

Dip Coated Superhydrophobic and Anticorrosive Silica Coatings

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Abstract: The present paper reports a simple and low cost method for the fabrication of superhydrophobic coating surface on different metal substrates via sol-gel dip coating method at room temperature. The prepared substrates are characterized by Field-emission scanning electron microscopy (FE-SEM), Atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), water contact angle (WCA) measurements. Sol-gel dip coated substrates showed high water contact angle with value about $161 \pm 2^\circ$ and low sliding angles for deposited metal substrate. A chemical aging test is carried to study anticorrosive properties of prepared coatings.

Keywords: Superhydrophobicity, dip coating, contact angle, anticorrosive.

1. Introduction

Metals have great demand in the chemical and microelectronics industries due to their high thermal and electrical conductivities. A notable disadvantage in the use of metals is that they are easily corroded in aqueous atmospheres. Corrosion control is an important subject of increasing interest to the modern metal finishing industry. The development of coatings that provide the necessary protection of the metal surface is essential for its efficient use in these applications [1]. Surface modification of metallic substrates by organic or polymeric coatings is an essential approach for enhancing surface properties such as wear, oxidation, and corrosion. Various conventional techniques are utilized to deposit the desired materials onto the metallic substrate for achieving surface modifications with better protection for the substrate. Corrosion is a natural process that has troubled human beings ever since the use of metals. Hence, efforts to develop more efficient and environmentally compatible methods to prevent corrosion have been ongoing throughout this century [2]. In the past few decades, a great number of synthetic methods have developed to fabricate non-metallic surfaces with special wettability. The construction of special wettability on metallic substrates is a scientifically and technologically challenging target. Recently, in order to extend the applications of metals, a variety of metallic surfaces with special wettability has constructed by using different synthetic processes [3]. These metallic surfaces with special wettability exhibit some important applications such as anti-corrosion, oil-water separation, friction reduction, liquid transportation, and microfluidic materials. Until now, different

approaches are described in the literature for the fabrication of superhydrophobic metal surfaces. The use of conducting polymers as advanced coating materials for corrosion protection of oxidizable metals has become one of the most exciting new research fields in recent times [4–9]. Qu et al. have reported a novel mixed-solution system for the fabrication of the superhydrophobic surface on steel, copper alloy and titanium alloy by a chemical etching method [10]. Zheng et al. have fabricated inorganic-organic coatings by sol-gel method for corrosion protection [11]. The sol-gel coating on metals is relatively recent and has not sufficiently investigated, in spite of its potential technological interest. The basic concept of chemical conversion of metal surface is based on the deposition of a hydrophobic sol-gel barrier layer for surface protection and corrosion prevention [12].

Sol-gel derived coatings have been found to be useful for a number of applications mainly due to the simplicity of solution based processing and the synthesis flexibility, which can be used for forming a wide range of thin films and coatings by using dip, spin or spray methods [13]. In addition, the use of organically modified precursors provide unique opportunities to tailor the physical and chemical properties of the final materials. Due to the presence of an organic component, the organosilica coatings dry evenly and are uniform and crack-free as compared to pure silica coatings. While there has been significant research activity in the use of sol-gel coatings for corrosion protection [14–16]. In the present study we reported, the methyltrimethoxysilane based superhydrophobic silica coatings on different metal substrates for anticorrosion purpose with the simple dip coating method. The aim of this study is to test the capability of sol-gel coatings to improve corrosion resistance of the different metal substrates. It is found that the coatings are effective at preventing corrosion of copper, aluminium and bronze substrates. In addition, the reproducibility is very good and we can get the similar results in every experiment under the preparation conditions. Overall, the strategy presented herein may provide a generic approach for fabrication of protective coatings on different metallic surfaces.

2. Experimental

2.1. Materials

The chemicals used are methyltrimethoxysilane, (Sigma–Aldrich Chemie, Germany), methanol (Loba Chem Limited, Mumbai), and ammonia (NH₃, sp.gr.0.91, Qualigens Fine Chemicals, Mumbai). Polymethylmethacrylate (PMMA). Double distilled water is used for all the experiments. All reagents are used as received. Different metal substrates such as, copper, aluminium and bronze are taken for the deposition.

2.2. Preparation of Coating Surfaces

The aluminum, bronze and copper substrates are cleaned in order to get uniform deposition. Pieces of 1 cm × 5 cm are cut from above mentioned metal sheets and these are used as substrates. These substrates are mechanically polished using zero grade polish paper as an abrasive. This practice removed the grease and the native oxide layer from the surface of the metal plates.

2.3. Synthesis of Superhydrophobic Coatings

In the present investigation, our approach is to develop transparent anti-corrosive superhydrophobic coatings on a various metal substrates through the two-step sol-gel based simple dip coating method. Such coatings consist of a low energy material and dual scale surface roughness in a hierarchical manner. The preparation conditions of superhydrophobic silica coating are discussed in the following paragraph.

The methyltrimethoxysilane (MTMS) based organically modified alcosol is used for the deposition on a different metal substrates. A coating sol is prepared by keeping the molar ratio of MTMS: MeOH: H₂O constant at 1: 5.63: 1.58, respectively with PMMA 7 wt% and 0.5 M NH₄F as a catalyst for which we get maximum hydrophobicity. Single layer silica coatings are deposited on cleaned metal substrate at an

optimized lifting rate from 8 cm/min by using a dip coater. Further; these substrates are annealed at 150 °C for 3 h to remove residual solvent.

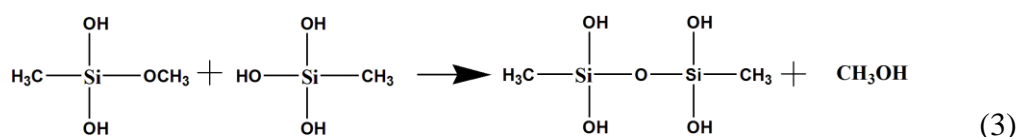
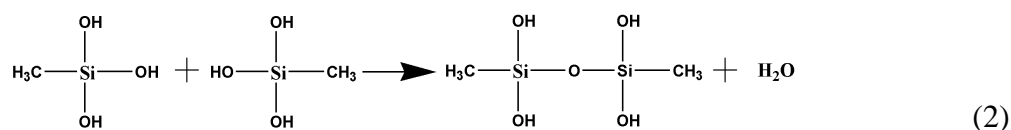
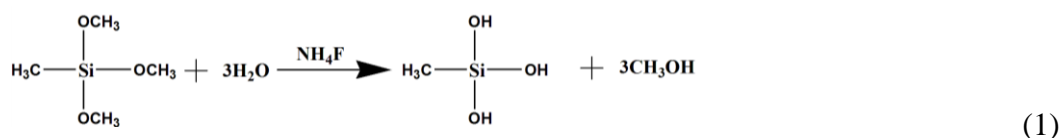
2.4. Methods of Characterization

The surface morphology of coating is examined by Field emission-Scanning electron microscopy (FE-SEM) (JEOL JSM- 7001F, Japan). The three-dimensional topo-graphic image is recorded using atomic force microscopy (AFM) (Nano scope E, Digital Instruments, USA) operated in contact mode. AFM image is obtained with 2 μm × 2 μm scan sizes at a scan rate of 10 Hz. Fourier Transform Infrared (FT-IR) spectrum are recorded with a Perkin-Elmer, model no. 783, USA in the range of 4000–500 cm⁻¹. The sessile drop method is used for measurements of contact angle by utilizing deionized water (>18 Mcm), the experiments are performed with help of goniometer (rame-hart Instrument Co., Model 501F1, USA). A drop size approximately equal to 0.5 μL of water is placed on the coating surfaces using a syringe. Static contact angle values are calculated from dynamic video files captured at 60 frames/s using software (Drop image advanced Version 2.1.3) provided by the manufacturer (rame-hart, USA). All samples are annealed using three stages programmed NeyTech Vulcan benchtop Muffle Furnace (VULCAN Model 3-550PD, USA).

3. Results and Discussion

3.1. Reaction Mechanism

The hydrolysis of methyltrimethoxysilane precursor and condensation reactions of water and methanol during polymerization silica network in the presence of PMMA and NH₄F are shown below [17],



Polymerization reaction between the hydrolyzed and partially hydrolysed MTMS molecules is as shown in the reaction (3). The addition of PMMA in the MTMS sol enhances the viscosity and helps to get adherent coatings on different substrates [17]. The surface –OH groups are replaced by the CH₃ groups of the PMMA in order to achieve the inherent superhydrophobicity as well as nanostructured silica network resulted on the substrate surface with release of two molecules of carbon dioxide, water and hydrogen atom. This reaction mechanism is responsible for the gelation.

3.2. Surface Morphological Studies

The two dimensional morphological studies of water repellent silica coatings have studied using FESEM micrographs as shown in Fig. 1 (a) to (c). Static contact angles of all substrates are above 150°. FESEM

images of a top view of the coatings on different substrate shows that the surface is microscopically rough, which has a porous morphology [18]. The morphology of the coatings involves both micro-nano scale hierarchical structures and methyl groups as revealed from FTIR analysis. Therefore, it can be expected to show superhydrophobicity. The water contact angle of coatings above 150° are indeed in the superhydrophobic range.

3.3. Atomic Force Microscopy

Fig. 2 (a, b and c) shows the three dimensional atomic force micrographs of the silica coatings on aluminium, bronze and copper respectively. Micrographs are recorded at $1 \times 1 \mu\text{m}^2$ planar in contact mode. The surface of the films has many dispersed islands that are distributed on the film surface. The root-mean-square (RMS) surface roughness of the substrates were analysed with AFM. The roughness for aluminium, copper and bronze metal substrates coated with silica coating are 10.67, 15.06 and $0.41 \mu\text{m}$, respectively. High surface roughness are observed for all films and value varies with different metal substrates. The thickness of coatings for different substrates was approximately similar as same silica sol used for all substrates. In addition, the agglomeration of silica particles did not observed visibly as seen from the photographs of substrates (Fig. 1). Therefore, a superhydrophobic silica coating can be applied on any shape of substrates using dip coating method.

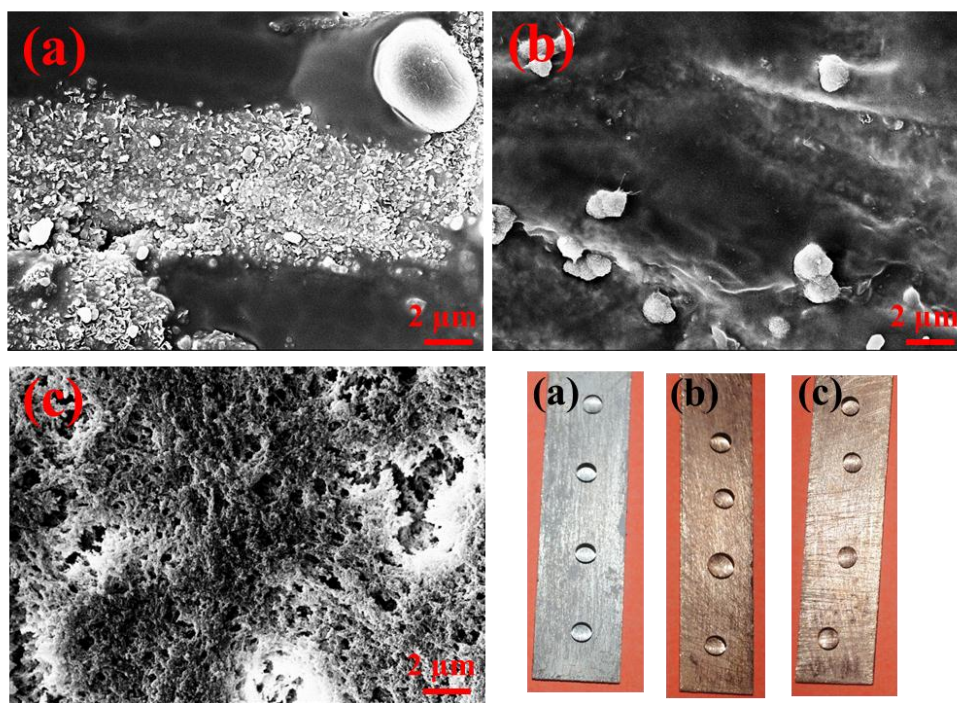


Fig. 1. FESEM image of the silica film prepared on (a) Aluminium substrate (b) Bronze substrate and (c) Copper substrate

3.4. Fourier Transforms Infrared Spectroscopy Studies

The chemical composition of the films deposited on aluminium, copper and bronze substrates were investigated by the FT-IR spectroscopy using the KBr method in transmission mode. Several characteristic absorption peaks were observed in the range 450 to 4000 cm^{-1} indicating the presence of methyl groups in the sample. The FTIR spectra of the silica films prepared with different metal substrates are shown in Fig. 3 (a-c), respectively.

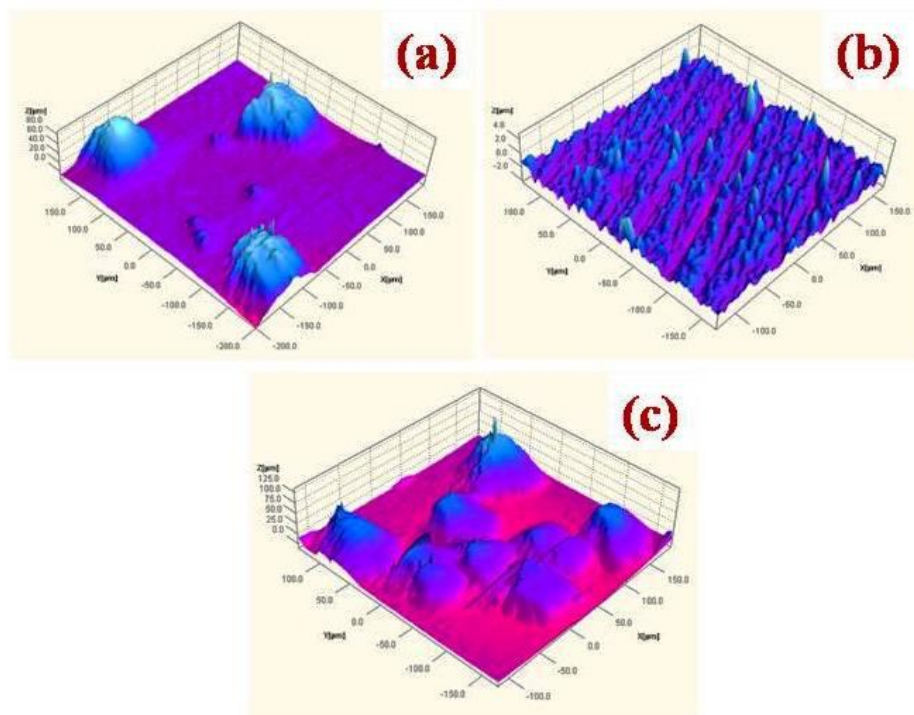


Fig. 2. AFM image of the silica film prepared on (a) Aluminium substrate (b) Bronze substrate (c) Copper substrate

The peak at 1122 cm^{-1} corresponds to the Si-O-Si asymmetric stretching vibration [19]. The presence of this peak confirms the formation of a network structure inside the film. The absorption bands observed at around 2950 cm^{-1} are due to stretching of C-H bonds, the peaks observed at 1274 , and 782 cm^{-1} are due to the Si-C bonds [20]. The broad absorption band at around 3400 cm^{-1} is due to the -OH groups [21]. The residual Si-OH groups are the main source of hydrophilic character. The intensity of the peak at 3400 cm^{-1} of -OH group is low as compare to the intensities of the C-H absorption peak at around 2950 cm^{-1} and Si-C absorption peak at around 782 cm^{-1} . The Si-OH band seen in the FT-IR spectra indicates that surface hydroxyl groups are still exist, even though the materials show the strong hydrophobic properties.

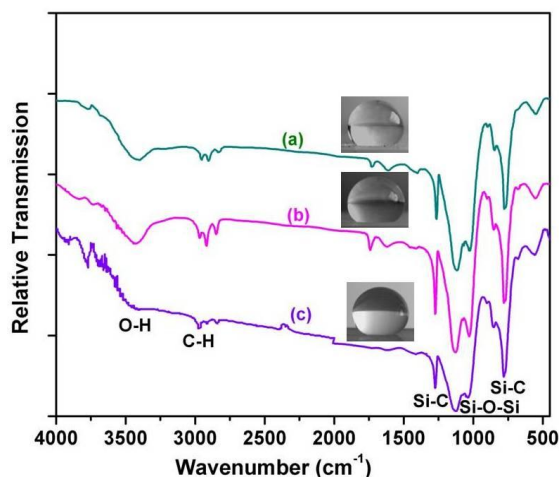


Fig. 3. FTIR spectra of silica coating on different metallic substrates (a) alluminium substrate, (b) bronze substrate and (c) copper substrate

3.5. Static and Dynamic Water Contact Angle Measurements

This composite surface has a higher contact angle because of the air/liquid interface and can result in superhydrophobicity. Thus, Cassie-Baxter state is preferred rather than Wenzel state due to very small hysteresis and excellent rolling behavior even at tilting angles of a few degrees. The surface wettability for film prepared on various metal substrates were observed by contact angle and sliding angle measurements before and after deposition, and a related contact angle and sliding angle are listed in a Tables 1 and 2. In addition, images of water droplet on coated samples were shown in Fig. 3, which confirms the superhydrophobic nature of prepared silica coatings.

Table 1. Comparisons of Contact Angle (CA) and Sliding Angle (SA) before and after Deposition on of a Various Metal Substrates with Water and After Exposure to Acid

Metal	Contact angle			Sliding angle	
	before deposition ($\theta \pm 2^\circ$)	after deposition ($\theta \pm 2^\circ$)	Contact angle after 100 h exposure in acid ($\theta \pm 2^\circ$)	before deposition ($\theta \pm 2^\circ$)	after deposition ($\theta \pm 2^\circ$)
Aluminium	69	164	151	36	7
Bronze	58	153	135	32	5
Copper	61	161	148	33	3

Table 2. Maximum Frictional Force Required to Slide Water Droplet on the Metal Substrates after Deposition

Metal	Sliding angle ($\theta \pm 2^\circ$)	Maximum frictional force f_{\max} (μN)
Aluminium	7	11.94
Bronze	5	8.54
Copper	3	5.12

3.6. Chemical Aging Test

The stability of the water contact angle over time is a very important factor for superhydrophobic surfaces, providing information about the long-time surface dynamics. Unfortunately, results from long-time stability measurements are seldom reported [22]. The anticorrosive performance of the sol-gel coating is tested by direct exposure of the coated metal substrates to corrosive media. The anticorrosive performance of the sol-gel coating was tested by direct exposure of the coated metal substrates in 50 % of HCl solution for 100 h. Interestingly, chemical aging test demonstrated that the superhydrophobic nature is maintained even though the deposited film was soaked for 100 h in 50% of HCl solution. This is expected as organically modified silica network is unreactive for the HCl acid. However, we found that the water contact angle decreased by 10° to 15° after 120 h of exposure to the acid environment.

4. Conclusions

The sol-gel process offers many potential avenues for the conservation of art objects. We have successfully

fabricated a anticorrosive, superhydrophobic silica coating on aluminium, bronze and copper substrates without any surface modification agent. We demonstrated that best on our approach, plain metal substrates can be easily altered into superhydrophobic metals stable with corrosive liquids. The selection of precursor, PMMA mixing and sol-gel composition yielded coatings found adhesive, water-repellent, and effective at preventing corrosion of coated metal substrates. With careful selection of the combination of starting alkoxides and appropriate synthesis conditions, such strategies open a new field of application for sol-gel technology.

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