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Fabrication of Namib Beetle Inspired Biomimetic Amphi-Phobic Surfaces Using Adsorbed Water as a Monomer

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Abstract

Chemical grafting of small molecule reagents onto polymeric fibrous materials, like paper, has been used to modify their wetting properties. Several reagents like trichlorosilanes, which can react with water or hydroxyls, have been used with the expectation that a monolayer, single molecule or polymerized single-molecule layer, is formed on the paper fiber surface. Presence of adsorbed water, however, would complicate the formation of a monolayer, especially in case of polyvalent reagents. We hypothesized that adsorbed water is a good co-monomer for polyvalent water-reactive reagents, therefore chemical grafting with polyvalent molecules would give polymeric gels instead of a monolayer. Reaction of trivalent reagents with paper *in vacuo* leads to formation of polymeric gels. By optimizing surface energy mismatch, through felicitous choice of chemical moieties on the monomer, self-assembly leads to formation of nano- to micro particles on the surface of paper fibers. We observe that, as expected, the wetting properties correlate well with the size and distribution of particles. We conclude that the recently reported ultra-hydrophobicity of chemically modified paper is not only due to inherent roughness of the paper fibers, but also due to a secondary roughness introduced by surface polymerization. Using this technique, we prepared amphi-phobic biomimetic surfaces inspired by the namib beetle. This talk will also address potential utility of such surfaces.

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1. Introduction

Since the existence of human kind, Nature has been a great source of inspiration for technological advances. Evolution, and the need to survive, has led to development of complex surface properties in some animals. In the case of the Namib Desert beetle, *Stenocara gracilipes*, surviving in harsh environments is largely due to its ability to harvest water from fog.[1-2] The surface structure of the beetles wings are Biphobic, that is, it has hydrophilic bumps that helps in water droplet adhesion/collection and hydrophobic valleys that act as collector channels for the water droplets. This beetle has been the inspiration for developments of various materials, such as metal surfaces for use in aerospace engineering and self-cleaning materials for biological purposes.[2-5] These applications, however, often require sophisticated nano-patterning, expensive equipment, and a skilled personal to reproducibly generate these kinds of surfaces. The ability to create energy efficient materials, in a sustainable and affordable approach that can be applied in remote areas is desired.[5-6]

Amphiphobic surfaces have a wide range of applications and methods to fabricate these important materials are highly limited, and often employ complex and/or expensive methods or technology.[5-6] The process of self-assembly is one that has been used over the past years due to its advantages in ease of use and cost.[7-9] Surface modification of paper, and analogous fibrous polymeric materials, with poly-functional reagents has the potential to create textured materials, which in turn would be amphiphobic.[9-10] Reaction of

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polyvalent (here valence means number of reactive units) molecules, like trichlorosilanes and water, can lead to significant cross-linking that in turn can lead to gel formation under the correct proportions. Where such a process involves step-growth polymerization, with its inherent large range in low degrees of polymerization, one can envision formation of gel particles of different sizes in a controllable manner. We hypothesized that during the surface functionalization process, the size of surface adsorbed particles can be controlled by controlling the degree of polymerization which in turn can be controlled by the reaction time. To test our hypothesis, we employed the synthesis of polysilsesquioxanes with concomitant surface energy driven self-assembly, to synthesize particles on paper.

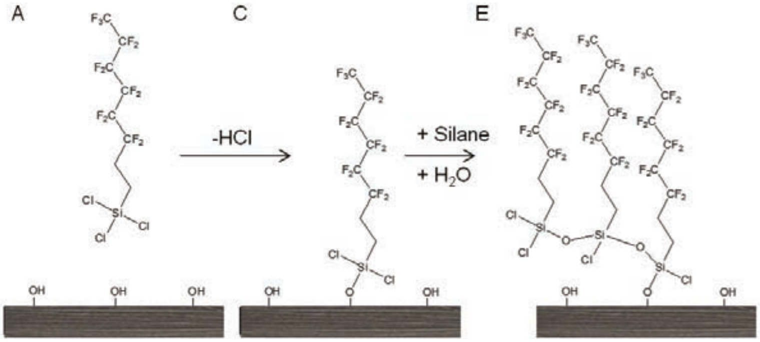

Figure 1. Reaction of surface hydroxyl groups with fluoroalkyl silane vapor to form hydrophobic surface. Condensation of the silane with any available hydroxyls releases HCl and gets cross-linked to give a polymeric layer.

2. Results and Discussion

First, we treated different types of papers with perfluoro octyltrichlorosilane (PFOTS) and observed that most of the papers became ultra-hydrophobic (static contact angle with water, θ_s, > 120).[11-12] To understand the origin of this ultra-hydrophobicity, we compared different types of paper; i) chromatography paper – 100% cellulose, high porosity, ii) card stock paper –cellulose with fillers, and, iii) NYX beauty paper – high density with infused fillers. We also used a perfluorinated and non-fluorinated reagents to investigate the role of surface tension of the reagents, relative to that of the surface, on the gel formation which we had hypothesized to be the origin of the ultra-hydrophobicity.

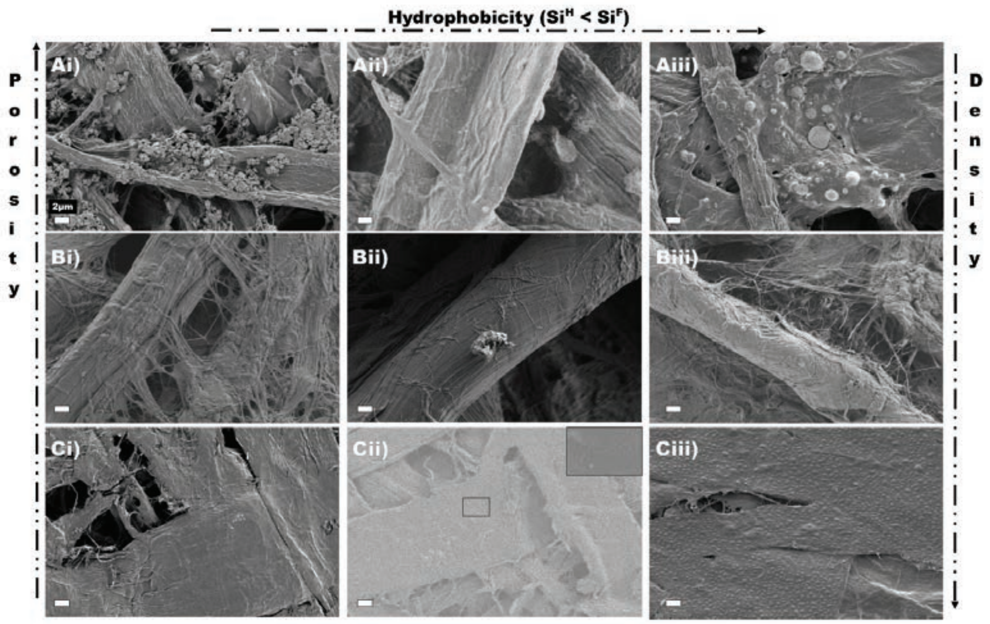

Figure 2. Chemical modification of representatives types of paper with non-fluorinated silane and fluorinated silane. Ai) highly porous, mostly cellulose paper represented here by chromatography paper No. 1. Aii) Chromatography paper upon chemical modification with non-fluorinated silane (Si^H) and Aiii) Chromatography paper upon chemical modification with fluorinated silane (Si^F). Bi) A porous paper containing filler materials represented by cardstock paper which contains PCC filler material. Bii) Cardstock paper upon salinization with Si^H, occasionally particulate were observed in the surface of the paper while in Biii) A more noticeable particle formation can be observed with the fluorinated silane (Si^F). Ci) Dense paper represented by NYX blotting paper. Cii) Upon silanization with the Si^H presence of particles are shown while in Ciii) Upon treatment with Si^F large amount of particles are formed.

Absorbed surface water: Scanning electron microscopy (SEM) images were collected from the control paper and the treated ones over different reaction times. Imaging the control paper, showed anisotropy in fiber orientation and structural composition. As