

Self-assembled perpendicular growth of organic nanoneedles *via* simple vapor-phase deposition: one-step fabrication of a superhydrophobic surface†

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We demonstrate a simple vapor-phase fabrication of self-assembled perpendicular organic nanoneedles on various substrates to generate superhydrophobic surfaces on them.

Wettability is a very important property of surfaces that strongly depends on both surface chemical composition and geometrical microstructure.¹ Superhydrophobic surfaces with a water contact angle (CA) larger than 150° have attracted extensive attention because of their potential applications in self-cleaning surfaces, microfluidic devices, and other important industrial processes.² It is well-known that superhydrophobic surfaces can be fabricated by carrying out nanoscale surface roughening followed by specific chemical modification with materials with low surface free energy such as fluorinated or silicon compounds.³ Various techniques have been applied to the fabrication of superhydrophobic surfaces, such as plasma etching,⁴ colloidal assembly,⁵ electrospinning,⁶ sol-gel processing,⁷ chemical vapor deposition,⁸ electrodeposition,⁹ and anodic oxidation.¹⁰ However, most of these approaches require special equipment and complicated process control.

Very recently, Nakano *et al.* demonstrated a simple one-step method for the fabrication of superhydrophobic surfaces that used a self-assembly process in the solution phase.¹¹ A superhydrophobic surface with a water CA of 154° was easily prepared *via* the formation of a three-dimensional (3D) network of a long perfluoroalkyl-based organogelator by implementing a simple film-casting method.

In general, the wetting of rough surfaces can be explained with one of two models. A homogeneous wetting model is used when the liquid completely penetrates the fine roughness morphology,^{12a} and a heterogeneous wetting model is used when the liquid does not fill the crevices of the rough surface, because air is trapped underneath the liquid inside the rough morphology.^{12b} It is widely known that heterogeneous wetting surfaces exhibit higher CAs than homogeneous wetting surfaces.¹³ According to the heterogeneous wetting model, the optimal CA arises when the surface is covered with perpendicular fine nanoneedles.

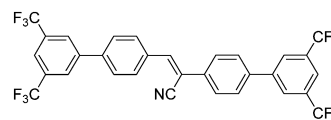
In this study, we demonstrated the simple and facile vapor-phase fabrication of a superhydrophobic surface consisting of

perpendicular organic nanoneedles produced by using π -conjugated organic molecules with extremely strong self-assembly tendencies. To the best of our knowledge, this is the first report of the perpendicular growth of a one-dimensional (1D) organic nanostructure on a substrate surface by using a simple physical vapor deposition (PVD) method. Yao *et al.* have previously reported the growth of crystalline nanowires of small organic molecules with the absorbent-assisted PVD method,¹⁴ which is essentially an epitaxial process and is thus different from our self-assembly process. Our process is carried out in the vapor-phase, and does not require any absorbents, templates, epitaxial surfaces, post treatment or catalysts.

As a promising candidate for a vapor-phase self-assembling molecule, we selected 1-cyano-*trans*-1,2-bis-(3',5'-bis-trifluoromethyl-biphenyl)ethylene (CN-TFMBE, Scheme 1), which has been shown to have a strong tendency to form nanowires in solution.^{15a} The self-assembly of CN-TFMBE arises from the combined effects of the strong π - π stacking interactions of its rigid rod-like aromatic segments and the supplementary intermolecular interactions of the four CF₃ units, which result in uniaxial nanowire growth.^{15a} Interestingly, it has also been shown that remarkable fluorescence enhancement is achieved in these unidirectional aggregates due to aggregation-induced enhanced emission (AIEE).¹⁵ Based on these considerations, we attempted to use CN-TFMBE for self-assembled nanoneedle formation in the vapor-phase.

Fig. 1 shows the morphologies and the water CAs of as-prepared films of CN-TFMBE nanoneedles for various film thicknesses. Note that the CA increases as the length and number of CN-TFMBE nanoneedles increase. When the evaporated film thickness is less than 50 nm, no needle-shaped aggregate is observed on the silicon substrate. At this thickness, there is negligible hydrophobicity, with a water contact angle of 86°. A closer inspection of the field emission scanning electron microscopy (FE-SEM) image in Fig. 1a reveals that the CN-TFMBE nanoscale ribbon consists of spherical nanoparticles (see the photo in the inset in Fig. 1a). Some of these particles are likely to be stacked on the surface, and act as seeds for the growth of the nanoneedles.

As the thickness of the vapor deposited CN-TFMBE film is increased to 500 nm, relatively longer ribbon-shaped



Scheme 1 Molecular structure of CN-TFMBE.

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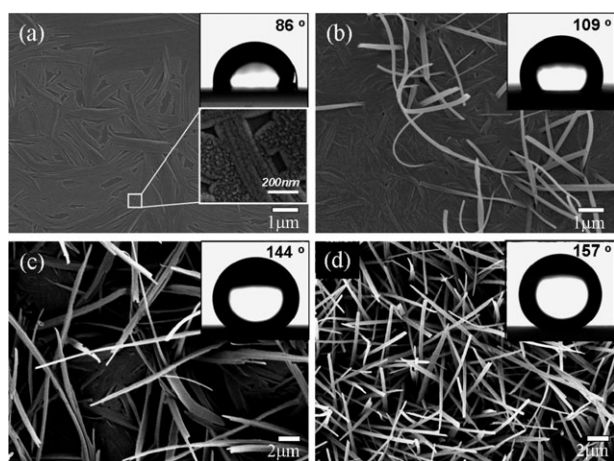


Fig. 1 SEM images of vapor deposited CN-TFMBE surfaces for various film thicknesses: (a) 50 nm, (b) 500 nm, (c) 1.9 μm , (d) 8.0 μm . The insets show images of water droplets (10 μL) on the vapor deposited CN-TFMBE films.

aggregates with an average width of 250 nm start to grow sparsely on the substrate (Fig. 1b). These self-assembled ribbon-shaped aggregates appear to be similar to inorganic nanowires grown with the epitaxial growth method.¹⁶ However, the growth of these CN-TFMBE nanoneedles does not require a catalyst or template, in contrast to the vapor-phase epitaxial method.¹⁷

With increases in the film thickness from 50 nm to 8 μm , the needle-shaped nanostructures become more upright and the number of needles increases. At the same time, the CA increases markedly up to 157° and sliding angle less than 4° (the advancing water contact angle: 158.2°; the receding water contact angle: 155.9°). In this superhydrophobic surface, pine-needle-shaped CN-TFMBE covers the whole surface of the substrate uniformly and compactly (Fig. 1d).

The CN-TFMBE nanoneedles have diameters in the range 250 to 500 nm, with lengths up to $\sim 8 \mu\text{m}$ with rather sharp tips. It is noteworthy that the tips of the nanoneedles are very strongly fluorescent, which is due to AIEE effect.¹⁵ (see ESI†).

The self-assembled vertical nanoneedle surface could be fabricated on various substrates with different surface energy under the same fabrication condition. Originally, substrates such as glass, silicon, PMMA coated- and perfluoropolymer (Cytop)¹⁹ coated-silicon substrates have different contact angles at 42, 50, 67 and 106°, respectively. However, after the vertical organic nanoneedles were deposited on them, all of them showed exactly the same CAs (151° at 5 μm film thickness) and surface morphology as shown in Fig. 2 (see ESI†).

To better evaluate the effects of the vertical alignment of the nanoneedles on the formation of the superhydrophobic surface, we also fabricated a 3D CN-TFMBE nanowire-covered surface with the solution self-assembly method. This CN-TFMBE xerogel-coated surface was prepared with the method reported in a previous communication.^{15a} To prepare the 3D network films, the CN-TFMBE was well dissolved in 1,2-dichloroethane (0.6 wt/vol%) by gentle heating (60–70 °C), and then the warmed solution was spread out on the silicon substrate without any difficulty. After approximately 1 min,

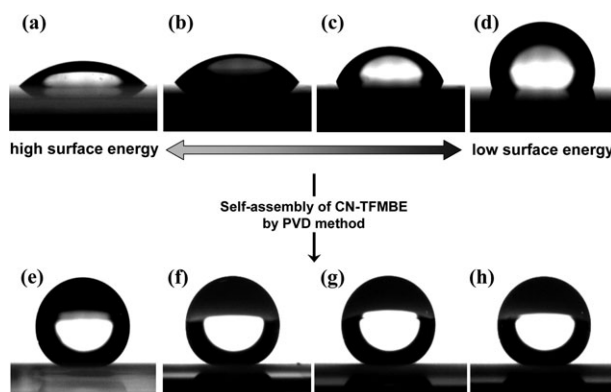


Fig. 2 Water contact angles before (a–d) and after (e–h) the deposition of perpendicular nanoneedles on different substrates; (a) glass, (b) Si, (c) poly(methyl methacrylate) on Si and (d) perfluoropolymer on Si, respectively. (e–h) CN-TFMBE coated surfaces on (a–d), respectively.

the solution on the silicon substrate turned into an organogel. Then, slow evaporation of the residual solvent within the organogel provided the xerogel coating on the silicon substrate. As shown in Fig. 3b, many fibrillar aggregates with diameters of 100 to 700 nm are present, and are entangled with each other resulting in a 3D network structure. This xerogel film has a smooth surface and is somewhat hydrophobic: the CA is 124°. It is known that the hydrophobicity of a surface can be enhanced by carrying out a chemical modification that lowers the surface energy. However, this approach has certain limitations. Chemical modification results in an increase in the water CA, with a maximum value of approximately 120° reported for smooth CF_3 -terminated surfaces.^{3,18} Clearly, the morphology of the coated xerogel film is totally different to that of the perpendicular nanoneedles surface prepared with the PVD method and shown in Fig. 3a at the same magnification.

By comparing Fig. 3a and b, it can be seen that the presence of nanometre scale surface roughness strongly influences the wetting behavior of water on the surface of the CN-TFMBE evaporated film. The properties of CN-TFMBE make it suitable for fabricating superhydrophobic surfaces in the form of arrays of pillars, with CAs in excess of 150° possible. The needle-shaped morphology produces trapping of air components within the surface, which results in an increase in the water CA according to Cassie's law.^{12b} The CA of the needle-shaped nanostructure surface is 157°, *i.e.*, it is a superhydrophobic surface.

In general, a superhydrophobic surface can be fabricated by controlling both its chemistry and modifying its geometrical

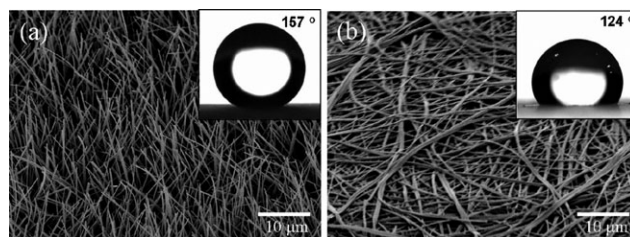


Fig. 3 Surface morphology and water contact angle of CN-TFMBE films prepared with (a) the simple vapor-phase deposition method, and (b) the solution self-assembly method.

roughness. In our simple PVD method, superhydrophobicity is achieved by the simultaneous control of the chemical composition and the geometrical morphology. It is clear that the CN-TFMBE aggregates exhibit unidirectional growth due to their excellent self-assembly tendencies in both the vacuum deposition and solution self-assembly processes.

In conclusion, we have demonstrated a one-step fabrication method for preparing superhydrophobic surfaces with a simple vapor deposition process. The superhydrophobic surface consists of vertically grown needle-like aggregates of simple π -conjugated CN-TFMBE molecules. These materials are potentially very useful in industrial applications.

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