LETTER

Compressed Metal Powders that Remain Superhydrophobic after Abrasion

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ABSTRACT Superhydrophobic "lotus effect" materials are typically not sufficiently robust for most real world applications because their small surface features are both easily damaged and vulnerable to fouling. Here, a method for preparing a new type of superhydrophobic ($\theta > 162°$) composite material by compression of superhydrophobic metal particles is reported. This material, which has no natural analogue, has low-surface-energy microstructures extending throughout its whole volume. Removing its outer layer by abrasion or cutting deep into it does not result in loss of superhydrophobicity because it merely exposes a fresh portion of the underlying superhydrophobic material. The high contact angle is therefore retained even after accidental damage, and vigorous abrasion can be used to restore hydrophobicity after fouling.

KEYWORDS: Superhydrophobic surfaces • Composite materials • Hybrid materials

INTRODUCTION

The field of superhydrophobic materials has grown enormously in recent years (1−3). In particular, huge effort has been expended in creating artificial "lotus effect" materials that mimic the properties of naturally occurring systems (4−6). These mimics usually comprise a low-surface-energy microstructured surface layer on a solid substrate (7−9). Indeed, it is not possible to achieve contact angles >120° without using the physical effect of surface roughness to augment low surface energy (10). The highest contact angles are obtained for Cassie-Baxter type materials, in which the water sits on top of a composite surface composed of solid microstructures with low surface energy and air-filled voids (11). Superhydrophobic Cassie-Baxter systems based on Si (12), metals (13), and their oxides (14), polymers (15), and waxes (16) are now known. However, regardless of whether they are natural or artificial, Cassie−Baxter surfaces are much more vulnerable to environmental degradation (1, 2, 17−19) than simple water-repellent materials, such as PTFE, whose hydrophobicity is due only to the chemical properties of the bulk material (17). This is because any mechanical damage to the inherently fragile small structures that comprise the surface layer will either change the structure of the layer (1, 2, 18, 19) or remove it completely, revealing the bulk substrate. Similarly, any fouling that fills the voids also dramatically reduces the contact angle. In plants, the problems caused by cumulative damage and fouling are minimised by their ability to repair or grow new structures (20), but this is difficult to achieve in artificial superhydrophobic systems. Indeed, the damage and fouling problem has been identified as the main barrier to widespread use of superhydrophobic materials in industrial applications (1, 2, 17−20). The approach of increasing mechanical robustness of the microstructures has limited potential. For example, although some abrasion resistance has been demonstrated for aluminium sheets coated with a composite alumina/chitosan/POMA, this resistance was at the level which could be tested with a velvet-covered roller (21). Similarly, highly porous gels (22) and solid foams (23) that can be cut with a razor blade to expose superhydrophobic interiors have been reported but the fact that they can be cut in this way also indicates the limit of their mechanical strength. Our focus has been on the production of mechanically robust superhydrophobic metallic coatings using processing steps that can be readily scaled, which should allow them to be produced on industrial scales. Here, we report the development of a material in which the metallic superhydrophobic outer layer sits on a substrate that also has the same composition and microstructure, so that there are effectively multiple potentially superhydrophobic layers extending down into the bulk material. In such materials the outer layers could be removed as necessary with standard metal working tools to expose a fresh surface. We have termed these "ecdysiastic materials" after 'ecdysis', the process in which reptiles shed their old skins and arthropods moult their outer cuticles.

EXPERIMENTAL SECTION

Copper powder, 99% −200 mesh (Aldrich) was coated in >50g batches. Experimental details here are for a 70 g batch. The powder was washed with 0.5% HNO_3, filtered, washed with water, and dried in an oven at 70 °C. Seventy milliliters of 0.02 M $AgNO_3$ was added to the powder, and the mixture shaken for ~2 min. The powder was allowed to settle for several minutes and the solution was carefully decanted off. Another 50 mL of 0.02 M $AgNO_3$ was then added to the powder, and the mixture shaken for ~2 min. The powder was then filtered

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off, washed with deionized water and dried in an oven (∼1−2 h). One-hundred milliliters of 0.1 M decanethiol (Alfa Aesar) in ethanol was added to the powder in a sealed flask, shaken, left for 24 h with occasional agitation, filtered, and dried in an oven.

To prepare the discs, we placed ∼1 g of copper powder into a standard die (13 mm, Specac Ltd, Orpington, U.K.), which is normally used for preparation of KBr discs, and pressed for 2 min. Mechanical abrasion was carried out using standard abrasive paper (100 grit, ca. 150 μm particle size, Klingspor Abrasives Ltd, Worksop, U.K.) or conventional double cut (10 teeth per cm) metal working files. Disks were cut using a hacksaw (10 teeth per cm).

SEM was preformed using a JEOL 6500 FEG SEM operating at 5.0 kV accelerating voltage. Particle diameters were measured using Image-pro Plus 4.5 (Media Cybernetics, Bethesda, U.S.A.). Contact angles were measured with an FTA200 instrument (First Ten Angstroms Inc, Portsmouth, U.S.A.). Twenty-four values were recorded for each sample and the reported values are the average of the middle 10 values within this set. Three -point bending tests were carried out using a Lloyds materials testing machine LRX, three replicates were carried out on each type of sample.

RESULTS AND DISCUSSION

The main challenge in preparing ecdysiastic materials is to find a method to retain the texture and low surface energy of superhydrophobic layers when they are assembled into a bulk material. Our approach has been to use the superhydrophobic metal powders whose preparation has recently been described (24). These powders are composed of small [average diameter 14.9 ± 4.2 μm] copper particles that are covered with an electrolessly deposited, textured silver overlayer <5 μm thick. The surface features are in turn coated with a covalently attached self-assembled monolayer of a low surface energy alkylthiol modifier. The particles would be expected to be superhydrophobic since copper sheets treated in the same way have contact angles >170° (25) and although it is very difficult to measure the contact angles of individual particles (26, 27), a flat bed of the powder adhered to a planar substrate has a contact angle of 152.7° ± 1.2°. Similarly the particles and planar substrates have similar nanostructure (24, 25). The most obvious way to build up a superhydrophobic material from these particles would be to use adhesive to stick them together. Unfortunately, although this gives a material whose outer surface is superhydrophobic, we have found that all the adhesives that were tested fouled the surfaces of the internal particles, so that when they were exposed, the surface they provided was no longer superhydrophobic. However, pressing the powder in a standard die (applied pressure, 18.8 MPa) gives compacted discs in which the particles bind to their neighbours to give a dense, apparently solid material (28). These solids should still present a quasi-continuous layer of low-surface-energy microstructured silver to any water coming in contact with the outer surface (as shown in Figure 1), but have the potential to be regenerated by exposing the inner particles. Electron micrographs show that the particles that are in contact with the die wall are noticeably flattened during the pressing process (Figure 2a), which results in a reduced contact angle of 143.0° ± 1.2° for the as-prepared discs, compared to 152.7° ± 1.2° for a flat bed of powder.

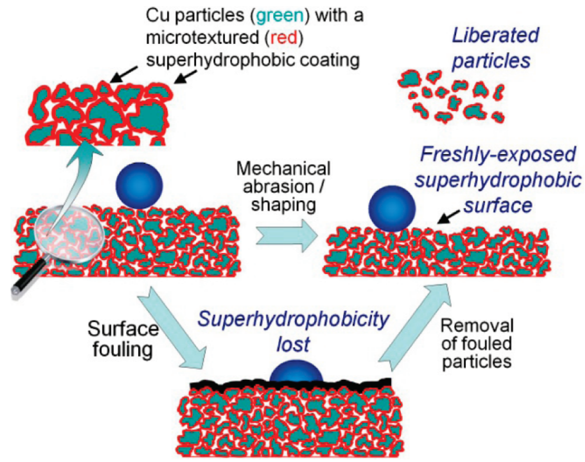

FIGURE 1. Cartoon representation of the behaviour of an "ecdysiastic" (skin shedding) superhydrophobic material prepared by compressing copper particles that have superhydrophobic microtextured silver surfaces. The surface of this material presents a quasi-continuous layer of superhydrophobic particles to a water droplet, giving a high contact angle. Importantly, abrasion of the surface does not result in loss of superhydrophobicity because the freshly exposed surface created by abrasion is also superhydrophobic. Similarly, if the surfaces of these materials become fouled, the high contact angle can be restored by mechanical abrasion.

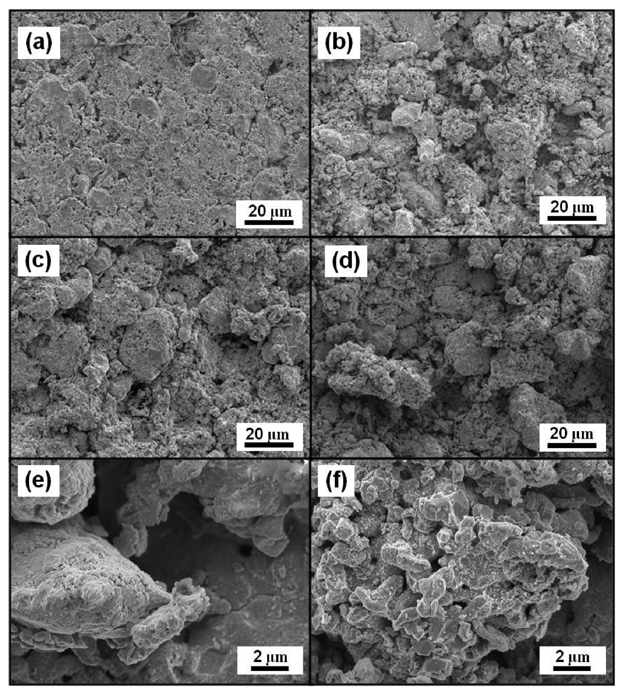

FIGURE 2. Abrasive regeneration of multi-scaled roughness. SEM images of discs prepared from compacted (18.8 MPa) superhydrophobic Cu powders. (a) As-prepared, the surface layer of particles has been flattened during preparation, (b) the same material after abrasion to remove the damaged surface layer, (c, d) the surface after two and three abrasion cycles, respectively. (e, f) Higher-magnification images of discs that were pressed then abraded. (f) Particle whose microtextured silver/alkylthiol coating has remained intact through the compaction/abrasion process; (e) similar view of the exposed particles in an uncoated sample, which are much smoother.

However, this flattening effect is confined to the outermost layer of particles, and these can be removed by rubbing the discs with abrasive paper or by using a metal file. This abrasion breaks away the damaged particles to reveal the underlying aggregated superhydrophobic particles, as illustrated in Figure 1. SEM of the newly exposed surface shows that the abrasion does indeed reveal a fresh set of copper particles which have retained the textured silver deposits on their surfaces (Figure 2b, f), even in areas that were in contact with other particles in the compressed solid. Although the low-surface-energy alkylthiol monolayer on the microstructured coating is not visible under SEM, it is also clearly retained on the particles in the discs since the newly exposed surfaces are found to be superhydrophobic, with the classic characteristics of a Cassie–Baxter surface, i.e., a high contact angle of 162.9° ± 1.0° and low (6.4° ± 0.6°) sliding angles (29). Indeed, the contact angle values are marginally higher than those for the uncompressed powder, showing that both the Ag microstructure and low-surface-energy alkylthiol coating are able to withstand the compression/abrasion steps remarkably well. Moreover, because the discs are essentially three-dimensional assemblies of these superhydrophobic particles, any portion of the solid which is exposed to water gives a high contact angle. This means that the abrasion process can be carried out repeatedly, each time removing a few layers of particles and generating a new superhydrophobic surface which is similar to the previous one, as shown in images c and d in Figure 2. Weighing the powder removed after a few seconds abrasion showed that approximately 100 μm or 7 layers of particles were removed in each cycle. Table 1 shows contact angles for a surface which was repeatedly abraded yet maintained the same high (162–163°) contact angle and low 5–6° sliding angles after each cycle. Indeed, even after the materials are cut with a saw or filed for several minutes down to a depth of 0.5 mm, the exposed surface is found to be superhydrophobic (see Figure 3(d), as is the powder, which is broken away from the solid during abrasion.

The pressure used to prepare the materials is critical since this determines the cohesive force between the particles, which must be set at a level where the particles can break cleanly away from the surface but only do so when required. The applied pressure also determines the physical strength of the materials (see Table 1 which collates physical data for discs prepared with 7.5, 18.8, and 37.5 MPa applied pressures). If too low (7.5 MPa) a pressure is used, the particles readily break away from the surface of the resulting material. Although this means that the potential for damaging underlying layers either during the pressing process or during abrasion is reduced, the resulting material is friable and also has low mechanical strength. Conversely, although higher pressure gives materials with increased mechanical strength, too much pressure leads to the particles becoming too firmly attached to each other. This means that even under conditions where the abrasion is sufficiently forceful to damage the particles' textured superhydrophobic surface features, the damaged particles remain attached to the surface, rather than breaking away. This prevents effective ecdysis (complete regeneration of the surface by exposing undamaged underlying layers). For example, even after abrasion, the contact angle of the disc formed at 37.5 MPa is only 133° (Table 1) and the sliding angle increases to 36.5°.

Optimum particle cohesion is achieved at an applied pressure of 18.8 MPa, which gives samples with a density approximately half that of copper metal. Three-point bending tests (EN ISO 6872:1998) show that the tensile strength of this material is 2.0 ± 0.03 MPa, which is similar to that of cement (31), whereas its high compression strength is indicated by the 18.8 MPa pressure, which is needed to prepare the discs. However, most important in this context is the combination of strength or hardness with the ability to maintain function after repeated abrasion, which minimizes the effects of any physical challenge to the surface and also means that they can easily be regenerated after fouling. For example, Figure 3 shows a series of photographs where a clean disc was deliberately fouled by drawing an ungloved

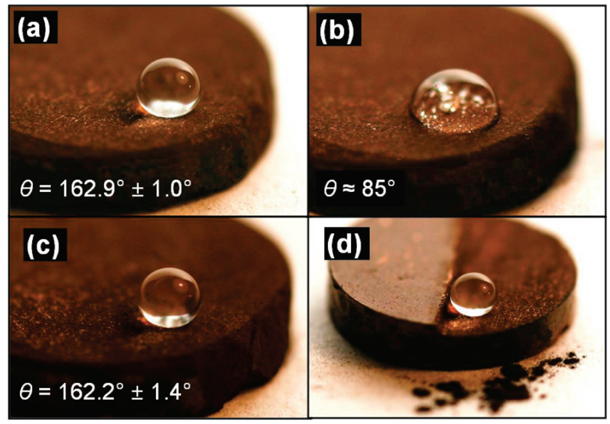

FIGURE 3. Regeneration of superhydrophobicity. (a) a water droplet on a freshly abraided surface, (b) a water droplet on the same surface after it was fouled by sebaceous oils from an ungloved finger, (c) the same material after a few seconds of abrasion with a metal file, (d) a sample that was filed to a depth ~0.5 mm but retained its superhydrophobicity; some of the powder generated by abrasion is shown in the image.

Table 1. Physical Properties and Contact Angles of Powder Discs Prepared with Different Compaction Pressures

forming pressure (MPa)	density (g)	tensile strength (MPa)	treatment	contact angle (deg)	sliding angle (deg)
7.5	4.7 ± 0.1	0.20 ± 0.03	as-prepared	134.6 ± 2.4	
			abraded	150.3 ± 0.8	4.2 ± 1.1
18.8	5.6 ± 0.2	2.0 ± 0.3	as-prepared	143.0 ± 1.2	
			abraded 1x	162.9 ± 1.0	6.4 ± 0.6
			abraded 2x	162.2 ± 1.4	6.3 ± 1.1
			abraded 3x	162.0 ± 1.3	5.5 ± 2.4
37.5	6.6 ± 0.2	7.4 ± 0.4	as-prepared	120.7 ± 1.8	
			abraded	132.7 ± 1.4	36.5 ± 5.8

fingertip over the surface. The sample was sufficiently robust that there was no mechanical damage but the contact angle dropped dramatically due to sebaceous oils fouling the surface. However, a few seconds of abrasion with a standard metalworking file restored the contact angle to its original high value (Figure 3c). This process works equally well for other forms of fouling and can be repeated numerous times because even filing down ∼0.5 mm below the surface exposes a superhydrophobic surface (Figure 3d).

Overall, these ecdysiactic materials give excellent contact angles >160° but also circumvent the damage and fouling problems traditionally associated with superhydrophobic materials. They are more than simply abrasion resistant, they can be cut, drilled and shaped by conventional metal-working tools such as files and saws but retain their original level of water repellency. They clearly have potential for large scale application, since they can be manufactured at low cost and without the use of any fluorinated compounds, but they also provide a novel approach that may inform the design of other materials that combine mechanical strength with extreme hydrophobicity that can be maintained even in challenging real-world conditions.

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(28) Although the discs appear solid, they are porous, as indicated by their lower density compared to bulk copper and the fact that discs pressed from untreated copper powder are capable of completely adsorbing water drops placed on their surface within a few seconds.
(29) Moreover, the discs displayed a highly reflective “silver mirror” effect when immersed in water and viewed at an oblique angle, because of the substantial air contribution for these Cassie–Baxter surfaces (25, 30).
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