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Particle Interactions

Sheets of Large Superhydrophobic Metal Particles Self Assembled on Water by the Cheerios Effect**

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Surface tension in water gives rise to a variety of phenomena some of which, such as the rise of water inside hydrophilic tubes under capillary action[1] or the ability of pond skaters to walk on the surface of water,[2–3] are so familiar that they seldom excite comment. However, there is still potential for new insights and discoveries to be made in this area. Two recent examples are the discovery that liquid marbles can be prepared by coating solvent droplets with powder[4–6] and the elucidation of a general mechanism for the attraction of buoyant objects in liquids, the "Cheerios effect".[7] Here we report a method for preparing large (up to 0.4 mm diameter) superhydrophobic copper particles and show that these particles, which have extraordinarily large contact angles but are much denser than water, give rise to a range of striking effects, including the ability to self assemble into sheets which can support objects that normally sink in water.

Here we present data for commercially available copper powders comprising either ≤75 μm diameter particles or ≤400 μm granules (which are fused aggregates of the smaller particles, but for simplicity we also call particles). Due to the manufacturing process, the particles have large pores, but on the micron-scale their surfaces are smooth (see Figure 1 a). We found that immersing the particles in a solution of silver ions resulted in Galvanic deposition of a thin textured silver metal coating (Figure 1 b) which was sufficiently robust to withstand the mechanical abrasion associated with subsequent rinsing and reaction steps. Following silver deposition, the surface energy of the particles was reduced by shaking them in a dichloromethane solution of 1-decanethiol which formed a self assembled monolayer on the surface. This simple process allowed the gram-scale synthesis of particles which had superhydrophobic surfaces and could be stored as dry powders for months with no indication of degradation. We have not measured the contact angles of individual particles, but the morphology of the deposited silver coating is identical to that found on planar copper substrates[8] that were treated in a similar manner and which have contact angles of 173° when treated with a polyfluoroalkylthiol. The apparent contact angle of a water droplet placed on a bed of dry particles is 157.3 ± 2.5°. The dry powders have an unremarkable dull brown/grey appearance, but when the powder is scattered thinly on a water surface, the particles spontaneously (within seconds) move towards each other to assemble into a close-packed sheet which is one particle thick (the Cheerios effect).[9] Since the particles are irregularly shaped, even when they close-pack there are still voids within the layer (Figure 2 a). However, the hydrophobicity of the particles prevents water from penetrating these voids. The sheets have a metallic appearance when viewed from beneath

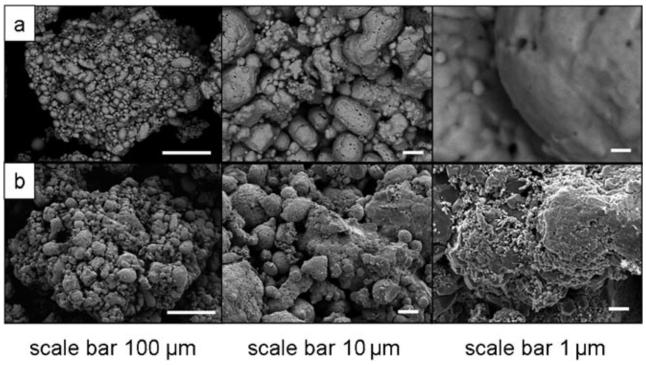

Figure 1. SEM images at different magnifications of a) an uncoated ≤400 μm copper particle and b) a similar particle following electroless deposition of Ag onto its surface. The macroscopic granular structure is not changed by the coating process and does not contribute to the hydrophobicity, which arises only as a consequence of the nano-textured Ag deposit.

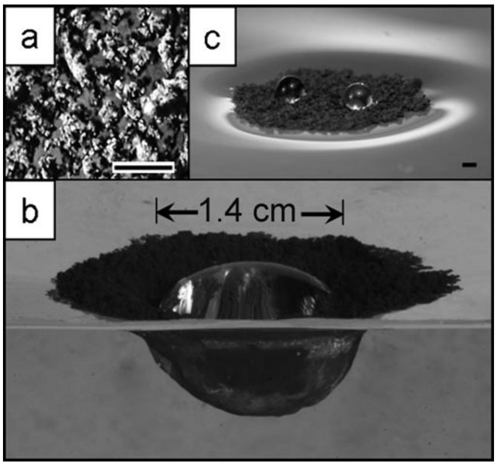

Figure 2. a) Packing within a superhydrophobic particle sheet made up of ≤400 μm copper particles. The scale bar is 500 μm. b) A 1 mL water drop supported by a film of ≤75 μm superhydrophobic particles. c) Water drops on a sheet of superhydrophobic ≤400 μm copper particles. The scale bar is 1 mm.

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the surface at a glancing angle. The same effect has previously been observed for superhydrophobic coatings on solid planar substrates and is due to reflection from the air layer which sits at the solid/liquid interface of immersed Cassie–Baxter surfaces.[8]

The most striking property of the sheets is the extent to which they can support objects. Figure 2b and c show sheets composed of small ($\leq 75\ \mu m$) and large ($\leq 400\ \mu m$) particles, respectively, supporting water drops at the surface. This effect is not confined to liquid droplets and photographs of a 1 cm irregular cement fragment supported by a sheet are shown in the Supporting Information. The particle sheets are capable of supporting surprisingly large loads; the water drop shown in Figure 2b was 1 mL. Moreover, a drop will remain supported for weeks if the system is sealed to prevent evaporation. The behavior shown in Figure 2b is reminiscent of liquid marbles prepared by coating small water drops with silane-treated *Lycopodium* spores which can be placed intact on the surface of water.[4] However, *Lycopodium* spore-coated marbles will survive for up to only one minute before collapsing, and denser objects, such as drops of salt water, placed on top of a thin layer of *Lycopodium* spores on water fall straight through.

We believe that the superhydrophobic copper particle sheets support objects to this remarkable extent because they satisfy two linked criteria. First, the particles in the sheet have sufficient buoyancy to support the external load. Second, under loading conditions the sheets do not tear or develop holes which are large enough for the supported object to contact the water beneath. Preventing this contact is important, because as soon as it occurs the supported objects fall through the sheet. The forces which oppose tearing of the sheets are not unique to superhydrophobic particles but detailed consideration of their origin allows us to understand why these forces are much larger for copper particles than for *Lycopodium* spores.

The most recent treatment of the Cheerios effect has shown that spontaneous aggregation of floating particles at liquid surfaces can be explained by considering the balance of both horizontal and vertical forces on the particles.[7] Essentially, any particle denser than the surrounding liquid medium will cause the meniscus to deform downwards and any similar particles nearby will feel an attractive force as they fall down the curved meniscus. For two spheres the attractive force is proportional to Σ^2, where Σ is given by Equation (1), where D is the ratio of the densities of the sphere and the fluid (ρ_S/ρ_W) and θ is the contact angle (see Supporting Information and ref. [7]).

$$\Sigma = \left(\frac{2D-1}{3} - \frac{1}{2}\cos\theta + \frac{1}{6}\cos^3\theta\right) \tag{1}$$

Equation (1) shows that the higher the density of the particles the stronger the inter-particle force. There is a practical limit to the strength of the interaction that can be induced in this way because increasing the density will eventually lead to the particles sinking. However, the density values at which this occurs can be pushed much higher than might be expected if the particles are superhydrophobic. This is because even a dense particle will float if its weight can be balanced by the weight of the fluid it displaces (Archimedes' principle)[10] plus the vertical component of the surface tension acting along the particle | liquid contact line.[11] It has been shown that the maximum density $D_{\max}$ for a sphere of radius r to remain buoyant is given by Equation (2), where ρ_w and ρ_A are the densities of water and air and γ_{AW} is the surface tension.

$$D_{\max} = \frac{3}{4}\left(\frac{\gamma_{AW}}{(\rho_w - \rho_A)\,g}\right)\frac{1}{r^2}(1-\cos\theta) \tag{2}$$

Since the copper particles approach the limiting value for θ they benefit from the largest contribution to the buoyancy from surface tension so they float despite a density of $8.96\ \mathrm{g\,cm^{-3}}$ (neglecting the air voids). Indeed, even using a worst-case value of $\theta = 157°$ and 400 μm particles gives a limiting $D_{\max}$ ($\approx \rho_S/\rho_w$) of 264, so that even these metal particles, which are ca. 9 times more dense than water, are still very far below the high-density limit. This is the reason that they are able to support large additional external loads.

Equation (1) shows that it is the high density of the copper particles, rather than their hydrophobicity that creates the strong cohesive forces observed in the particle sheets. For example, the smallest metal particles available possess similar contact angles and radii to *Lycopodium* spores ($\theta = 157°$ and 153°, $r = 10.5$ and 16.3 μm, respectively). However, the difference in the densities (8.96 vs. $0.55\ \mathrm{g\,cm^{-3}}$)[12] results in Σ values of 5.97 (copper) and 0.36 (*Lycopodium* spores). Consequently the Σ^2 contribution to the attractive force between two copper particles is a factor of 273 greater than that between two *Lycopodium* spores, although other differences in the overall expression (see supporting information) reduce this to a factor of 42.

These strong forces make the particle sheets robust but they are not completely rigid, which is important because it means they can deform to follow the contours of an object, which helps to prevent tearing and cracking of the sheet under loading. Figure 3 shows schematic diagrams for objects of different density reaching equilibrium at various immersion depths. These diagrams are equally valid for the stages of a particle sheet wrapping around a solid object at various stages of lowering. The latter case is shown in the photographs on the right of the figure, where a Teflon-coated magnetic follower was lowered through a sheet of 400 μm particles coated in 1-decanethiol. For the purposes of this discussion it is more useful to consider the deformations in the context of loading the sheets with objects of different mass/density.

If objects with low mass are placed on the sheets they remain essentially planar, apart from a local small distortion (Figure 3a). Heavier objects cause a more profound deformation (Figures 2b and 3b) creating a steep sided (even vertical) meniscus which remains covered in particles. It was found the object needed to be lowered sufficiently slowly that the sheet was able to deform so as to conform to the required shape. Close observation showed that the local expansion and contraction of the sheets to allow them to fit around the objects did not result in the particles moving apart in the areas where they needed to stretch. Similarly, in the areas where

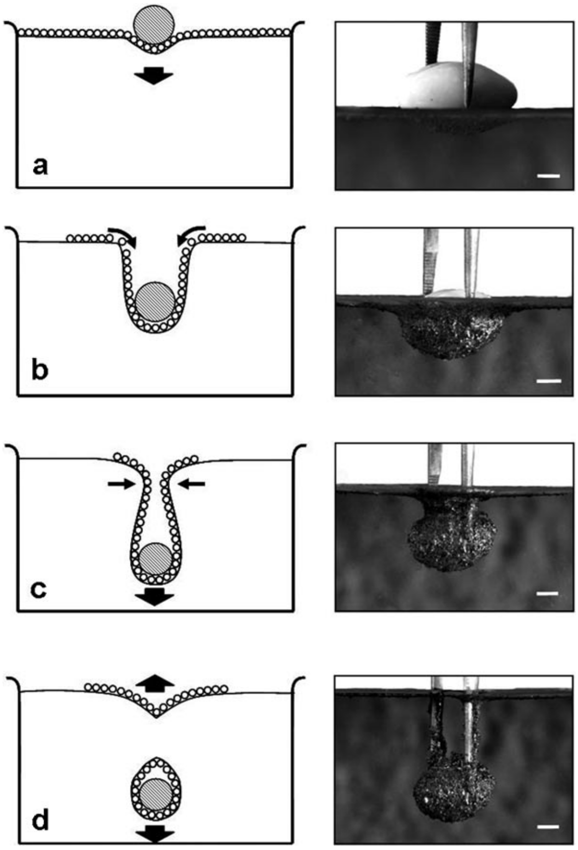

Figure 3. Diagram showing the effect of placing spheres with different densities onto a superhydrophobic particle sheet and photographs of a magnetic follower at stages of immersion on a sheet of coated ≤ 400 µm copper particles. The scale bar is 10 mm.

they needed to contract, they did not form wrinkles in the way previously observed for particle sheets in uniaxial compression.[13] Instead, the particles were free to reorganize into new close-packed layers, with the appropriate geometry, at the point where they fell over the curved junction between the surface and the vertical meniscus (Figure 3b).

In essence, as an object is lowered into the water it is coated in a robust and completely waterproof film that grows as required when the object is pushed further into the liquid but which falls off when it is raised. At higher mass the vertical meniscus curves inward (Figure 3c) until at a critical value the opposing surfaces meet and the neck closes (Figure 3d). Remarkably, at this point the object is seen to be completely enclosed in a sheet of particles which are held in place by the hydrostatic pressure. This effect is strikingly reminiscent of endocytosis, but on a macroscopic scale. A photograph further illustrating the effect is given in the Supporting Information.

The ability of the floating sheets to resist penetration of liquid water arises from the attractive forces which pack the particles sufficiently strongly that the voids which arise due to their irregular shape do not grow, even under reasonably high loads. However, the source of the attraction does not need to be the Cheerios effect. When the sheets wrap submerged objects they are held in place by hydrostatic pressure and we have found that fixing a single layer of particles to a solid support with adhesive also creates a water-resistant barrier despite the macroscopic (>100 µm) holes in the coating due to poor packing of the particles. Further studies, aimed at increasing the water resistance of the sheets by using spherical particles which will pack more efficiently, are underway. At a more general level these materials may provide useful macroscopic models for exploring interfacial phenomena normally observed only at the microscale, such as the stabilization of emulsions by colloidal particles.

Experimental Section

Superhydrophobic copper particles of all sizes were prepared by the same method; that for ≤ 400 µm particles is outlined. Copper powder (ca. 40 g, 400 µm, 99.5 %, Aldrich) was washed with 0.5 % HNO_3 (70 %, J. T. Baker) and deionised water. The particles were shaken in 0.02 M $AgNO_{3(aq)}$ (70 cm^3, AnalaR, BDH Chemicals Ltd.) for several minutes. The powder was filtered, rinsed with deionised water and dried at 70 °C. The powder was immersed in 100 cm^3 of a 0.1 M 1-decanethiol (96 %, Alfa Aesar) solution in ethanol (Absolute ACS grade, J. T. Baker). The mixture was shaken intermittently and left overnight. The powder was filtered, rinsed with absolute ethanol and dried at 70 °C.

Contact angles of *Lycopodium* spores (Fluka) and the coated copper particles were recorded by spray mounting the particles onto flat card. The angles were recorded on an FTA200 contact angle instrument and are the average of >10 angles. Scanning Electron Microscope images were recorded using either a JEOL 6500 FEGSEM operating at 5.0 kV or on a Hitachi TM1000 operating at 15.0 kV.

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