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Universal, geometry-driven hydrophobic behaviour of bare metal nanowire clusters

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Abstract
A parallel array of isolated metal nanowires is expected to be hydrophilic. We show, however, that a clustering of such nanowires brought about by vacuum drying produces a ‘dual-scale roughness’ and confers a strongly hydrophobic property to the surface. The mean size of the nanowire clusters as well as the contact angle are both found to be related to the wire length, and the critical wire length above which the surface becomes hydrophobic is \( \approx 10 \mu\text{m} \). Surface roughness is generally known to enhance water-repellent properties, but this is the first report of roughness-induced hydrophobicity on a bare (uncoated) metallic surface.

1. Introduction

Techniques for making a surface hydrophobic (non-wetting) are of great technological importance [1, 2], with applications in glass coating, microfluidics, pesticides and other areas [3, 4]. This has, in recent years, led to a study of the water repellent nature of certain naturally occurring surfaces [5, 6]. There are several reviews of the current status of this field [7, 8]. Since hydrophobic surfaces do not favour the formation of a hydrogen bond network with water molecules, they orient themselves so as to minimize the area of contact with such surfaces, which are therefore not wetted by water. On the other hand, a typical metal such as copper allows the formation of hydrogen bonds and thus favours the wetting process. Previous attempts at conferring hydrophobic properties to metallic surfaces (such as copper) involved coating them with organic compounds [9] or chemically modifying the metal surface via complex formation [10].

The wetting property of a surface is characterized by the contact angle (\( \theta \)) between the liquid meniscus and the solid surface (see figure 1, inset). According to convention, the liquid is said to wet the surface when \( \theta < 90^\circ \) and to not wet the surface if \( \theta > 90^\circ \). For a smooth surface, the contact angle can be expressed in the form of Young’s equation: 
\[
\cos \theta = \left( \gamma_{SV} - \gamma_{SL} \right) / \gamma,
\]  
where the surface energies of the solid–liquid, solid–vapour and liquid–vapour interfaces are given by \( \gamma_{SL}, \gamma_{SV} \) and \( \gamma \), respectively. The nature of the surface roughness influences the contact angle in different ways. In the context of hydrophobicity, the following two types of surface microtexture have been studied in detail. In the first case, the liquid is in contact with the surface at all points and the hydrophobicity is enhanced merely due to an increased solid/liquid interfacial area arising from surface roughness. In this case, the effective Young contact angle is described by the Wenzel equation: 
\[
\cos \theta' = r \cos \theta,
\]  
where \( r (>1) \) is the ‘solid roughness’ (i.e. ratio of true and apparent surface areas). In the second case, the surface contains voids and air traps into which the liquid is unable to penetrate, such that the single solid/liquid interface is replaced by a composite solid/liquid and liquid/vapour interface. The effective contact angle in this case is described by the Cassie–Baxter equation: 
\[
\cos \theta' = -1 + f_S (\cos \theta + 1),
\]  
where \( f_S \) is the fraction of the solid actually in contact with the liquid. Generally, a pattern of tall, smooth pillars would behave like a ‘Cassie’ surface, while a pattern of short, squat pillars would act like a ‘Wenzel’ surface. The Cassie–Baxter model is usually more appropriate for distinctly hydrophobic solids, whereas the Wenzel model is more suitable for slightly hydrophobic or marginally hydrophilic surfaces (\( \theta \sim 90^\circ \)).

In this paper, we study a special type of microstructured surface consisting of a parallel array of bare (i.e. uncoated) metal nanowires growing out of a substrate of the same metal. We show that a particular type of self-organization of the metal nanowires occurs during controlled drying (in vacuum), provided the wires are taller than a certain critical height. Such a clustering of the nanowires makes the surface strongly hydrophobic (figure 1). Even though we present data mainly from a copper nanowire surface, we have observed similar

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effects in other metal nanowire surfaces, such as those of silver and cobalt. Thus, the observed phenomenon appears to be controlled by the surface microtexture rather than the nature of the material. To our knowledge, this is the only report of a bare metallic surface showing appreciable hydrophobicity.

2. Experimental details

The copper nanowire arrays were electrochemically grown within commercially available porous anodic alumina (PAA) templates (Whatman Anodisk), with a diameter of 1.3 cm and a thickness of 60 μm, containing parallel cylindrical pores with an average diameter of 200 ± 10 nm. The PAA templates were back-plated with a ≈200 nm copper layer that served as a working electrode during electodeposition. The nanowire array was electodeposited potentiostatically in an acidic copper sulfate bath (pH = 2.0) using a conventional electrochemical cell with three-electrode geometry, comprising a working electrode (copper back-plate), a counter electrode (99.9% pure copper plate) and a reference electrode (standard calomel). The PAA template was subsequently removed in an oil-free vacuum environment. The diameter (\(d_0\)) of the nanowire is defined by the pore size of the PAA template (≈200 nm), while the wire length (\(l\)) was varied by controlling the time of deposition. The mean spacing (\(d_0\)) between the edges of two adjacent nanowires grows in the PAA template is about 50 nm. During electodeposition, a 50 μm thick copper layer gets further deposited over the copper back-plate of the template, and this provides a firm substrate for the nanowires. The adhesion of the nanowires to the substrate is quite good, and even after completely etching out the PAA template, we observed no appreciable detachment of the nanowires from the substrate.

The contact angle (\(\theta\)) of water on the surface of the nanowire samples was measured using the ‘sessile drop’ method. Droplets of distilled water (average volume ≈2 μl) were placed on the surface using a syringe and the static contact angle was measured with a horizontal microscope equipped with a CCD camera. Images were processed and analysed using the ImageJ software [11, 12] in order to measure the angle of the liquid–solid interface.

3. Results

We observe that the free standing Cu nanowires, produced by completely etching out the template and drying in vacuum, exhibit a tendency to cluster due to the capillary force of the liquid acting between them. The nature and extent of clustering depends directly on the average length of the exposed parts of the nanowires. Figure 2 shows scanning electron microscope (SEM) images of the type of clustering observed on drying three nanowire samples with different average wire lengths (\(l\)). It is clear that the shorter nanowires (e.g., \(l = 9 \mu m\)) show hardly any clustering, while the longer ones (\(l = 17 \mu m\) and 45 \(\mu m\)) form well-defined, tapered clusters. We now show that well-clustered nanowire surfaces exhibit pronounced hydrophobic behaviour, while poorly clustered surfaces favour wetting. Column (iii) in figure 2 shows photographs of a ≈2 μl water drop on the nanowire surfaces of different lengths. We clearly see that the surface of the 7 μm long nanowire sample, in which there is almost no clustering, is relatively hydrophilic (row A). However, the nanowire samples with \(l = 17 \mu m\) (row B) and 45 \(\mu m\) (row C) show strong clustering tendencies and their surfaces are definitely hydrophobic. It is important to point out that, in samples in which the template is only partially etched, the nanowires are strongly anchored to the base and are not allowed to bend and form clusters: these samples therefore always exhibit very low contact angles.

In order to obtain an idea about the dimensions of the nanowire clusters, we performed a 2D fast Fourier transform (FFT) of the SEM images shown in column (i) of figure 2. Figure 3 shows the radially averaged FFT intensity for all three samples. The broad peak observed in the scattering intensity at \(k = k_p\) corresponds to a mean cluster size: \(\xi_m = 2\pi/k_p\), where \(k\) is the wavevector associated with the clustering process. We find that the mean cluster size \(\xi_m\) scales linearly with the length of the nanowires (figure 4). This is significant in the context of an earlier study of hydrophobicity induced by clustering and cellular pattern formation in carbon nanotubes [13]. By balancing the mechanical bending energy and capillary forces it was predicted that \(\xi \propto l^2\). The exponent \(\alpha\) was calculated to be 2 by Journet et al [14] and 1.5 by Zhao and Fan [15]. However, figure 4 clearly shows that the value of \(\alpha\) obtained from our observations is very close to 1, and the data cannot be fitted to either \(\alpha = 1.5\) or 2. Finally, we plot the measured contact angle against the length of the nanowires (figure 5) and show that the surface becomes progressively hydrophobic with an increase in the length of the nanowires (which, as shown earlier, leads to increased clustering). However, the value of the contact angle tends to saturate with wire length (above ≈35 \(\mu m\)) and the maximum contact angle observed by us is 141°.
Figure 2. Scanning electron micrographs (SEM) of an array of exposed and vacuum-dried, free standing copper nanowires with ≈200 nm diameter. Columns (i) and (ii) show SEM images at different magnifications from samples with different average lengths \( l \) of 9, 17 and 45 \( \mu \)m, arranged respectively in rows A, B and C. Column (iii) shows photographs of a 2 \( \mu \)l water droplet sitting on the top surface of the three nanowire samples of different lengths. The hydrophobic nature of the surface can be seen to increase with the extent of clustering.

Figure 3. Radially averaged intensity of a 2D fast Fourier transform (FFT) of the SEM images shown in figure 2 (column (i)). The squares, circles and triangles represent FFT results for \( l = 9, 17 \) and 45 \( \mu \)m, respectively. The peaks in the scattering intensity (marked by arrows) occur at \( k = k_p \) and determine the mean sizes of the clusters, \( \xi_m = 2\pi/k_p \).

Figure 4. Relation between the mean cluster size and the length of the nanowires, plotted on a log–log scale. The least squares fit straight line passing through the data points has a slope that is very close to unity.

We now refer to the schematic diagrams in figure 6 to understand our results. Figure 6(a) shows a liquid surface supported on parallel nanowires separated by a distance \( d_0 \), which determines the surface radius of curvature (\( R \)) of the supported liquid surface. The pressure difference across the liquid–vapour interface is given by the Laplace equation: \( \Delta p = 2\gamma/R \). A decrease in the distance between the surface features decreases the radius of curvature and
leads to an increase in the total pressure the structure can support. Figure 6(b) shows a schematic representation of the unclustered copper nanowires obtained by partial removal of the template from the sample. The presence of a part of the template prevents clustering of the nanowires and leads to a parallelly aligned array. In this case the distance between the nanowires \(d_0 \approx 50 \text{ nm}\) is such that the radius of curvature of the liquid surface on the metal wires is too large (i.e. \(\Delta p\) is too small) to support the liquid surface. This results in a total wetting of the surface. The entry of water into the crevices between the nanowires increases the effective contact area of the liquid with the metal surface and leads to a moderately small contact angle \([7]\). However, when the template is completely removed, the free standing nanowires can come together at the tips during etching and drying (see figure 2). Such nanowire clusters are schematically shown in figure 6(c). The clustering of the nanowires causes a reduction in the effective value of \(d_0\), which leads to a reduction in \(R\) and an increase in \(\Delta p\). Hence, water does not enter the crevices within each nanowire cluster, resulting in a large decrease in \(f_s\), the fraction of water in contact with the metal. This results in an increase in the effective contact angle. With an increase of the wire length and, consequently, the clustering tendency, there is, in effect, a crossover from the Wenzel scenario (figure 6(b)) to the Cassie–Baxter one (figure 6(c)).

To substantiate our conjecture that the air trapped within the voids in the nanowire clusters leads to an enhancement of the hydrophobicity of the metal surface, we studied the effect of thermal cycling on the contact angle of water drops \((\approx 2 \mu l)\) placed on the metal nanowire surface. We first lowered the temperature of the metal nanowire sample (with the water drop on it) by establishing thermal contact with a liquid nitrogen bath \((\approx 100 \text{ K})\). The water drop on the surface freezes but the contact angle of the solidified drop remains greater than \(90^\circ\), as seen in figure 7(A). The sample is then isolated from the low temperature bath and allowed to attain room temperature.

While warming up, the solidified water drop melts and the contact angle gradually decreases to lower values (figures 7(B) and (C)). This may be ascribed to the condensation of moisture on the surface of the individual nanowires, which leads to the expulsion of the trapped air. This allows the external water drop to penetrate into the crevices within the nanowires while the system warms up to room temperature and leads to hydrophilic behaviour.

When a bare metal surface (such as Cu) is brought in contact with the atmosphere, a layer of surface oxide is formed on it. What is the role of the surface oxide on the hydrophobic properties of the metal nanowires? At this stage, we have no direct evidence to either prove or negate the effect of the ubiquitous surface oxide. However, it is quite clear that such an oxide layer would be present both on the sharp and somewhat conically clustered structure (shown in rows B and C in figure 2) as well as on the comparatively less clustered nanowires shown in row A. Since the former structure is hydrophobic while the latter is hydrophilic, we may conclude that the observed water repellence is controlled by the prevalent geometry rather than the presence of a surface oxide layer.

In summary, we have demonstrated that, under specific conditions, a bare (i.e. not deliberately coated or treated) metallic surface can exhibit hydrophobicity when the surface in question consists of clusters of nanowires. The magnitude of the water repellence depends on the nature of the clustering
of the nanowires, which in turn has been shown to depend on the wire length. We observed that, below a critical length ($\approx 10 \mu m$), the clustering is either non-existent or random and the nanowire surface favours wetting. On increasing the length of the nanowires, the cluster size increases and the surface develops water-repellent properties. Apparent contact angles for water greater than 140° have been observed. We have shown that the observed hydrophobicity is a purely geometrical phenomenon related to the nature of clustering and is therefore not affected by the inherently hydrophilic nature of the metallic (copper) surface. We may therefore expect to observe this phenomenon for geometrically similar clustered nanowires’ surfaces of any metal. We find that the cluster size ($\xi$) scales linearly with the length ($\ell$) of the nanowires. This observation cannot be understood from a simple model based on balancing the mechanical and capillary energies [14, 15] and requires further theoretical work.

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