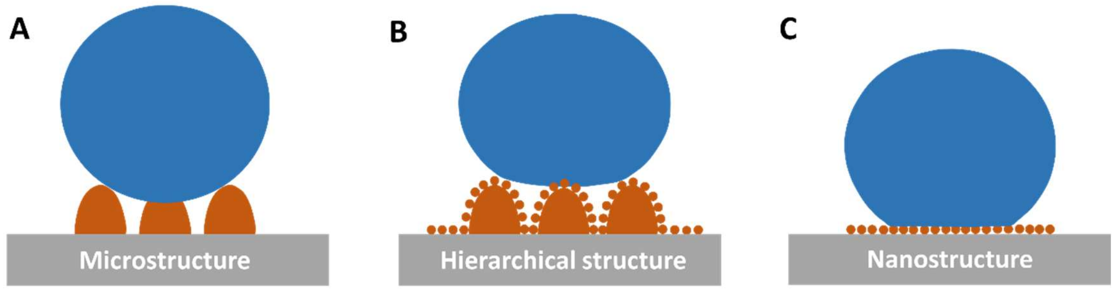
How contact angle measurements can help to develop water resistant paper.

Conventional paper is widely used in our daily life, unfortunately it can be easily destroyed when exposed to water due to the hydrophilic hydroxyl groups of its main component cellulose. Many efforts have been devoted to rendering paper more stable towards water and also heat. So far researchers have mainly applied two general methods to construct hydrophobic paper with comprehensive performance:

1. Incoorporation of inorganic nanoparticles modified by hydrophobic modification agents
2. Micro-/nanoscale hierarchical structures coated with low surface free energy materials.

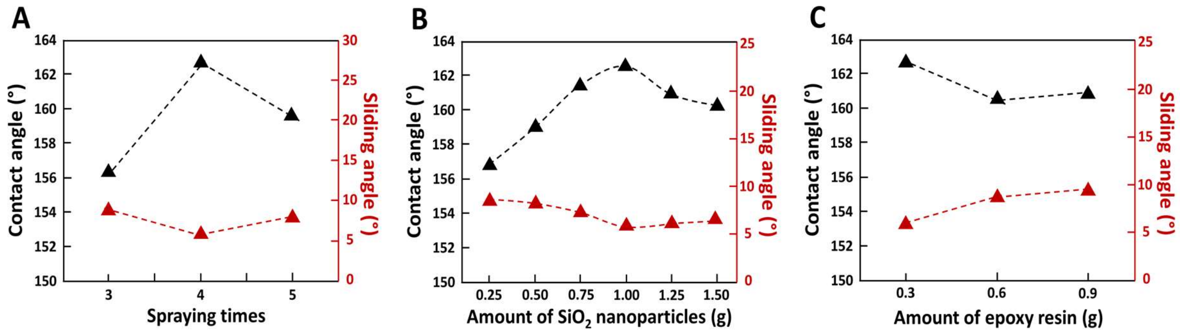
However, the toxicity of these modification agents (fluorine-containing) and weak adhesion hindered the practical application. Recently, Jiao et al. have come up with a novel strategy to solve above problems by building hierarchical structures and incorporating adhesive materials.

In this work, the authors developed multifunctional superhydrophobic paper by a two-step spray-deposition method. SiO_2 micro-/nanoparticles were used due to their low production costs, high thermal stability and optical transparency. The SiO_2 microparticles and nanoparticles were modified with hydrophobic methyl groups on the surface by mixing SiO_2 microparticles with fluorine-free hexamethyldisilazane (HMDS). Epoxy resin (ER) was added as the adhesive agent. Finally, by spraying suspensions of the modified micro- and nanoparticles onto standard A4 printer-grade paper, a superhydrophobic paper (BSP) with hierarchical structures was obtained (**Picture 1B**).



Picture 1*: Scheme of the simplified wetting models for three surface structures. (A) Micro-structured surface, (B) Hierarchical structured surface, (C) Nanostructured surface*

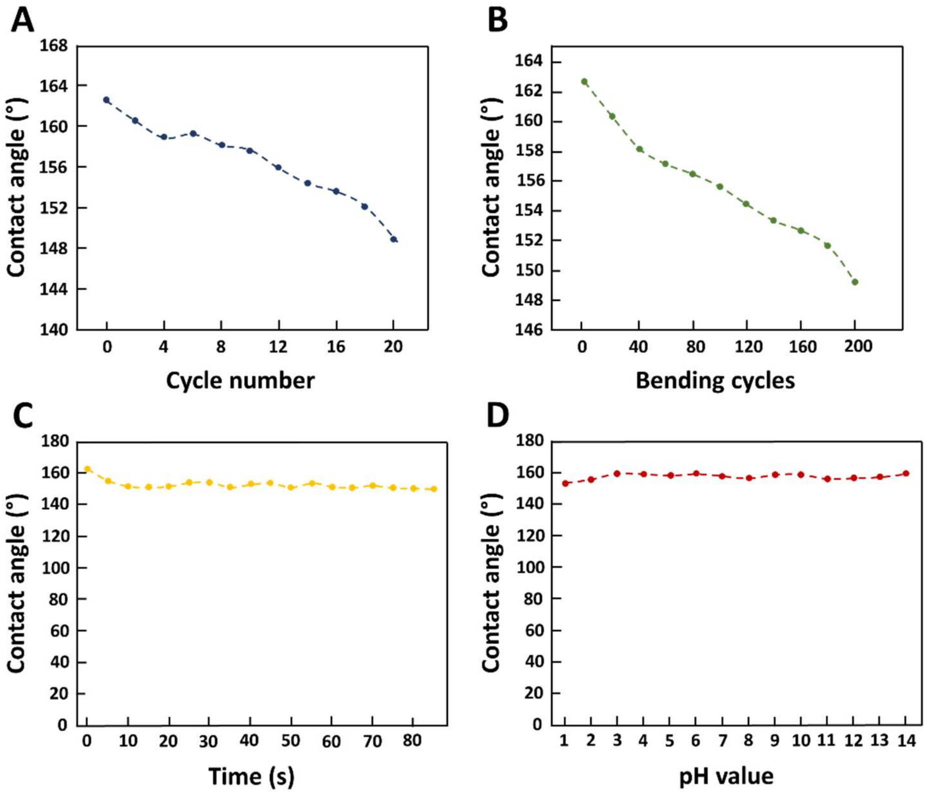
To better illustrate the surface wettability also papers with microstructures (**Picture 1A**) and nanostructures (**Picture 1C**) were made. As expected, the surfaces with hierarchical structures were found to be more hydrophobic than the two control groups. Furthermore, they evaluated the effects of suspension spraying times, amount of SiO_2 nanoparticles and amount of epoxy resin on the water contact angles (WCA) and sliding angles (SA) of BSP (**Picture 2**).



Picture 2: *WCAs and SAs of the BSPs as a function of (A) different times for spraying SiO_2 nanoparticles, (B) various amount of SiO_2 nanoparticles, (C) the amount of epoxy resin*

Most notably when adding 1.0 g SiO_2 nanoparticles, the fraction of the trapped air between the micro-/nano hierarchical structures would reach the maximum (91.3%), leading to the best hydrophobicity. The amount of epoxy resin had no significant effect in the tested range.

They further studied the mechanical abrasion durability, chemical durability, boiling water resistance and corrosion solution resistance of BSP by measuring WCAs before and after treatment (**Picture 3**). BSP could bear abrasion tests for up to 20 cycles and bending tests for up to 200 cycles with slight decreases in the WCAs. An excellent durability over the whole pH range or in boiling water was detected. Interestingly, when they wrote on BSP underwater, they found the area with and without words could both maintain the superhydrophobicity.



***Picture 3**: WCAs of the BSP (A) after each wear test cycle, (B) as a function of bending cycles, (C) as a function of the immersion time in boiling water, (D) after soaking in the corrosion solutions with the pH values varying from 1 to 14 for 3 min*

Overall, the authors improved the comprehensive performance of conventional paper by introducing hierarchical structures on the paper surface. They finally obtained multifunctional superhydrophobic paper with multiple liquid-repellency, heat-resistance, good chemical stability and mechanical robustness. This work provides us a novel method to design water resistant paper with robust fluorine-free superhydrophobic coatings and holds considerable promise for fabricating multifunctional paper for more potential applications.

An optical contour analysis system OCA (DataPhysics Instruments GmbH, Germany) was used in this research.

For more information, please refer to the following article:

Underwater writable and heat-insulated paper with robust fluorine-free superhydrophobic coatings; Z. Jiao, W. Chu, L. Liu, Z. Mu, B. Li, Z. Wang, Z. Liao, Y. Wang, H. Xue, S. Niu, S. Jiang, Z. Han and L. Ren, *Nanoscale* **2020**, 12, 8536–8545; DOI: 10.1039/C9NR10612J