



# Polystyrene assisted superhydrophobic silica coatings with surface protection and self-cleaning approach

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## ABSTRACT

Both surface morphology and surface energy of solid surface conclude its wettability, either in Wenzel's hydrophobic or Cassie–Baxter's superhydrophobic wetting state. The superhydrophobic silica coatings were prepared by spin deposition technique from a mixture of hydrophobically modified silica particles and polystyrene. To enhance the adherency of the coating on the substrate and also to improve the durability of the coating, polymer is especially utilized in the coating solution. The durability of the superhydrophobic coating was confirmed by resistency towards water jet impact. The consequence of number of spin deposited layers on the wettability of the coatings was precisely studied. The static and dynamic water contact angle of 158° and 9° were achieved on the coating surface. Freely rolling spherical water drops on the non-wettable solid surface are favourable for the self-cleaning effect and so the prepared superhydrophobic coatings revealed superior self-cleaning performance. An anti-corrosion performance of the superhydrophobic coating was also confirmed using electrochemical corrosion experiments in 3.5% NaCl solution with long immersion time.

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## 1. Introduction

In recent years, superhydrophobic coatings have aroused abundant interest both in fundamental research as well as industrial viewpoint due to their variety of applications in self-cleaning, anti-corrosion and anti-fouling coatings, microfluidic or biomedical devices, waterproof textiles, and in the printing and packaging industries [1–5]. In general, rough hierarchical solid surfaces with low surface energy would show superhydrophobic wetting properties. Depending on the wettability of the solid surface, a shape of water drop varies from concave (complete or partial wetting) to convex (complete non-wetting) shape. Water drops quickly begin to run off the superhydrophobic surface at very miniature disturbance due to its round shape possessing contact angle above 150°. Such low water adhesion originating from high contact angle

and small sliding angle is quite often observed on many biological plant and insects surfaces [6]. This low adhesion of water drop on the surface favours self-cleaning properties to the biological surfaces, where dirt particles adhered on the surface might be certainly removed by merely rolling water drops. In addition, the self-cleaning behaviour observed in nature can be mimicked, which can find potential industrial application for self-cleaning door and window glasses, windshields of automobiles, roadside mirrors, glassware, sport equipment's, solar panels, apparels and many [7–10].

Various efforts have been devoted to fabricate the superhydrophobic surfaces and optimize their structure, predominantly those based on sol-gel techniques to improve the water repellency and self-cleaning features [11]. Several inorganic nanosize particles, such as SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZnO have been utilized for regulating a material's surface roughness [12]. In general, silica based materials are ideal to form superhydrophobic coatings as its offering tunable refractive index and thickness with excellent adhesion to the base substrate. Silica coatings are advantageous to apply the homogeneous, stable and large-area coating on the solid sur-

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face of any type, shape and size with ease. Lavish scientific reports on superhydrophobic silica coatings on glass, papers, metals, wood, textile, meshes, and polymeric substrates are available [13,14]. The simple and conventional dip, spin, and spray coating methods are perfectly compatible with the sol–gel systems. In particular, the formation of superhydrophobic coatings on metal substrates has recently received high attention since it can be used as protective coatings [15]. In general, superhydrophobic coatings are known to be highly resistant to water absorption which is directly relevant to its protection against corrosion attack.

Several reports are available in the literature which specifies the improved durability of the nanocomposite coatings by appropriate addition of polymers in nanoparticles suspension or the other way [16–19]. In this study, we demonstrated a feasible strategy to develop superhydrophobic coatings with self-cleaning and anticorrosion features using modified silica particles in different concentrations with polystyrene. The significance of number of spin coated layers on the wetting characteristics of the coatings were studied in details. Further the self-cleaning property and stability of the superhydrophobic coatings was also discussed. In addition, the prepared superhydrophobic coating was applied on mild steel (MS) substrates in order to assess the corrosion protection performance using electrochemical impedance spectroscopic measurements in 3.5% NaCl solution with long immersion periods.

## 2. Experimental section

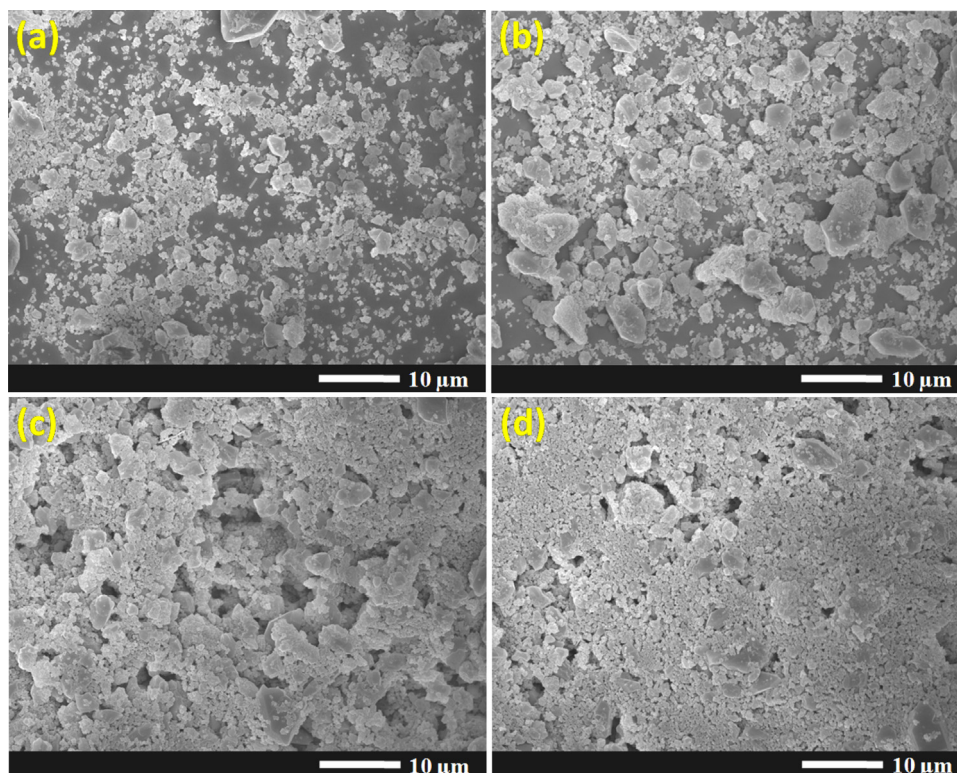
### 2.1. Materials

Silicon dioxide particles (~99%) with diameter in the range of 0.5–10  $\mu\text{m}$  (approx. 80% between 1 and 5  $\mu\text{m}$ ), Polystyrene (Mw ~192,000), Methyltrichlorosilane ( $\geq 97\%$ ), Tetrahydrofuran, Hexane (anhydrous, 95%) were purchased from Sigma Aldrich, USA. The elemental composition of MS was specified in wt% as 0.040C, 0.350 Mn, 0.022 P, 0.036 S and remaining Fe. These substrates (size

$\approx 1\text{ cm} \times 1.5\text{ cm}$  and 0.5 mm thick) were mechanically grounded using 320–2000 grit standard abrasive papers, washed with deionized (DI) water, followed by ultrasonic cleaning in acetone for 5 min and dried under atmosphere condition. Prior to each electrochemical measurements, MS substrates were utilized as designated and freshly used without any additional storage.

### 2.2. Preparation of coatings

Silica particles (4 g) were mixed in hexane (40 ml) and kept for ultrasonic bath for 30 min. Methyltrichlorosilane (3 ml) was added drop wise in above mixture and again kept for 3 h ultrasonication. The modified silica particles were dried and annealed at 150 °C for 6 h. The annealed silica particles were then grinded using mortar and pestle. The modified silica particles were mixed in THF with different concentrations of 10, 40 and 80 mg/ml and in each above prepared solution, 0.5 ml of polystyrene (20 mg/ml in THF) was added. These particle–polymer mixtures were ultrasonicated for 1 h before spin deposition. The glass substrates were cleaned by the same procedure defined in our previous article [20]. The glass substrates were spin coated with 1, 2, 3 and 5 spin coating layers from the above prepared solutions. The substrates were spin coated with 500 rpm for 5s, 1500 rpm for 15 s and 1000 rpm for 5s. Finally, all the coatings were annealed at 150 °C for 4 h. It is important to mention here that the coating prepared without PS polymer showed absolute no adherency towards glass substrate. For electrochemical corrosion measurements, the same procedure was adopted to coat on MS substrates. All the coatings prepared with 10, 40 and 80 mg/ml of modified silica particles and PS was denoted as SHC1, SHC2 and SHC3, respectively. Further, the thickness of the SHC was found by using an Elcometer instrument. The average thickness of SHC was found to be about 14–15  $\pm 0.2\ \mu\text{m}$ , respectively. In order to inspect the adhesion between the SHC and MS substrates, the ASTM D 3359 standard tape adhesion test was performed and the magnitude of the adhesion remaining (AR%) were found to be 95% with



**Fig. 1.** FE-SEM images of SHC2 Coatings with (a) one, (b) two, (c) three, and (d) five spin coating layers.

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