A General Chemical Approach for the Controlled and Extreme Regulation of Liquid Wettability in Air and Under water†

Abstract

Controlled regulation of both oil (under water) and water (in air) wettability is an emerging approach to design several functional materials for various prospective applications such as oil/water separation, anti-corrosive coating, underwater robotics, drug delivery, open microfluidics etc[1-2]. Herein, we report a 'reactive' and covalently cross-linked polymeric coating through a facile and robust 1, 4-conjugate addition reaction, which is appropriate for the regulation of the extreme wettability of both in air and underwater. The special liquid wettability of the multilayer can be tuned (i.e. extremely liquid repellent—but with controlled adhesive property) by strategic post-chemical modifications. The super-wetting properties of the materials were able to withstand various physical abrasions and harsh chemical environments unlike most of the reported materials where this property is compromised under such circumstances[3-4]. Besides, this current method has been proved to be a substrate-independent approach that enables us to decorate various flexible and rigid substrates (i.e. wood, Al-foil, synthetic fabric etc.), irrespective of their composition as well as innate characteristic wettability with various bio-inspired wettability properties[5]. This single polymeric coating would be useful in various prospective and relevant applications in practical scenarios.

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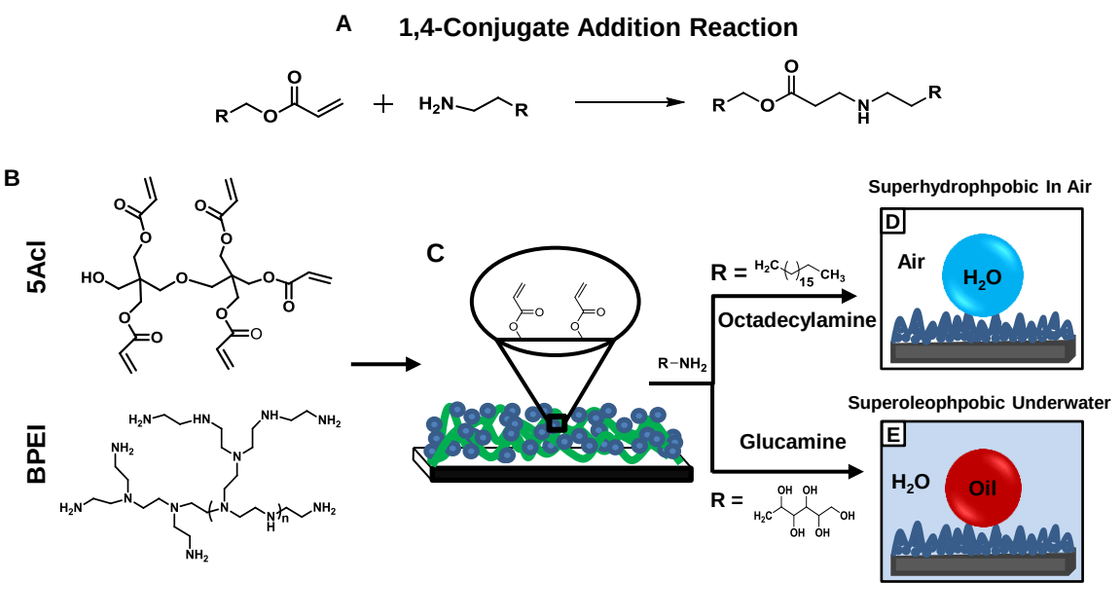
Methods



Scheme 1. A) 1,4 conjugated addition reaction (Michael addition) between primary amine and acrylate moieties. (B) Structural formula of Dipentaerythitol penta-acrylate (5Acl) and branched polyethyleneimine (BPEI) consisting of several acrylate and amine groups respectively. (C) Schematic representation of the multilayers assembly of BPEI/NC having reactive acrylate groups. (D--E) Illustrating the post-chemical modification of the multilayers assembly of NC with different small molecules to adopt the superhydrophobicity in air and superoleophobicity under-water.

Results

Figure 1. A-B) Graphical representation of (A) size-growth of the nano-complex and (B) the growing thickness of the multilayers assembly both with salt (black) and without salt (red) contamination, with increasing bilayer deposition. (C-H) FESEM images of the post-functionalized polymeric multilayers with salt (C-E) and without salt (F-H) contamination in low (C,F scale bar 20μm ; D,G scale bar 15μm) and high (E,H scale bar 500nm) magnification. (I) The reactivity is revealed by the FT-IR analysis of untreated (black), ODA-treated (blue) and glucamine treated (red) multilayers of NC with salt contamination.

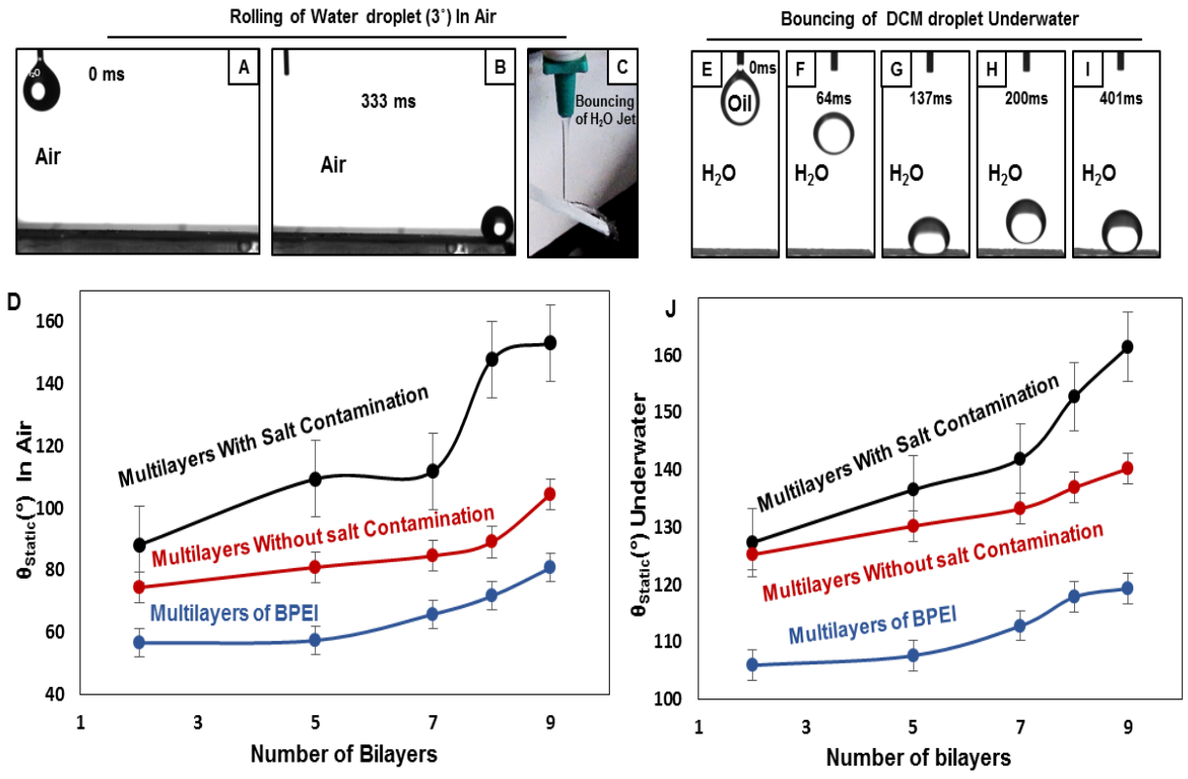


Figure 2. A-B) Rolling of a water droplet (5μL) after hitting a tilted surface of 3˚.(C) Bouncing appearance of a water jet over the superhydrophobic surface. (D) The variation of contact angle measurement plot of water droplet (4.5μL) with increasing bilayer deposition for the multilayers of NC in air . (E-I) Bouncing of the oil droplet (DCM, 11μL) after a strong impact on a super-oleophobic surface under-water. (J) The change in contact angle measurements plot with increasing bilayer deposition for the multilayers of NC under-water.

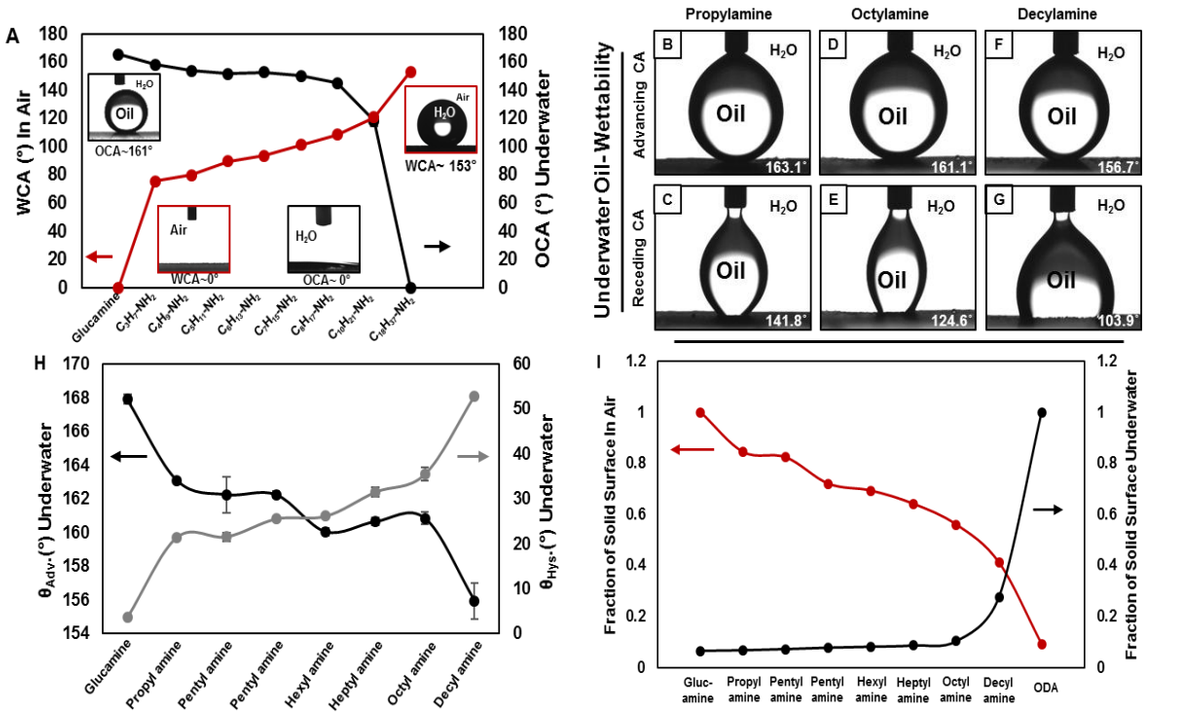


Figure 3. A) The variation of WCA in air (red) and OCA under-water (black) of the multilayers of NC after complete post-functionalization with several small molecules starting from hydrophilic (glucamine) to extreme hydrophobic (octadecyl amine ; $C_{18}H_{37}$-NH_2). (B-G) The effect of adhesiveness on the OCA under-water with changing the chemistry of post-modification from C_3-hydrophilic (propyl amine; $\theta_{Adv.}$ B , $\theta_{Rec.}$ C) to C_8-hydrophobic (octylamine; $\theta_{Adv.}$ D , $\theta_{Rec.}$ E) to C_{10}-hydrophobic (decylamine; $\theta_{Adv.}$ F , $\theta_{Rec.}$ G) small molecules. (H) The change in advancing OCA (black) and respective contact angle hysteresis (grey) under-water by altering the post-modified chemistry. I) Graphical overview of the variation of the fraction of the solid surface area in contact with the water droplet in air (red) and oil droplet under-water (black) with varying of post-modified chemistry.

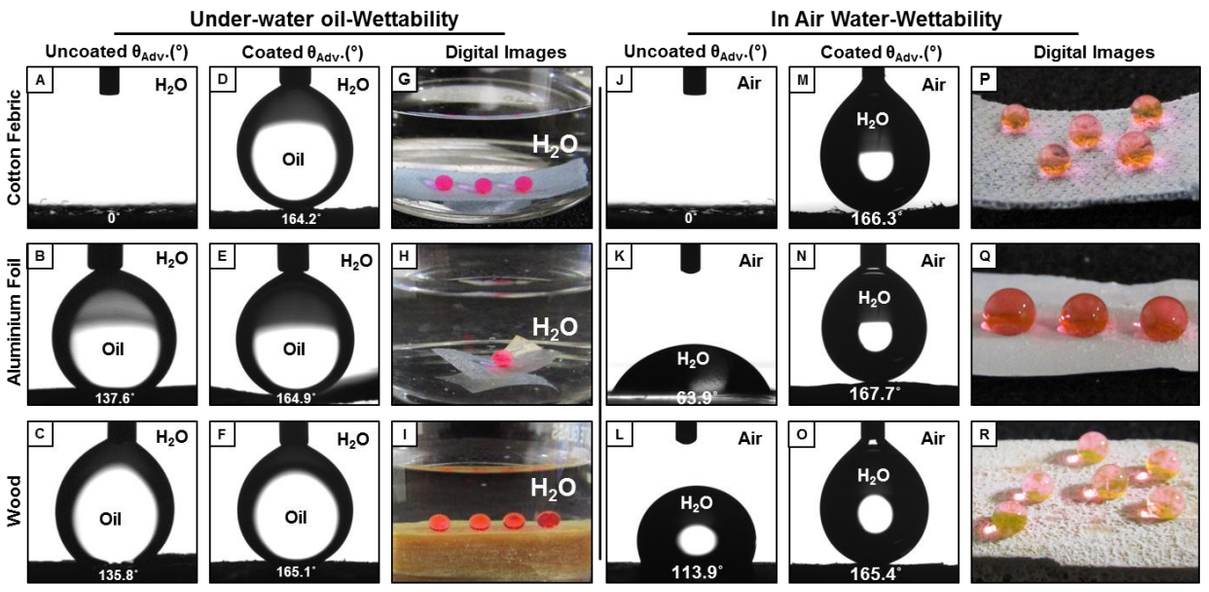


Figure 4. A-F,J-O) Contact angle measurements and (G-I, P-R) digital images of both bare (A-C, J-L) and coated substrates (D-I, M-R) like cotton-febric (A,D,G,J,M,P), aluminium foil (B,E,H,K,N,Q) and wood (C,F,I,L,O,R) in air (J-R) and under-water (A-I).

Publication

†**A General and Facile Chemical Avenue for the Controlled and Extreme Regulation of Water Wettability in Air and Oil Wettability under Water. Chem. Sci., 2017, 8, 6542–6554.**