Structure Hierarchy

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From Fluidic Self-Assembly to Hierarchical Structures—Superhydrophobic Flexible Interfaces

Ulrich Jonas and Maria Vamvakaki*

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Throughout human history, living organisms have often served as sources of inspiration for the technological development of biomimetic materials and devices.[1] In particular, the ability of an organism to self-assemble from smaller components into a complex hierarchy of structural levels with an intriguing wealth of functionality has been a challenge to mimic in artificial systems. For many years chemists have investigated the self-assembly of molecular entities into larger, defined supramolecular structures by the so-called "bottom-up" approach.[2] Gradually the small molecular building blocks have been expanded, by a fluidic self-assembly process, into larger units reaching far into the colloidal domain in which the dimensions of the individual components range from nanometers up to many micrometers.[3] The air–water interface, with its strong surface tension, has proved to be particularly instrumental in the assembly process, since the capillary forces between floating objects extend over several millimeters and enable the self-assembly of macroscopic objects.[4] Cleverly designed centimeter-sized building blocks with well-defined shapes and chemical surface patterns, which control the wetting at the contact line between the floating object and the water surface, can self-assemble into sophisticated superstructures.

Control over the wetting of solid surfaces with water droplets has also been at the focus of scientific research. One of the goals is the transfer of the water-repellent and self-cleaning properties of the lotus plant to technical applications, such as self-cleaning windows and coatings. Research on superhydrophobic surfaces has identified both the surface morphology and the surface chemistry as key prerequisites for obtaining extreme wetting behavior, as described by the Wenzel and Cassie–Baxter theories.[5]

The insightful report by Kim et al. has joined aspects of self-assembly and superhydrophobicity in a powerful yet convenient strategy for the preparation of flexible particle layers at the air–water interface; one face of these layers is strongly bound to water, whereas the other face (oriented towards the air) is extremely hydrophobic.[6]

The key component of this system are so-called "Janus" particles with two different faces, one face is attracted to water, while the other hemisphere strongly rejects water (Figure 1, center). These Janus particles exhibit a sophisticated anisotropic architecture with hierarchical structure elements of small holes and needlelike protrusions in combination with hydrophobic surface groups on the water-repelling hemisphere (Figure 1 B and Figure 2), while the water-attractive face features only the small holes surrounded by planar and hydrophilic surface material (Figure 1 A and Figure 2). Upon deposition of these intriguing little balls, only 80 micrometers in diameter, at the air–water interface, they spontaneously aggregate into a compact particle film driven by the attractive capillary forces between the particles (Figure 2,(2)). The upper surface of this flexible but sturdy layer is so water-repellent, that a small deposited water droplet will rest on the floating layer as a little sphere (Figure 1 C). If a glass rod is pushed through the particle layer, the layer coats the immersed fraction of the rod as a compact film and effectively separates the glass from the aqueous

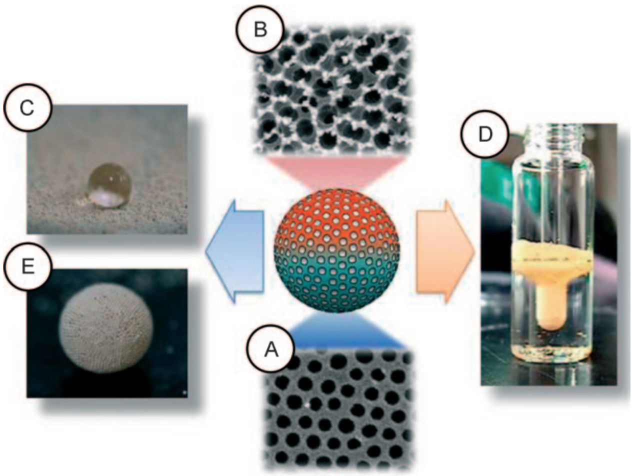

Figure 1. Illustration of a Janus particle (center) with its hydrophilic face in blue and its hydrophobic face in red. Scanning electron micrography images of: A) the hydrophilic and B) the superhydrophobic surface topography. Photographs of: C) a water droplet resting on a floating monolayer of Janus particles; D) deformation of the particle layer with a glass rod; E) a water marble coated by a monolayer of Janus particles.

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[*] U. Jonas, M. Vamvakaki
Bio-Organic Materials Chemistry Laboratory (BOMCLab)
Institute of Electronic Structure & Laser (IESL)
Foundation for Research and Technology – Hellas (FORTH)
Nikolaou Plastira 100, Vassilika Vouton, 71110 Heraklion, Crete
(Greece)
Fax: (+30) 2810-39-1876
E-mail: ujonas@iesl.forth.gr
Homepage: http://www.iesl.forth.gr

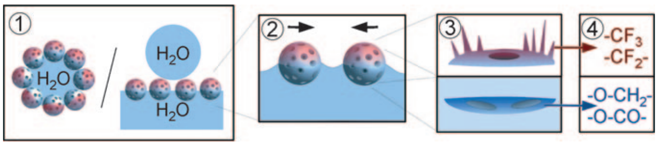

Figure 2. Structural hierarchy: 1) Janus particles at the air–water interface; 2) capillary forces between Janus particles, 3) dual-scale surface roughness with spikes and holes on the hydrophobic hemisphere (red) and smooth areas between the holes on the hydrophilic side (blue); 4) hydrophobic fluorocarbon groups (red) and hydrophilic ether/ester surface functions (blue).

phase (Figure 1D). Upon retraction, the particle layer reforms at the air–water interface and the glass rod is recovered in its original uncoated state. The flexible particle layer is so robust that a whole water droplet can be enclosed within a compact particle shell, and the resulting “liquid marble” can be manipulated with a pair of tweezers without disintegration (Figure 1E). Since these Janus particles are also magnetic, both the floating particle layer and the water marble can be manipulated by a magnet.

An ingenious sequence of process steps was developed by the authors[6] to fabricate these microspheres starting with a dispersion of 250 nm silica particles and magnetic iron oxide nanoparticles in a polymerizable oil phase. This oil phase is extruded through a capillary into a water phase to form emulsion droplets about 80 μm in diameter. Within minutes the hydrophilic silica particles inside the oil droplets accumulate at the oil–water interface to form solid-particle-stabilized oil droplets, known as a Pickering emulsion. Upon subsequent UV irradiation, the oil droplets photopolymerize and are thus converted into hard spheres covered with the silica particles. Next, the silica particles on the surface of the polymer sphere are dissolved to leave voids at the polymer–water interface (Figure 1A). Finally, to generate the needle-like topography in the areas between the voids and to convert the hydrophilic polymer into a hydrophobic surface coating with fluorine groups (Figure 1B), one side of the holey polymer spheres is selectively exposed to a reactive ion etch with SF_6. For this purpose a monolayer of the holey spheres is deposited onto a silicone film; the polymer particles adhere strongly enough to prevent rolling or detachment during exposure to the directed flow of reactive ions. This procedure ensures precise hydrophobization and topographic etching of only one hemisphere of the polymer particles, while the other side retains its hydrophilic character.

The remarkable properties of these Janus particles, which have rather simple spherical geometry, at the air–water interface document the potential of combining complex structural hierarchy with chemical diversity (Figure 2). The underlying features of superhydrophobicity—the propensity for forming self-cleaning, nonfouling, and antisticking surfaces—have initiated considerable research in the design of surfaces exhibiting a dual-scale roughness on the micro- and nanometer scale following appropriate chemical modification with low-surface-energy materials. Kim et al. have cleverly implemented this concept in their fabrication of the Janus particles. Owing to their anisotropic surface properties, which introduce an extra design parameter beyond size and shape, Janus particles have been extensively envisioned investigated as building blocks in hierarchical self-assembled superstructures.[7] Many methods for the preparation of Janus particles have been developed: 1) adsorption of a particle monolayer and selective shading of one hemisphere, 2) stamping of one hemisphere, 3) immobilization at the interface between two phases (like Pickering emulsions) and face-selective modification, 4) phase separation of immiscible phases in small particles, 5) electro-jetting of a biphasic system in the form of particles, and 6) microfluidic fabrication with photopolymerization. In particular, the latter technique has been demonstrated for the preparation of complex particle architectures having both intriguing shapes and chemical compartmentalization, with large potential for scale-up.[8]

In conclusion, Janus nanoparticles like those described by Kim et al. are attractive for a variety of applications in the fields of drug delivery, catalysis, materials science, surface engineering, and microelectronics. One of their unique properties is their self-assembly into fascinating hierarchical assemblies and complex superstructures upon dispersion in media selective for only one of the hemispheres. These small superhydrophobic objects have great potential for the preparation of size-dependent semipermeable membranes at interfaces between immiscible fluids, as buoys for micromachines that float on water, and in various superhydrophobic coatings, especially in the context of rain- and tear-resistant makeup. Moreover, their hierarchical assembly at the interfaces of immiscible polymer blends bears great potential for blend stabilization.

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