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Influence of silanes on the wettability of anodized titanium

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ABSTRACT

A facile method was adapted to make superhydrophobic (SHP) titanium in which a synergistic combination of surface roughness and surface chemistry was utilized. In the first step, titanium was mechanically polished and pickled followed by anodization. The next step was to dip coat the samples with silane solution and then were cured at 110 °C. Influence of different synthesis parameters such as silane concentration, number of dip coating and curing temperature on water contact angle (WCA) was studied and conditions were optimized to achieve a WCA of 150°. The wetting properties of the samples were elucidated using contact angle meter and the water just rolled off the modified titanium surface with a slight tilting. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to study the morphology and surface roughness of the silane coated titanium samples. Grazing incidence X-ray diffraction (GIXRD), energy dispersive spectroscopy (EDS), attenuated total reflection-infrared spectroscopy (ATR-IR) and X-ray photoelectron spectroscopy (XPS) were used to analyze the chemical composition of the coatings which confirmed the presence of silicon along with titanium and oxygen. Immersion studies in sea water and nitric acid medium for 15 days indicated the stability of the coatings with minimal variations in contact angle.

1. Introduction

Nature has its own 'Nanotechnology' revealed in different objects for different purposes. A specific example is the lotus leaf which is considered as a sacred flower in East Asian countries. Its peculiarity arises from the fact that it grows in murky waters and yet the lotus leaves are free from impurities. Water droplets falling on the lotus leaf bead up and roll off taking away all the dirt. This phenomenon is called the 'Lotus effect' and the lotus leaves are said to be superhydrophobic. When the WCA is above 150°, the surface is superhydrophobic, water drops simply bounce-off the surface. This phenomenon is exhibited by a wide range of plants and a few insects for self-cleaning purpose. In nature, the leaves of plants like *Nelumbo nucifera* [1], *Colocasia esculenta, Brassica oleracea*, the wings of butterflies, and the legs of water striders are all superhydrophobic. A detailed microscopic examination of the lotus leaves revealed a micro-nano rough feature namely papillae and a wax-like coating [2]. They have papillose epidermal cells and an additional layer of epicuticular waxes that provide the water repellence. As air is trapped between the micro-nano features, the water drops rest only on the tip of the surface microstructures, thereby minimizing the interfacial area between the surface and the water drop. But without micro-nano architecture there is also a possibility of exhibiting superhydrophobicity as in the case of the wings of butterflies.

Superhydrophobicity could be generated in two steps: (i) creating micro-nano roughness and (ii) coating with a low surface energy material. These steps could be achieved by a number of experimental techniques and materials. The first step is usually achieved by mechanical polishing or electro polishing and then a suitable technique is used to create micro-nano roughness followed by dip coating or spin coating the low surface energy materials. At the same time, a number of sophisticated experimental techniques are also employed to create superhydrophobic surfaces; plasma enhanced chemical vapor deposition, magnetron sputtering, self-assembly, laser treatment, photo catalytic lithography, anodization, electrospinning, electrostatic spinning and spraying, chemical vapor deposition, electroless replacement deposition, wet chemical reaction, sol–gel method, polymer replication method, electroless galvanic deposition, plasma arc deposition, polymerization, and atomic layer deposition are some of the techniques used to roughen the surfaces or to coat a low surface energy material, or both [3,4].

On the other hand, some techniques are used to roughen the surfaces alone (the materials need not necessarily be low surface energy materials) including mechanical polishing, laser/plasma/chemical etching, lithography, sol–gel processing,

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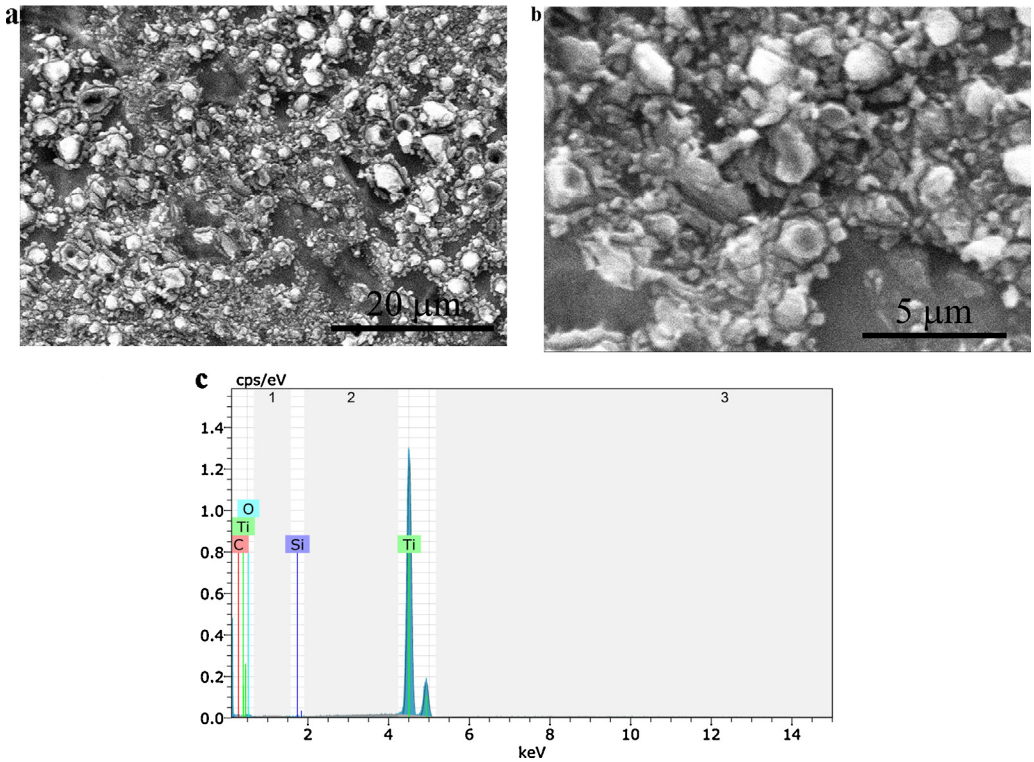

Fig. 1. (a and b) SEM images of silane coated titanium anodized in 0.3 M H_2SO_4 and (c) the corresponding EDS spectrum.

layer-by-layer or colloidal assembly, electrical/chemical reaction and deposition, electrospinning, and chemical vapor deposition to name a few. Having created the necessary roughness by these techniques, the next step is to coat them with low surface energy materials like myristic acid, stearic acid [5–9], silica coatings [10], octadecyltrichlorosilane (OTS) [11,12], perfluorooctyltriethoxysilane (PFOTES) [13], polydimethylsiloxanes (PDMS) [14,15], non-fluorinated alkylsilane [16], silicone nanofilament [17], porous polymer coatings [18], nano-titania coatings [19,20], polymethylmethacrylate (PMMA) coatings [21], carbon nanotube based composite coatings [3,22,23], tetrafluoroethylene (Teflon) coating [24], and polystyrene [25] which are some of the common materials coated on the mechanically polished surfaces to yield superhydrophobicity. In addition, superhydrophobic surfaces were also prepared using one-step processes predominantly on copper substrates [9], which involve longer process time ranging from a few hours to few days, special substrate preparation, and stringent experimental conditions. A bio-inspired approach is also utilized for the one step surface modification of substrates using soft lithography and polymer coating which in turn mimic the adhesive pads of the Mussels [26]. In the present study, the fabrication of superhydrophobic titanium is prepared using a simpler and faster two step method which neither requires sophisticated instruments nor laborious experimental procedures.

The 'lotus effect' has been successfully employed for superhydrophobic surface modification of titanium [5,6], a significant material used in nuclear power plants and reprocessing plants. In the case of stearic acid coated titanium anodized in H_2SO_4, the maximum WCA obtained was 149°. To further improve the uniformity and stability of the coatings as well as the tilting angle on titanium, stearic acid coating was replaced by silane coating. A two step surface modification involving anodization and coating with silane was employed for titanium in the present work. Though a considerable amount of work was reported in the literature on silanes, titanium modified using silanes was the first of its kind and the experimental parameters were optimized especially for titanium. The morphology, surface roughness, contact angle measurements, and chemical composition analysis were carried out for surface modified titanium using silanes. In addition, the superhydrophobic coatings developed on titanium were tested in nitric acid and sea water for long term stability, and the morphology variations and changes in WCA before and after immersion were recorded.

2. Experimental

2.1. Sample preparation

Commercially pure grade 2 titanium (1.5 cm × 1.5 cm × 0.05 cm) coupons were used for the present investigation. Highly pure analytical grade chemicals such as hydrofluoric acid (HF, 40%), sulfuric acid (H_2SO_4, 99%), hydrochloric acid (HCl, 90%), nitric acid (HNO_3, 90%), ethanol (90%), and perfluorooctyltriethoxysilane (PFOTES, 97%, Alfa Aesar) were used. Deionized (DI) water was used for the preparation of the electrolytes. The titanium coupons were mechanically polished on both sides using SiC paper upto 1000 grit. After polishing, the samples were consecutively washed in soap solution and DI water and degreased with acetone. The polished titanium samples were pickled in 400 g/L HNO_3, and 40 g/L HF followed by washing in DI water and dried in air at room temperature.

2.2. Superhydrophobic surface modification

2.2.1. Step 1 Anodization

Anodization was carried out using a two electrode set up with polished Ti coupon as the anode and stainless steel (SS) as the cathode. The electrodes were connected to a DC voltage source (Aplab, Model L3230). The experiments were carried out at room temperature in 0.3 M H_2SO_4 electrolyte at 30 V for 1 h duration. The anodized samples were washed in DI water and dried in air.