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Silica based superhydrophobic coating for long-term industrial and domestic applications

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ABSTRACT

In this work, multifunctional superhydrophobicity coatings have been produced on germanium, brass, steel and copper substrates with the help of simple sol–gel spray coating method. A simple testing, artificially simulated corrosive solution continuously exposes with coating surface for six months, it reveals the excellent anti-corrosion performance against corrosive salt solution at room temperature. The as-prepared superhydrophobic coating surface shows outstanding long-term durability, mechanical stability, self-clean ability, thermal stability and acid resistance. We will present how the sol–gel spray coating approach has been integrated into advanced multifunctional material to improve their stability performances against critical conditions and to extend their applications by introducing additional functionalities.

1. Introduction

As a crucial aspect of surface Science, the wettability control of a surface shows enormous value in fundamental and practical applications. Since the discovery of the superhydrophobic surfaces with water contact angles ($\geq$150°) and sliding angles ($\leq$10°) have earned rapidly expanded interest in fundamental and technical research [1,2]. Superhydrophobic surface has been promised a wide range of applications in non-wetting, anti-oxidation, anti-corrosion, self-cleaning surface, anti-fogging, anti-icing, drug delivery system, biosensors, antireflective optical devices, anti-biofouling, anti-staining surface, immiscible liquid separation, and coating on the aquatic surface [3–6]. From the past decade, a large amount research is devoted to this issue, and researchers from various multidisciplinary fields are engaged, including technicians, theoreticians, chemists, physicists and engineers.

A huge number of superhydrophobic coatings have been produced by mimicking the Lotus leaf textures in special ways. However, the susceptibility to environmental degradation forces like thermal degradation, corrosion, mechanical damage and acidic degradation severely hindered the use of superhydrophobicity in industrial and practical uses. Physical and chemical contact could destroy the hierarchical texture and a hydrophobic layer on the surfaces that are essential for establishing superhydrophobicity. Nowadays, industries are suffering from a massive economic loss caused by corrosion and oxidation and for their maintenance cost., Various conventional coating materials have been accounted for producing wear resistance coating by using phosphates, chromates, aluminum, nitrites, zeolites, cationic clays, self-assembled mono-layer's (SAM), anionic clays and molybdates, on the surface of metals and alloys [7–11]. The conventional coating materials are still at the premature stage, mainly due to lack of environmental stability, duration, robustness, acid impressiveness, heat resistance, toxicity and opacity of the prepared superhydrophobic structures [12–22]. Therefore, awarding synthetic superhydrophobicity with a long-term durability and robustness ability is believed to provide an efficient and long-desired way to solve these problems. However, as per our knowledge, there are only few attempts has been paid to the key issue except for some reported reports [23,24]. Recently, D. wang and co-workers achieved a remarkable effort that superhydrophobic coatings with a liquid polysiloxane (PSO) were fabricated via a simple solidification-induced phase separation method, and the organically modified silica (ORMOSIL) coating material is intrinsically hydrophobic without surface modification with expensive fluorinated reagents [25]. Additionally, it should be

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mentioned that the groups of Ludmila Boinovich [26] prepared a regenerative superhydrophobic coating from several siloxane-based hydrophobic and superhydrophobic surfaces, and the different deterioration mechanisms of wettability were discussed successfully. However, in their efforts, while the techniques preferred are relatively costly and non-hazardous chemicals, some specific chemicals are still restricted, and not apply in domestic life. Consequently, it would be desired and urgent to develop real facile approaches towards large area fabrication of the multifunctional superhydrophobic surface with the durability, thermal stability, for a wide range of applications [27]. The sol–gel is a simple method, low cost, and commercially available method for the large-scale of applications, which is not restricted to a specific surface area and can be effortlessly expanded to huge and complicated surface, moreover, it do not typically require any other complicated instruments, critical and tedious conditions.

In this paper, a simple sol–gel spray coating method has been adopted to fabricate durable superhydrophobic coatings with using a methyltrimethoxysilane (MTES) as silica precursor, which is non-poisonous and easy to handle. The MTES based superhydrophobic coating shows outstanding stability with artificial corrosive salt, long-term durability, mechanical stability, anti-corrosion, acid imperviousness and thermal stability. Despite using a simple method before, this work describes to develop different properties and functional applications of typical materials. Thus, this work is assuring for huge amount production, long lived and applicability to make a large of number potential applications in science and technology.

2. Experimental

2.1. Materials

Commercially available germanium, copper, steel and brass (thickness 0.5 mm) substrates were purchased from the local market. All chemical reagents and solvents were used further synthesis without any purification. Methyltriethoxysilane (MTES 99% Sigma–Aldrich Chemie, Germany) was used as silica precursor. The liquor ammonium (NH_3, Sp. Gr.0.91 Qualigens Fine Chemicals, Mumbai) and oxalic acid (99% Sigma–Aldrich Chemie, Germany) were used as a base and acid catalyst respectively. A typical corrosive solution was prepared from combination of calcium chloride (Fluka chemicals, Switzerland, 98.5%), sodium sulfate (Fluka Chemie, Switzerland, 99%), and sodium chloride (Fluka Chemie, Switzerland, 99.5%). The nitric acid (Thomas Baker, Germany 69–70%) was used to test acid impressiveness at different concentration.

2.2. Surface characterization

An automatic homemade spray system with air compressor (TOYO model STY-4) was used to produce superhydrophobic coatings on metals and alloy substrates. The water contact angle on the coatings were measured by a contact angle meter (Rame hart Instrument Co., Model 501 F1, USA) at surroundings temperature and were recorded immediately after placing a 3 μL deionized water droplet (1.8 MΩ cm) on the surface. SEM images of the superhydrophobic coatings were gained on an SEM, JEOL JSM-6360, Japan at 20 KV. IR spectroscopic analysis of the MTES based material was performed in reflection mode using a Fourier transform infrared (FTIR spectroscopy, Perkin–Elmer, Model no. 783, USA) spectrometer. The mean surface roughnesses (Ra) are measured with a Mitutoyo Surftest SJ-201 M (Japan) portable surface roughness tester instrument. The surface roughness is an average taken from 5 different measurements. The optical transparency of the coated glass substrate was studied with a UV–Vis spectrophotometer (UV-3000, Shimazdu Co. Japan). Finally, thermal degradation of was successfully studied using the TGA-DSC analysis (USA). Finally, thermal degradation of coating material was recorded as a function of temperature using TGA-DSC (TA Instrument, Q600, USA), which was performed under an inert atmosphere up to 1000 °C at a rate of 10 °C/minute. The corrosion behavior of coatings was successfully studied by exposing with an artificial corrosive solution for six months and measures their wettability studied after soaking period.

2.3. Treatment of coating surfaces

Aluminum, copper, steel, germanium and brass metal substrates (dimension: 5 × 1 cm) were polished with paper grit (SiC#800) to produce micro-scale rough surface. The only glass substrate was cleaned by scrubbing with detergent and then in distilled water. All substrates were afterwards immersed in ultrasonic baths of ethanol and acetone, each for about 25 min. The surface was cleaned with cotton and then the surface was successfully dried with the help of the dryer. Finally, all substrates were exposed to a heat at 50 °C in oven over 2 h.

2.4. Synthesis

To produce the superhydrophobic coatings, the sol solution with a molar composition of MTES: MeOH: H_2O (0.1 M oxalic acid): H_2O (13.36 M ammonia base) = 1:24.59:2.76:1.40 was prepared by drop wise addition of aqueous H_2O (0.1 M oxalic acid) as an acid catalyst to MTES and methanol solution with rigorously stirring, where oxalic acid promoted the early hydrolysis of MTES. After hydrolysis reaction for 5 h, the linear polymerization was accelerated by the slow addition of a quantity of aqueous ammonia base solution as a base catalyst to the above mixture, and then reacted at room temperature for the next 10 h. The transparent and viscous solution, which was gained before gelation time at room temperature over a fixed period, sol was sprayed into a different substrates for 2 min, it passed through the fine nozzle has a diameter of 0.5 mm under compressed air pressure around 30 psi. The distance between the nozzle tip to the substrate was kept about 30 cm and moving with 60 RPM. The temperature and relative humidity were fixed about 125 °C and 40%, respectively. Afterwards, the coated substrates were placed in an oven for about 2 h at 150 °C (to evaporate methanol), resulting in a coating with a rough surface composed mainly network of low-surface-energy MTES material.

3. Results and discussion

3.1. Surface morphology and wettability of coatings

Fig. 1 (a–d) shows scanning electron microscopy (SEM) images of superhydrophobic coatings that are produced by sol–gel spray coating deposition onto different types of substrates. We coated metal substrates with hierarchical texture of MTES for its high stability against heat. From Fig. 1 (a), we can see clearly observing that hierarchical textures are formed on the germanium substrate, showing interesting marigold flower shapes with nano-scale swellings. Similarly, for other substrate like brass, steel, and copper, the sol tended to spray as fine drops and then collected into irregular textures with porous nature residues on the coating surface (Fig. 1b–c).

Cassie and Baxter have drawn Equation (1) to express the correlation among the CA of a water droplet on a plane surface (θ_s) and the CA on a hierarchical texture (θ_r) composed of a solid and air [28].