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Comparative studies on water repellent coatings prepared by spin coating and spray coating methods

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ABSTRACT

TiO_2 and SiO_2 based water repellent coatings were prepared on various metal and ceramic substrates via spin and spray methods through sol-gel route. Compared to the spin coatings, the spray coatings were able to regenerate superhydrophobicity and to maintain self-cleaning properties while being stable in outdoor environment. The spin coatings appeared to be more mechanical resistant under the impact of water drops and barely reduced the optical transmittance of the substrate. The SiO2 coatings were also more thermal stable than the TiO2 ones and maintained the water repellent properties after 6 months of outdoor environment

1. Introduction

Nowadays there has been deep understanding in developing water repellent coating with unique wetting properties for both industrial and domestic applications. Superhydrophobicity with the dual scale morphology containing observed in nature have inspired scientific and engineering advances in fields such as optics, hydrodynamics, nanotechnology, surface science, and materials science [1,2]. In recent literature, a broad range of interesting properties has been attributed to superhydrophobic surface, including self-cleaning, anti-sticky, anti-corrosion, oxidation resistance surface, drag-reduction surface energy conversion, and protection of electronic devices [3–5]. Synthetic superhydrophobic surfaces are generally obtained by combining micro- or nano structures with low energy surface, on which air pockets are packed underneath droplet in a Cassie or composite state, resulting in superhydrophobic surfaces with large contact angles (>150°) and low sliding angles (<10°). These binary structures have been shown to enhance the contact angle (CA), trim down the CA-hysteresis, and get better stability [6].

Therefore, many materials have been reported for observing lotus effect on low energy surface of hierarchical morphology. Many efforts have been made to fabricate superhydrophobic surfaces bio-inspired by the lotus leaf effect. Starting from a polymer solution, superhydrophobic coarse surfaces are fabricated by simple electro-spinning or phase separation methods [7]. Papillae-mimetic polyaniline particles are assembled in the presence of perfluoro-octane sulfonic acid to build up highly water repellent coatings in situ [8]. Assembling the surface of nano-particles and subsequent surface modification leads to coarse superhydrophobic surfaces [9]. A superhydrophobic coating can be easily fabricated by commanding their crystal dynamics growth from melting [10], or by means of electrochemistry onto metallic substrates [11]. The current methods have their own drawbacks, either involving expensive facilities or the process being time consuming and complicated. Some methods are specially designed for mechanistic study, which is not applicable at large scale. Furthermore, most of the reported superhydrophobic coatings are not robust enough to resist water flushing. How to regenerate the superhydrophobic performance of a coating after being scratched becomes a key concern. It is urgently required to develop a facile approach towards large-scale fabrication of robust highly water repellent surfaces on various substrates. To the best of our knowledge, there is no report dealing with comparative studies of TiO_2 and SiO_2 based water repellent coatings on various types of substrates with focus on

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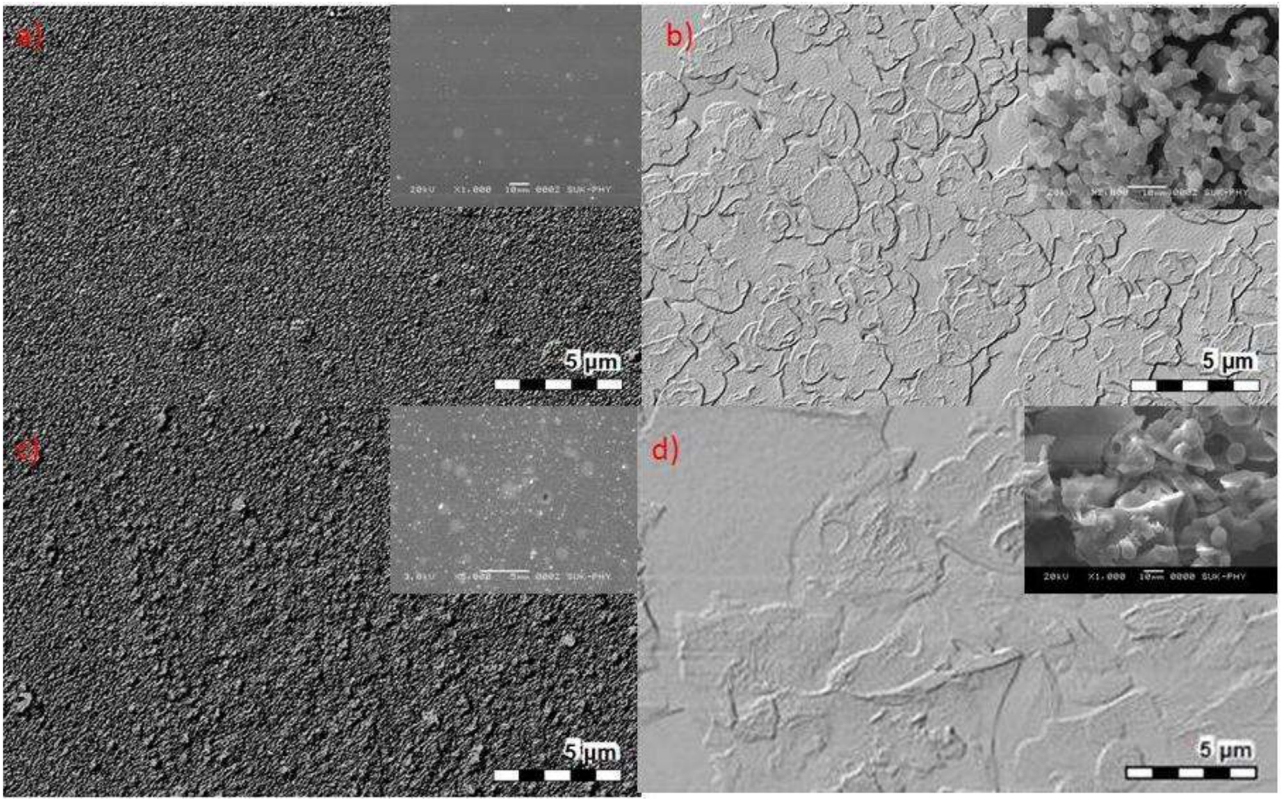

Fig. 1. Surface topography and morphology (inset figures) of glass substrate coated with TiO_2 by a) spin method, b) spray method and similarly SiO_2 on a glass substrate by c) spin method, d) spray method.

their high performance and comparative surface properties, optical transmission, mechanical and thermal stability on different substrates.

In this work, we present comparative studies of TiO_2 and SiO_2 based water repellent coatings fabricated on different substrates by spin coating and spray coating methods via single step sol-gel process. The procedure is fairly facile to run; no complicated procedure without any high-tech, and costly instruments. The hydrophobic and superhydrophobic coating surfaces will be easily produced on various metal and ceramic substrates to result in low sliding angle (high slippery surface), high thermal stability, and highly transparent surface while being stable in outdoor conditions for long time.

2. Experimental section

2.1. Materials

Glass, quartz, alumina and germanium, copper, steel and brass (thickness 0.5 mm) substrates were purchased from the Blue Star factory (Mumbai) and the local market. All chemicals, reagents and solvents were used for further synthesis without any post purification process. Methyltrimethoxysilane (MTMS), and titanium butoxide (TBT), (99%, Sigma-Aldrich Chemie, Germany) were used as precursors, and Trimethylchlorosilane (TMCS, 99%, Sigma-Aldrich Chemie, Germany) was used as silylating agent. Ammonia (NH_3, Sp.Gr.0.91 Qualigens Fine Chemicals, Mumbai) was used as base catalyst. Methanol and hexane (S. D. Fine-Chem Ltd., Mumbai) were employed as solvent for sol-gel process and surface modification, respectively.

2.2. Fabrication of water repellent coatings by sol-gel method

Titanium butoxide (TBT) and Methyltrimethoxysilane (MTMS) were used as starting materials for the preparation of titanium (TiO_2) and silica (SiO_2) based coatings. Single molar ratios 1:8.15:20.24 of TBT: H_2O (13 M NH_4OH) were employed to successfully fabricate the TiO_2 coatings. The ingredients were stirred at room temperature for 2 h using a magnetic stirrer. Similarly, the alcosol for SiO_2 based coatings were prepared from the constant molar ratio of MTMS: MeOH: H_2O (13 M NH_4OH) at 1:138.6:146.95, respectively. The components were stirred for 24 h using a magnetically stirrer at room temperature. Both sols were then deposited on various substrates by spin and spray coating techniques at optimized deposition conditions. A spin coater (CHEMAT, KW-4A, USA) was used to produce the spin coatings. At low rotation speed (<2000 RPM), the sol-gel coatings were seen to be non-uniform. Hence, a rotational speed of 2000 rpm and a holding time of 1 min were optimized. In case of spray method, the 10 mL of TiO_2 and SiO_2 alcosols were sprayed separately on various substrates at 100 °C for 45 s through a fine spray nozzle at optimized pressure (90 psi) obtained by using an air compressor system (Air compressor, TOYO model. STY-4). The as-deposited coatings were annealed at 150 °C for 2 h in a stove (NeyTECH, Vulcan, Benchtop model 3-550, USA) in order to remove trapped ethanol and improve the bonding strength of materials with substrates.

2.3. General characterization techniques

The measurement of static and dynamic water contact angles with double step distilled water droplets of 5 μL measured by using commercial instrument (Rame hart Instrument Co., model 501 F1, USA). The experimental data were represented as mean ± standard deviation (SD) for n = 5. The outdoor exposure was carried out

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