Modified Zinc Oxide Nanoparticles for Corrosion Resistance Applications

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Summary: Atmospheric corrosion is a big threat to the steel structures. This is because it compromises its structural integrity, aesthetic aspects and overall efficiency. An attempt has been made to counteract this through surface engineering of substrates including glass and steel by using modified zinc oxide nanoparticles to increase hydrophobicity. The synthesis of zinc oxide nanoparticles is carried out by using sol-gel method, thereafter these particles were modified by using stearic acid; a fatty acid. The zinc oxide nanoparticles were characterized by using X-ray diffraction analysis (XRD) which confirms the presence of hexagonal wurtzite structure. Moreover, the Scanning Electron microscopy (SEM) reveals the hexagonal wurtzite morphology of as prepared nanoparticles. Fourier transform infrared spectroscopy (FTIR) confirms the grafting of stearic acid on the surface of ZnO in bidentate form. The water Contact Angle obtained by using sessile drop method gives a statistical value of 140° which is of great interest due to higher water repellency and lower surface contact area. Finally, corrosion test was carried out on the coated steel substrate by means of conventional corrosion testing technique and it is observed that the coated sample decays three times slower than that of its bare steel counterpart.

Keywords: Hydrophobicity, Contact angle, Corrosion, ZnO nanoparticles, Self-cleaning, Stearic acid.

Introduction

Zinc oxide nanoparticles have excellent antibacterial, anti-corrosive [1], anti-fungal and UV resistant properties. Zinc oxide nanostructures are investigated for their antimicrobial effect against multiple foodborne pathogens and food contaminants [2].

Zinc oxide can be found in one-dimension (1D), two-dimension (2D), and three-dimension (3D) structures [3]. 1D structure has the most significance in the overall categories including Nano rods, Nano strips, Nano ring and Nano spring, Nano helixes, Nano needles, Nano belts, Nano wires, Nano tubes and Nano brushes [4]. Zinc oxide is further acquired in 2D structures, for instance Nano pellets and Nano sheets [5]. The domain of 3D structures of Zinc oxide includes snowflakes, coniferous urchin-like bloom and dandelion [6]. It gives the most extreme varieties in the form of different morphologies. The decent variety of structures of Nano-size implies that Zinc oxide have the capacity to be grouped among imaginative materials by methods for potential applications in most of the fields of Nano innovation [7, 8].

The coating prepared by modifying the surfaces of Zinc oxide nanostructures has wide range of applications from biomaterials [9] and industrial area to corrosion resistant application [10-12]. The surface modification results in reduction of agglomeration of nanoparticles in sol gel matrix [13]. The prepared modified coating is expected to have high degree of hydrophobicity with water contact angle greater than 120 degrees which is an excellent approach for repelling atmospheric contaminants and avoiding corrosion on the substrate [14-16]. Coatings have excellent corrosion resistance [1, 12] and very good U.V. resistance and mechanical properties[17] that make it suitable for the cooling towers, anti-icing coating [18] on automobile & aircraft bodies, de-frost coating on power pipelines, anti-corrosion coating on construction material and anti-fouling coating on bio-material [2, 19] The surface that resist water retention is said to be hydrophobic [9] and if the water droplet on the coated substrate attains almost spherical shape and resist attraction on the substrate might have the static water contact angle greater than 120 degree with the sliding angle no more than 10 degrees is hydrophobic in nature [18, 20]. There are different methods to achieve these conditions which include physical operations [11, 18] plasma treatment [18], template method [21], chemical deposition [22], hydrothermal technique [23], layer by layer assembly coating [9] and sol-gel formation [19, 22, 24]. The hydrophobic coatings with a static Water Contact Angle (WCA) > 120◦ is prepared by modifying ZnO nanoparticles with fatty acids [19, 25, 26]. The synthesis of Zinc oxide nanoparticles was carried out by sol-gel method [19, 23, 27]. X-ray diffraction (XRD) study shows that the ZnO prepared by sol gel

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method has hexagonal wurtzite structure [14]. Scanning electron microscopy (SEM) shows the morphology of the prepared particles and the modified coatings exhibiting nanoparticles. In Fourier transformed infrared analysis (FTIR), the spectrum shows that the stearic acid ion coordinates with ZnO in the bidentate form which confirms the presence of zinc stearate *i.e*. a strongly hydrophobic compound [26, 28, 29]. The hydrophobicity of the sample is observed by measuring static water contact angle [9, 26]. The corrosion behavior of the coated sample is examined by the analytical corrosion testing method *i.e*. weight gain/ loss method.

Experimental

Materials for the synthesis

The synthesis of ZnO nanoparticles is carried out by sol gel technique. The whole procedure involves the use of Zinc Acetate Dihydrate (Zn $(CH_3COO)_2.2H_2O$) having purity of 99%, Sodium hydroxide (NaOH) having purity greater than 98%, alcohol *i.e*. Ethanol (CH_2COOH), fatty acid *i.e*. stearic acid ($2CH_3(CH_2)_{16}COOH$) and distilled Water. Zinc Acetate Dihydrate is used as a precursor with an alcoholic reagent *i.e*. Ethanol. The solvent medium is Distilled water while stearic acid is used for the modification of nanoparticles.

Synthesis of ZnO nanoparticles

The synthesis of ZnO Nano particles is carried out using sol-gel route. 4g of zinc acetate dihydrate is dissolved in 30 ml distilled water by stirring on a magnetic stirrer for 10 minutes. 16g of NaOH is dissolved in 20 ml distilled water separately on the magnetic stirrer for 10 minutes. Both the solutions are then mixed and stirred for 10 minutes to homogenize. Now the as prepared solution is titrated with ethanol until white precipitates are formed. As the solution becomes opaque, it confirms the formation of ZnO nanoparticles. The particles are then separated by means of filtration. The filtered particles are washed with distilled water to remove contaminants. Finally, the nanoparticles are dried in an oven at 80°C for 1 h and these dried particles are then calcined at 500°C in a furnace for 2 hs.

$(Zn\ (CH_3COO)_2.2H_2O) + 2NaOH \rightarrow ZnO + 2NaCH_3COO + H_2O$ ---- eq (1)

Modification of synthesized ZnO nanoparticles with Stearic acid

0.2g of zinc oxide nanoparticles that are synthesized above are suspended in 10 ml of ethanol and ultrasonicated for 15 min. 0.05g Stearic acid is dissolved in 15 ml ethanol and stirred on the magnetic stirrer for 15 min. The stearic acid solution is then mixed with the ZnO colloid. This mixed solution is stirred on the hot plate at 60° C for about 1 h. The prepared solution is aged for about 2 to 3 hs. Afterwards, the samples are coated by simple and effective dip coating technique. The sample is manually dipped three times in the prepared coating so that homogenous spreading and thickness is achieved. Then the samples are soaked in an oven at 80° C for 1 h to remove excess ethanol. No binder is added, the adhesion takes place through surface roughness.

$ZnO + 2CH_3(CH_2)_{16}COOH \rightarrow Zn\ [CH_3(CH_2)_{16}COO]_2 + H_2O$ ---- eq (2)

The thickness of the coating on substrate is around 12-15 micron after three dips. As the number of dips of the substrate in the coating increases the coating thickness increases but for a sound and homogenous coating, three dips are enough.

Testing and characterization

The as prepared coating is expected to have higher degree of hydrophobicity that will ultimately reduce the chances of corrosion due to water retention on the surface of steel. The water static contact angle on the surface of the coated substrate was measured by the sessile drop method at several positions on each sample using similar droplets of water. The synthesized ZnO via effective sol gel route for the synthesis of nanoparticles were characterized by X-ray diffraction analysis (XRD) and the crystalline size is calculated by using Debye Sherer equation. The particles ranging in the nanoscale are modified with the help of organic ligands that are fatty acids with long chain of carbon whose polar end has greater ability to remain undissolved in water. Fourier transform infrared (FTIR) spectrum was generated to characterize the modified particles and to study the coordination of zinc oxide and fatty acid. Morphology of the as-prepared zinc oxide nanostructure and the coated surfaces were observed by scanning electron micrographs (SEM). The corrosion rate determination of the sample is carried out by the conventional method *i.e*. weight gain/loss method [2, 19, 27].

Results and Discussion

X-ray diffraction (XRD)

XRD analysis determined the phases present in powder. XRD result as shows in Fig.3 below is the resulting pattern of ZnO powder synthesized by sol gel technique. The graph results in various profiles of peak and diffraction angle 2θ, which shows the diffraction of ZnO powder using Zinc Acetate dihydrate as a precursor. The XRD pattern of the powder was observed in the fraction angle range 20° to 80°. The figure shows dominant peaks of ZnO, which indicate that the synthesized powder is crystalline in nature. The synthesized ZnO powder showed a pattern with single phase in clear diffraction peaks. In our case all the diffraction peaks at angles (2θ) of 31.78° from planes (100), 34.48° from planes (002) , 36.3° from planes (101), 47.5° from planes (102), 56.67° from planes (110), 62.82° from planes (103) and 67.98° from planes (112) of the hexagonal wurtzite zinc oxide structure. The synthesized ZnO Nano-powder is the compound of Zinc Oxide with scoring 87%. [27, 30]

Fig.1: The image of calcined ZnO powder.

Fig. 2: The coating prepared by modifying ZnO particles with Stearic acid.

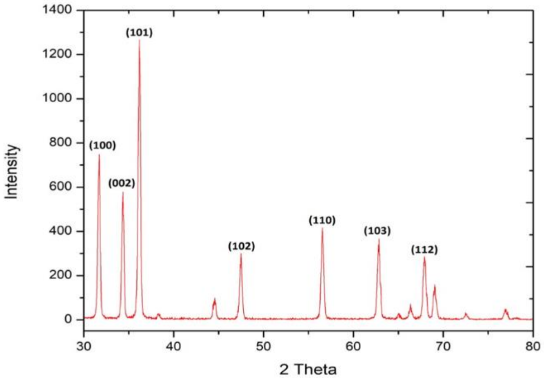


Fig 3: Shows the intensity vs 2 Theta plot of synthesized ZnO powder.

The crystalline size of as prepared Zinc oxide particles was calculated by Scherrer equation *i.e,*

D=Kλ/ (β cos θ) …………………… (eq 3)

where,

•D is the average crystallite size, which can be smaller or equal to the grain size
•K is a dimensionless shape factor, approximately unity
•λ is the wavelength of the X-ray
•β is the full wave at half of the maximum intensity (FWHM)
•θ is the diffraction angle

The value obtained by the powder diffraction are as follows,

K= 0.9, λ=1.54 A , β=0.33 , 2θ= 36.29

In order to calculate the crystalline size of ZnO above values are put in Debye-Scherrer equation.

The crystalline size obtained is 43.16 nm.

Fourier-Transform Infrared Spectroscopy

Fourier-Transform Infrared (FTIR) spectroscopy generates the infrared spectrum of absorption or emission over a wide spectral range. The deposition of fatty acid layer by collaboration of the carboxylate group with ZnO crystal on the surface was investigated by FTIR spectroscopy. FTIR is used in this research only to confirm the bond arrangements of stearate functional groups on ZnO crystalline material. Fig 4 represents the FTIR spectrum of ZnO with stearic acid hydrophobic coatings. Absorption band related to the -CH stretching mode peaks in the ranges of 2850 and 2910 cm^{-1} approximately. The untreated fatty acid was represented by the peak at 1700 cm^{-1}. The bands belonging to the COO- symmetric and asymmetric stretch can be showcased at about the range of 1539 and 1460 cm^{-1} approximately. Similarly, the stearate ion coordination with Zn=2 in bidentate form can also be confirmed due to the delta v (vas-vs) of RCOO-. In this way, Zn species are bonded with fatty acids by leaving their non polar tails reacting with air. The ZnO peak can be observed almost at 420 cm^{-1}[31].

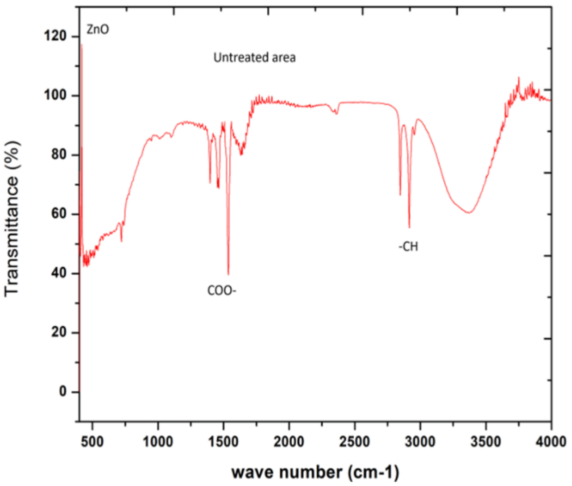


Fig. 4: The FTIR spectrum of ZnO modified with Stearic acid.

Scanning Electron Micrographs

SEM could be utilized for countless applications, commonly for morphological evolutions [31]. The SEM analysis is used to find out the morphology of the as prepared synthesized ZnO particles and the particles modified with stearic acid.

SEM micrographs of synthesized ZnO powder

The SEM analysis of the synthesized ZnO particles represents the zero-dimensional morphology of particles. The particles are seen to be agglomerated due to a huge extent that causes the joining and combining of particles into a lump resulting in the formation of porous structure like cluster. These clusters are shown in different sizes ranging from approximately 10 microns to maximum 200 microns.

SEM micrographs of modified ZnO particles

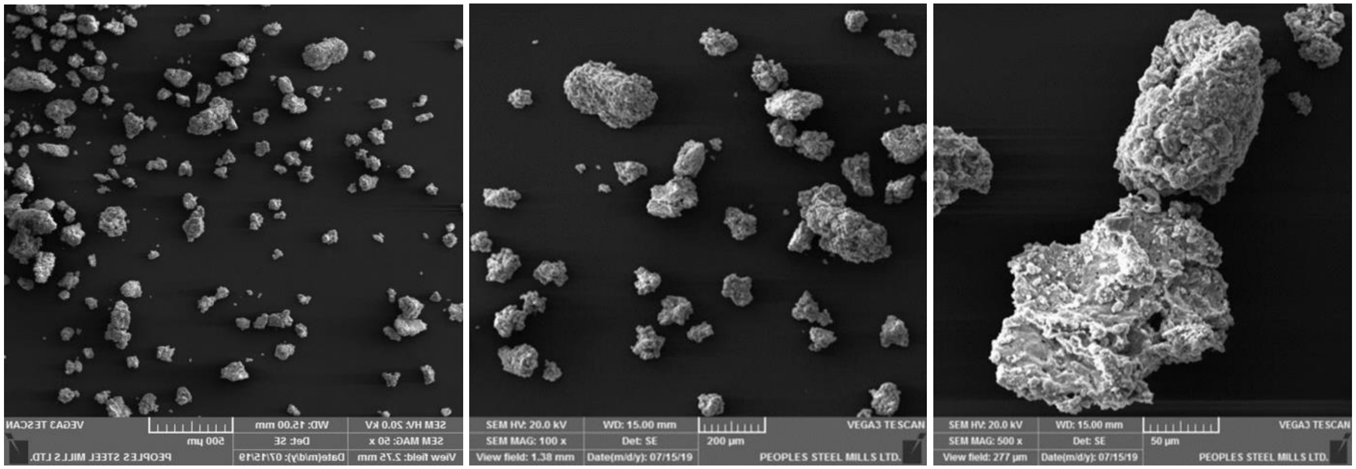
The modification of the synthesized ZnO with the stearic acid is the surface treating method of particles that would form a bidentate structure with the ZnO resulting in deagglomeration. The modification would result in the stearic acid cloud formation around each ZnO particle that will modify the surface ultimately increasing the hydrophobicity. The cloud can be seen in the SEM result images mentioned in previous chapter. The cloud formed is magnified at higher magnifications and the size of the cloud is found to be less than 2 microns.

Contact Angle

The static Water Contact Angle was analyzed by Sessile Drop observations. After coating the samples, water drop is placed on the surface of the sample using a precise syringe. A high-quality picture is taken from any side of the sample and the angle is measured by feeding the picture in AutoCAD software. Plenty of coated substrates were prepared by varying quantities of ZnO from 0.1g to 0.2g. Each substrate is analyzed by the similar method. The greatest static contact angle measured is 141.8 degrees on the substrate coated with 0.06g stearic acid modified with 0.2g ZnO.

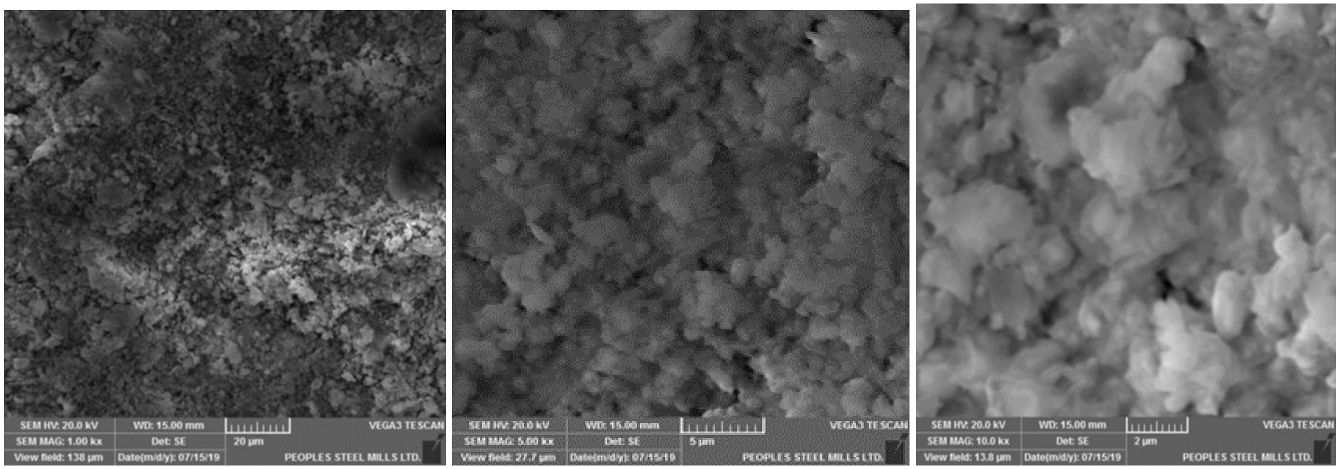
Furthermore, the relationship in Fig 11 illustrates that the hydrophobicity of the coating decrease with the increase in stearic acid concentration up to an extent. On the contrary, when we further increase the mass of ZnO from 0.2g, the hydrophobicity of the coating does not increase because the stearic acid becomes saturated and the excess ZnO does not form any bond with Stearic acid and remains untreated.

Additionally, stearic acid also contains two free hydroxyl groups which are hydrophilic in nature and can be used with ZnO nanoparticles to synthesize hydrophilic coatings which can attract water and prevent the substrate from corrosion. But to produce such coating, we must synthesize ZnO nanoparticles which are hydrophilic in nature and can only attract water. Although, it is a good approach to protect the steel but even a very small wear and tear can cause water to enter and ultimately corrode the steel.



(a) (b) (c)

Fig. 5: Shows the SEM micrograph of synthesized ZnO powder at 20 kV with the magnification of (a)50x, (b)100x, (c)500x.



(a) (b) (c)

Fig. 6: The SEM analysis of the ZnO particles modified with Stearic acid at 20 kV with the magnification of (a) 1000x, (b) 5,000x (c) 10,000x.

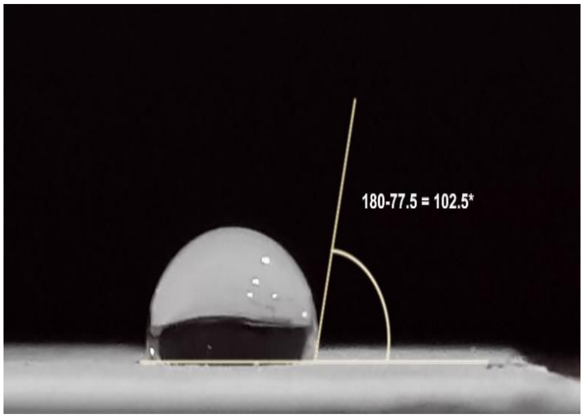


Fig 7: The Static Water Contact Angle on the coated substrate by 0.1g zinc oxide nanoparticles modified with 0.06g stearic acid.

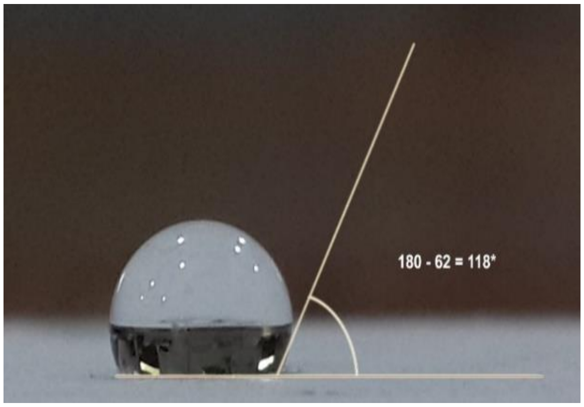


Fig. 8: The Static Water Contact Angle on the coated substrate by 0.12g zinc oxide nanoparticles modified with 0.06g stearic acid.

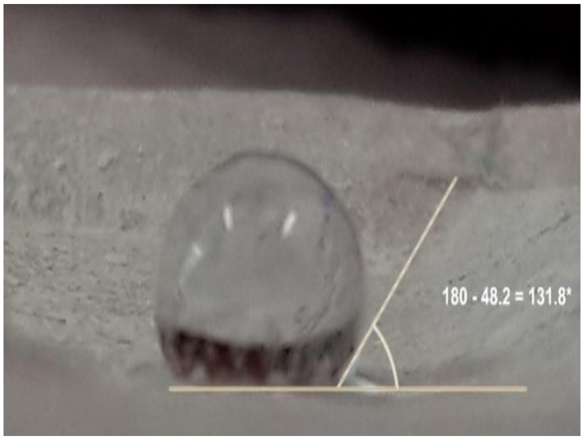


Fig 9: The Static Water Contact Angle on the coated substrate by 0.14g zinc oxide nanoparticles modified with 0.06g stearic acid.

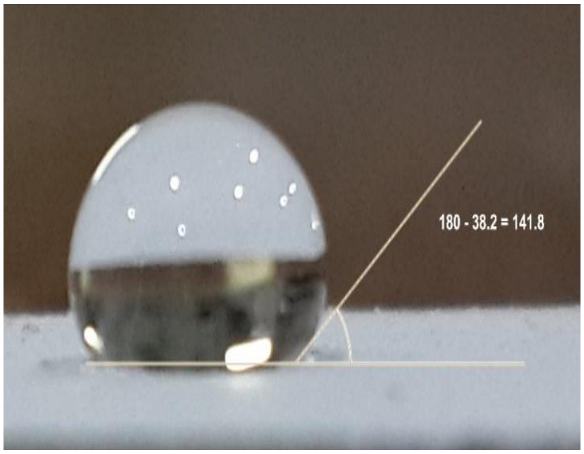


Fig. 10: The Static Water Contact Angle on the coated substrate by 0.2g zinc oxide nanoparticles modified with 0.06g stearic acid.

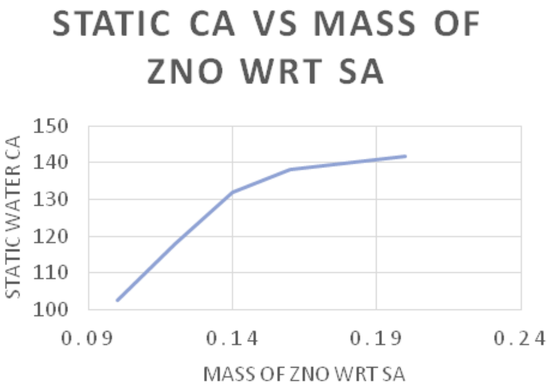


Fig 11: The relationship between static water contact angle and the concentration of Stearic acid.

Corrosion Test

The corrosion rate of the sample is obtained by the easy and effective conventional technique *i.e.* Weight loss method to obtain corrosion rate. In this method the sample of area 1 cm2 was prepared mounting the sample then grinded on emery paper of different roughness. The grinded sample is then polished on the polishing paper with the polishing medium of 1 micron and 0.5-micron colloidal alumina. The sample is then ultrasonicated in ethanol for about 30 minutes. The sample is then weighed. After weighing it is suspended in the prepared solution of 3.5% NaCl and Water for about 20 days. After the exposure time the sample is again weighed and the change in weight before and after suspension is calculated either in terms of weight loss or gain. By using the weight loss/gain with time, corrosion rate of the specimen can be calculated by the expression as follows,

CR = 87.6x(W/DAT) ………………. (eq 4)

where,
CR = Corrosion rate in mm/year
W= Weight loss of sample in milligrams
D= Density of sample in grams/cm^3
A= Initial Surface area of the sample in cm^2
T= Time in h

To observe the corrosion behavior of the coated sample, two samples are prepared, one is bare and the other is coated. Both are suspended in the same environment and the medium *i.e.* 3.5% NaCl solution in water. Weight loss is calculated, and the corrosion rate is measured.

The corrosion rate of bare steel is found to be 3.84 mpy while the corrosion rate for coated sample is found to be 1 mpy.

The corrosion rate of the bare sample is approximately 4 mpy while the coated sample has the corrosion rate of 1 mpy. A decrease in corrosion rate is observed as the coated sample degrade approximately three times slower than that of the bare sample.

Conclusions

A simple and facile technique to create surfaces that are superhydrophobic in nature was shown by utilizing ZnO nanoparticles altered with stearic acid to work as a corrosion inhibitor. The Powder X-ray diffraction analysis results affirm that the nano powder displays the hexagonal wurtzite structure. The FTIR spectrum confirms the bond arrangements of stearate functional groups on ZnO crystalline material in bidentate form. SEM images of unmodified nanoparticles shows agglomeration and cluster formation however, the modified particles are deagglomerated showing a cloud formation around zinc oxide nanoparticles. The static water contact angle of 140 degree proves to be an excellent approach in preventing corrosion of steel. The modified surface indicates increased roughness accompanied with lower surface energy as compared to the unmodified surface eventually increasing the hydrophobic and self-cleaning properties of coating. The corrosion test indicates that the life of coated steel increases 3 times in a 3.5% NaCl solution.

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