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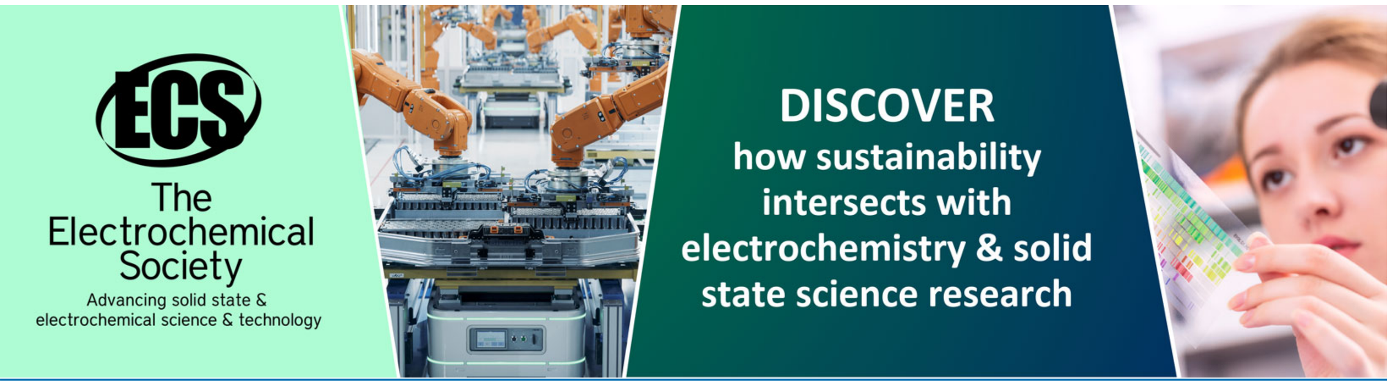

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Development and characterization of cobalt based nano-structured super hydrophobic coating

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Abstract. A super hydrophobic coating on the surface of glass substrate has been developed using chemical bath deposition (CBD) process. A water contact angle (WCA) greater than 150° has been achieved. Cobalt Chloride ($CoCl_2$) has been used as the main precursor to investigate optimum composition and high superhydrophobicity. The water droplet has been observed to slide with a sliding angle less than ~3°. This effect is particularly due to the surface morphology (roughness) and low surface energy that causes water droplet to form a large contact angle thus allowing the surface to show water-repellent properties. Deposition time is the primary parameter affecting the coating properties and a different WCA value has been observed by increasing time. Scanning Electron Microscopy (FE-SEM) images show the presence of a nano flower-like morphology that helps in imparting superhydrophobic behavior. Energy Dispersive X-ray Spectroscopy (EDX) indicate the coating to be composed of cobalt as the main constituent. Contact Angle Measurement confirms the contact angle value to be greater than 170°.

1. Introduction

Superhydrophobicity is defined as the state in which water shows a contact angle greater than 150° with the surface. Non-wetting surfaces having high contact and low sliding angles have received significant attention in recent years. Properties such as self-cleaning [1], corrosion resistance [2-3], resistance to frost formation and accumulation [4] and oleophobicity [5] have been studied. Naturally, plants such as lotus have been found to exhibit superhydrophobic behavior [6].

High surface roughness and low surface energy [7-9] are the requirements for a surface to be superhydrophobic. The surface roughness is provided by the morphology of the coating deposited on the surface while low surface energy is due to the attachment of certain molecules onto the tips of the surface. Cassie/Baxter model can be used to determine the water contact angle (WCA) with the surface [9]. This is given by (1) as:

$$\cos\theta_c = \varphi_s(\cos\theta_e) + (1 - \varphi_s)\cos\theta_x \qquad (1)$$

Where, θ_c is the WCA, φ_s (less than 1) is the fraction of area covered by solid at the top of the surface, θ_e represents the WCA with the solid, $(1 - \varphi_s)$ represents the fraction of area covered by air gaps at the surface and θ_x shows the WCA with the entrapped air (within the surface grooves).θ_x is normally taken to be 180° due to which the contact angle increases. In this case, the water drop remains in contact with the tops of the surface leading to the flow of air beneath.

To develop superhydrophobic coatings, both bottom up (sol-gel [10], layer by layer deposition [11], chemical vapor deposition [12]) and top down (plasma treatment of surfaces [13], templating [14], photolithography [15]) approaches can be used.

Cobalt based (cobalt hydroxide and cobalt oxide) coatings have been found to exhibit water-repellent properties. Saravani et al. [10] used cobalt chloride as the precursor for producing a superhydrophobic surface based on cobalt oxide (Co_3O_4) nanoparticles and reported a WCA of 153.45° along with a sliding angle of 2.5°.In a comparative study, Ho et al. [16] deposited layered cobalt carbonate hydroxide on a substrate using different precursors. The cobalt oxide films synthesized from these precursor salts were in shape of straight acicular nanorods, bending acicular nanorods, nanosheets, and net-shaped nanosheets. Chemical bath deposition (CBD) is an economical route for depositing oxide based coatings [17].A WCA of 178° has been reported by Zhou et al. [18] using CBD by developing cobalt hydroxide based coating. Joo et al. [19] synthesized cobalt oxide based coating with a thickness between 437-843nm.

In this study, cobalt based coatings have been developed by CBD using cobalt chloride as the main precursor. Moreover, cobalt nitrate and cobalt sulfate salts have also been used as precursors to see the difference in surface morphology of the coating. Stearic acid treatment has been used to impart superhydrophobic behavior. Deposition time has been varied to see the effect on WCA values.

2. Experimental

2.1 Materials

Cobalt chloride ($CoCl_2$), cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) and cobalt sulfate heptahydrate ($CoSO_4.7H_2O$) were procured from Sigma-Aldrich. Ethanol was procured from Scharlau and stearic acid was procured from BDH.

2.2 Development of the superhydrophobic coating

Cobalt based coatings were developed on a glass slide using CBD. The glass slide was first cleaned by rinsing with ethanol and drying in air. The solution for CBD was prepared by mixing known amount of $CoCl_2$salt (0.1 mol/dm^3) and CH_4N_2O(20 g) in 100 ml water. $CoSO_4.7H_2O$ and $Co(NO_3)_2.6H_2O$were also used as precursors. The solution was transferred to a sealed glass bottle (glass slide was immersed in the solution)and placed on a hot plate at 60°C for varying amount of time. The substrate was then removed, rinsed with ethanol and dried in air at room temperature. The dried coated glass slide was then immersed in an ethanolic solution of stearic acid ($C_{18}H_{36}O_2$) for 10 min and dried in air.

2.3 SEM analysis

The surface morphology of the coating was observed using a field emission scanning electron microscope (FEG-SEM).

2.4 EDX analysis

The composition of the coating was determined using energy dispersive X-ray spectroscopy (EDX) with a FEG-SEM equipment.

2.5 Contact angle measurements

The water contact angle with the surface was measured by sessile drop mode of Drop Shape Analyzer (KRUSS DSA-30).

3. Results and discussion

CBD process is highly favorable due to its low temperature and ease of operation. It is a two-step process involving nucleation and growth of the nuclei. The coating developed on glass substrate by chemical bath system (precursor plus activating agent i.e. urea) does not show superhydrophobic behavior unless further treated. The nuclei grow in the form of a flower composed of very fine nanopinswhen precursor is $CoCl_2$ as shown in Figure 1 in comparison to other precursor salts.

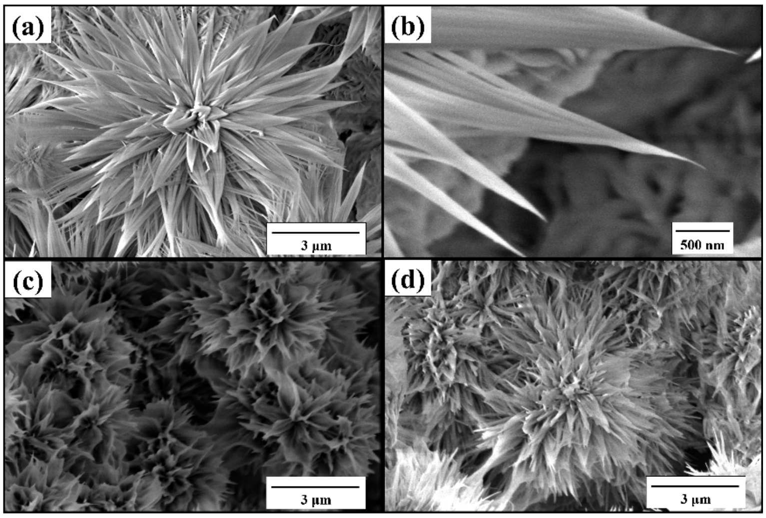

Figure 1. SEM image of Co based coating using (a), (b) $CoCl_2$, (c) $CoSO_4.7H_2O$ and (d) $Co(NO_3)_2.6H_2O$ precursor.

The WCA at this stage depends on the deposition time. A deposition time as high as 22 h causes the water droplet to spread leading to a contact angle value ~0°. At lower deposition times, the drop shows hydrophilic to hydrophobic behavior but tends to spread continuously making contact angle measurements extremely difficult as compared to an uncoated glass surface that exhibits hydrophilicity (WCA equal to ~55°) as shown in Figure 2.

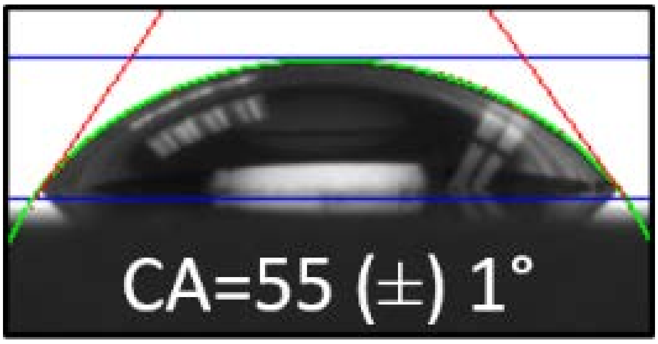

Figure 2. Water contact angle on an uncoated glass slide is ~55°

At this stage, one requirement of superhydrophobicity i.e. surface roughness is fulfilled. For satisfying the second condition, necessary treatment is required to ensure the lowering of surface energy. Treating the surface with ethanolic solution of stearic acid makes the coating superhydrophobic. Stearic acid molecule like all the fatty acid molecules is made up of two parts: a polar head which is hydrophilic in nature and a non-polar tail that has a hydrophobic nature. These molecules arrange themselves in such a way that the hydrophilic head attaches itself onto the surface features (nanopins in this case) while the hydrophobic tail is aligned away from the surface. These non-polar tails effectively decrease the surface energy so that when a water droplet comes into contact with the surface it forms a sphere and a high WCA is obtained.

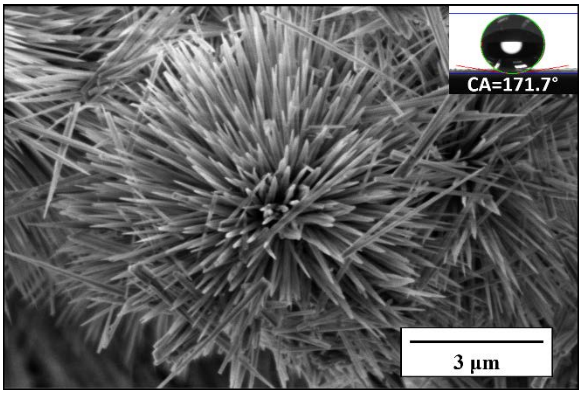

Figure 3. SEM image of Co based superhydrophobic coating using 0.1 M $CoCl_2$ at 22 h

Figure 3 shows the morphology of a superhydrophobic coating on glass (the pins become finer – rod like at the bottom and very fine at the tip). The fineness of the coating features is due the stearic acid treatment that deposits itself as a monolayer over the pins thus lowering the surface energy and allowing the surface to show water-repellent properties. A WCA value of 171.7° has been achieved at a deposition time of 22 h using 0.1 mol/dm^3 $CoCl_2$ as precursor. The water drop tends to roll off the surface even at very slight tilting of the glass slide. This indicates the sliding angle to be less than ~3°. The EDX (area scan) results indicate the coating to be composed of cobalt and oxygen as the main constituents with cobalt having the highest percentage (80 wt% and 52.93 at%) as shown in Figure 4. Oxygen also has a relatively higher proportion because of the stearic acid molecule that is rich in oxygen. Chlorine is also observed in the EDX scan that is indicative of the precursor ($CoCl_2$).

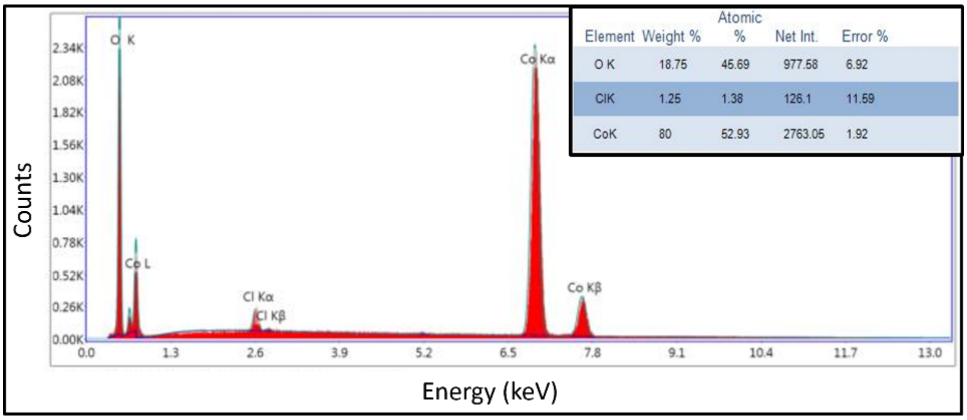

Figure 4. EDX scan indicating the relative proportions of the constituents in the coating

Deposition time is an important parameter that affects the coating properties. The WCA values tend to increase as the deposition time is increased and depends on the surface morphology (see Figure 5). This is particularly due to the increase in surface roughness i.e. formation of greater number of pins with time. A coating developed at 6 h has very few pins and the dominant morphology is bead type (interconnected flakes) but the coating shows superhydrophobic behavior with a WCA of 164.2°. On increasing the deposition time, pins begin to form and grow in the form of a flower-like arrangement. At 8 h, the coating is composed of maximum number of pins rather than beads but these pins appear to be in the initial stages of growth. Further increase in deposition time leads to further growth of the pins thus leading to an increase in contact angle values. The WCA does not increase very sharply with time as only a little increase in values is observed. Superhydrophobicity has been observed at a time as less as 6 h and the sliding angle in all cases was observed to be the same i.e. < ~3°. Increase in deposition time also tends to improve adhesion of the coating as observed by finger nail test. Figure 5 shows the effect of increase in deposition time on coating (stearic acid treated) morphology.

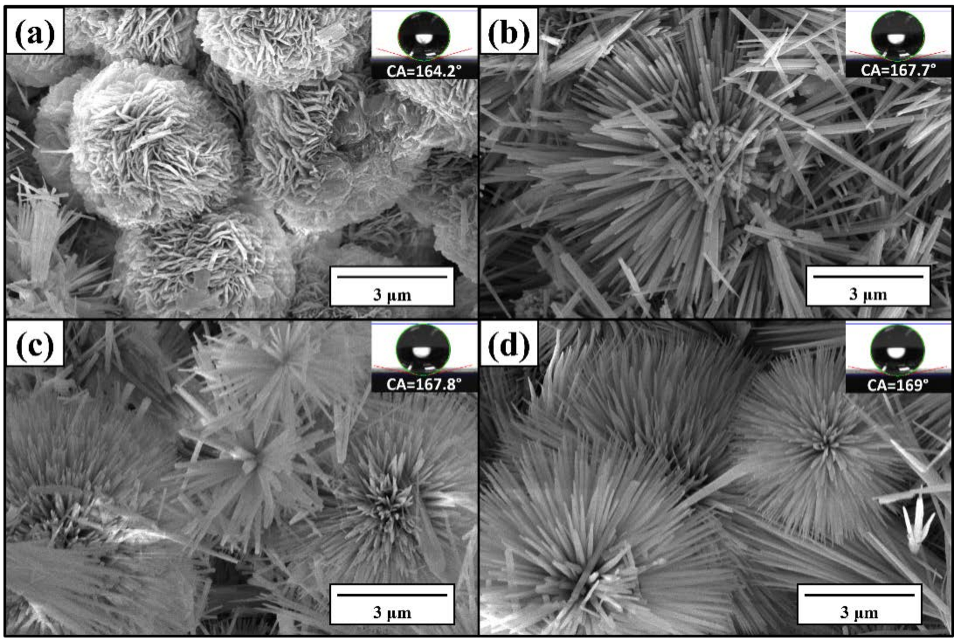

Figure 5. Evolution of superhydrophobic coating morphology with deposition time; (a) 6 h, (b) 8 h, (c) 10 h and (d) 12 h (insets show the images of water droplet on respective glass slide)

4. Conclusions
Superhydrophobic cobalt based coatings on glass exhibited a very fine nanopin flower-like morphology. A water contact angle of 171.7° was successfully achieved by the application of stearic acid. Stearic acid makes the pins very fine at the tip with rod like features at the bottom. The water droplet tends to roll off the surface at a sliding angle < ~3°. Increasing the deposition time tends to increase the contact angle due to increase in surface roughness by the formation of nanopins and their growth. EDX analysis confirms the coating to be composed of cobalt as the main constituent.

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