k) **OPV3**–CNT surfaces (side view from a goniometer measurement).

measuring the water CA of the nanocomposite on a glass surface. Photographs of a water droplet on the surface of CNT, **OPV1**, and the composite coatings are shown in Figure 4a–c, respectively. The water CA on the CNT coating is $(128 \pm 3)°$ and on the **OPV1** coating $(106 \pm 3)°$, which shows that both surfaces have hydrophobic character, but are not superhydrophobic (Figure 4d and e, respectively). Figure 4f, h, and j show water droplets on composite surfaces formed between the CNTs and **OPV1**–**OPV3** with advancing contact angles (ACA) of $(165 \pm 2)°$, $(164 \pm 2)°$, and $(164 \pm 2)°$, respectively. Figure 4g, i, and k show water droplets with receding contact angles (RCA) of $(164 \pm 2)°$, $(162 \pm 2)°$, and $(162 \pm 2)°$, respectively. The very small CA hysteresis of the nanocomposite surfaces makes the water droplets move freely on the surface at a very low SA ($< 2°$). The free rolling of the water droplets on the nanocomposite surface illustrates the self-cleaning effect, similar to the lotus leaf.

The water CA on a hydrophobic surface (θ_r) can be expressed by a modified Cassie equation [Eq. (1)].[1c] Here, θ_r

$$\cos\theta_r = f_1 \cos\theta - f_2 \qquad (1)$$

and θ are the CAs on the composite (rough) and OPV (smooth) surface, respectively; f_1 is the fraction of solid/water interface, while f_2 is that of the air/water interface (thus, $f_1 + f_2 = 1$). This equation indicates that when a rough surface comes in to contact with water, air trapping may occur, which would contribute greatly to the increase in the hydrophobicity.

According to Equation (1), the f_2 value of the composite surface can be estimated by using the CA values to be 0.953, which indicates that the fraction of air in the surface is very high.[5a,16] Water droplets could roll on the composite surface much more easily than on the CNT and OPV surfaces. This difference is explained by the difference in the CA hysteresis—the force required to move the droplets: $F \approx \gamma_{LV}(\cos\theta_R - \cos\theta_A)$.[2b] It takes a force about 44- and 24-times larger for the water droplets to move on pure CNT and OPV coatings, respectively, than on the nanocomposite surface.[4b,16]

Figure 5a shows the effect of CNT content in the composite on the superhydrophobicity. This graph shows that the water CA increases with an increase in the CNT content in the composite, and reaches the maximum of $(165 \pm 2)°$ at 50 wt% of CNT. Figure 5b illustrates the time-dependence of the water CA for the **OPV1**, CNT, and composite (1:1) coatings. It is observed that the water CA of the CNT coating decreases with time, from an initial value of 128 to 0° within 25–30 minutes, possibly because of the capillary action of the nanotube.[6b] However, the CA of water droplets on the composite film remains constant even after 24 h, thus showing a stable superhydrophobicity.

For any practical application, it is important to have a superhydrophobic surface which retains its inherent character under a variety of extreme conditions, such as varying

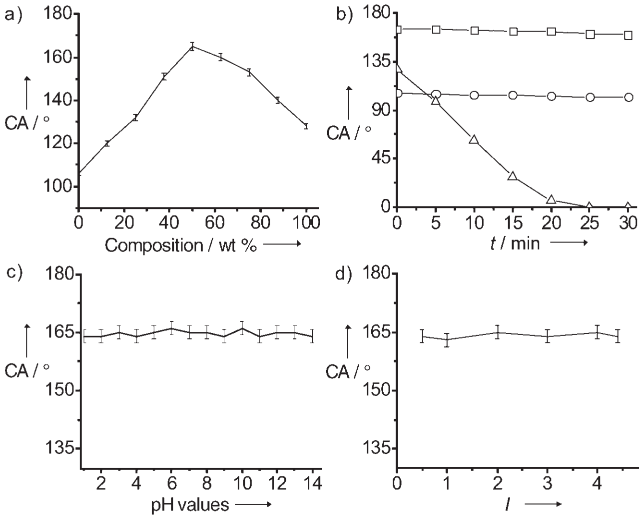

Figure 5. Plot of a) water contact angle against the CNT content in the composite; b) CA as a function of time: **OPV1**–CNT (1:1) □, **OPV1** ○, and CNT △; c) effect of the pH value on the CA; and d) effect of the ionic strength (NaCl solution) on the CA of a nanocomposite coating.

temperature, acidity, basicity, and ionic strength.[6c,17a] The relationship between the CA of water droplets on the composite surface and the pH value is shown in Figure 5c. The CA remains unchanged within experimental error (± 2°) when the pH value is varied from 1–14. The CA remains at greater than 160° not only for water but also for corrosive liquids, such as acidic and basic aqueous solutions. The effect of the variation of the ionic strength (I) on the composite coatings was tested by using aqueous solutions of NaCl, which revealed that the superhydrophobicity is retained with only a small variation in the CA (Figure 5d).

The superhydrophobic nature of the composite surfaces with water droplets were video recorded, which showed the bouncing and easy rolling of water droplets on the composite surface.[16] This observation indicates that the surface has no affinity for water and behaves like a highly water-repellent and self-cleaning surface. The rolling of a water droplet over a dusted nanocomposite coating showed the removal of the dust along the path of the rolled droplet (Figure 6a). The water-repellent nature of the composite surfaces was demonstrated by placing the composite in a petri dish followed by pouring water just above the surface level of the coating (Figure 6b). Water was seen to be reluctant to come into contact with the coating.[17b] The water-repellent nature is retained even after immersing the coating in a water bath for more than 24 h, thus indicating the robustness of the surface.

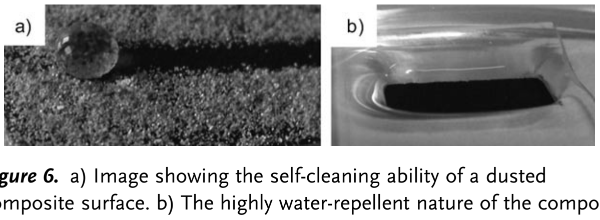

Figure 6. a) Image showing the self-cleaning ability of a dusted composite surface. b) The highly water-repellent nature of the composite surface when kept in a petri dish with water.

In conclusion, π interactions have facilitated the creation of a hydrophobic coating of CNTs with OPVs with a surface topography consisting of micrometer-sized hills and valleys with a nanoscale paraffin coating of hairy hydrocarbon chains akin to lotus leaves. The CNT–OPV nanocomposite surface gives high CAs and very small SAs, which allows the rolling of water droplets, thus imparting a self-cleaning ability with liquids having varying pH values and ionic strengths. Most importantly, it is demonstrated here that, in place of the regular micro- and nanostructured topography of natural systems, an irregular microstructure created by a nanostructured material is sufficient to mimic the superhydrophobic character of natural self-cleaning surfaces. The fact that superhydrophobicity is exhibited by the relatively cheaper MWNTs, compared to SWNTs, broadens the scope for potential applications of the composite.[18] The present strategy could be used as a general approach for the design of self-cleaning superhydrophobic surfaces. These self-cleaning, water-resistant coatings are expected to be useful in a variety of applications if they can be prepared on a large scale with improved adhesive properties.

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