



Smart Superhydrophobic Coating for Corrosion Protection

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ABSTRACT

The smart superhydrophobic coating was developed via nanocomposite approach using nanocomposite which is zinc oxide (ZnO₂) / epoxy with the simplest and inexpensive method involving simple equipment that convey superhydrophobicity properties which is hierarchical rough structures. However, most of the studies related to the fabrication of superhydrophobic coating are both including complex fabrication steps and multitudinous treatment steps including pre/post-treatment to develop superhydrophobicity. The physicochemical properties of the coating were studied in terms of wetting, morphological and structural bonding properties via FESEM, EDS and FTIR. The smart superhydrophobic coating exhibited excellent water adhesion, water repellence and self-cleaning property with WCA = 166.60° and SLA = 5° respectively. The corrosion performance of coating was investigated through salt spray condition, through visual inspection and study of wetting properties for 20 days of exposure times with ASTM B117 standard testing, 3.5 % NaCl solution. The WCA was observed and recorded to make sure the coating maintaining its superhydrophobicity even after being exposed harsh environment. The resulted coating function effectively as corrosion protection and perform a self-cleaning coating which also helps in reducing maintenance and corrosion-related costs.

1. Introduction

Metals are important construction materials in today's world, with steel appearing in almost every bridge, building and vehicle constricted. As a result, corrosion protection of metals has become a vital issue to ensuring the structural and vehicles safety as well as to a significant part, for economic reasons. In particular, improving the lifetime of steel in the environment has become a key issue due to its broad applications [1]. Conventionally, corrosion protection for metals has been achieved by the use of chemical or physical means, such as coating and cathodic protection. The use of coatings is the most widely used technique since it can provide protection against general environmental conditions and greatly improve the lifetime of structures through reduced maintenance efforts. In 2013, corrosion costs in the United States were estimated to be around 2.7% of (gross domestic product) GDP and now, corrosion costs in all industrialized countries range from 1% to 5% of GDP.

Superhydrophobicity is a widespread natural phenomenon that has been extensively investigated and researched for applications in a variety of fields for decades. Surface coating techniques, in

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particular, have piqued the curiosity of both industry and scientific researchers. The development of micro/nanostructures out of low surface tension materials is a common method for creating superhydrophobicity. In actuality, the majority of coating methods documented to date rely on either replicating pre-existing "rough" structures or producing roughness on existing materials through several procedure techniques. A coating method that is easy, low-cost, scalable and ecologically friendly is in great demand because to the paucity of outstanding natural templates and uncomplicated manufacturing processes [13]. Until recently, corrosion protection could be efficiently performed using a superhydrophobic coating with a different type of nanocomposite.

Smart coatings are unique films with predetermined characteristics that demonstrate their importance and react to external stimuli such as the environment [6]. Coatings with self-healing and self-repair characteristics are suitable for corrosion prevention, material protection and other surface enhancement applications. Smart coatings combine functionality with nature and contain both standard coating functions like protection and ornamentation, as well as unique capabilities targeted at environmental stimuli [5]. Smart coating allows materials to respond to changes in light, strain, chemical, heat and other stimuli. Coatings are categorised by functional elements, manufacturing procedures, application and other factors. Self-healing, self-cleaning, microcapsule healing and anti-corrosion coatings are examples of traditional coatings [6]. Smart coatings can assist improve a system's performance by decreasing inspection times, maintenance costs and downtime. In addition to increasing the service life of components and structures composed of corrosive materials, the smart coating reduces the requirement for repairing damaged areas. Other advantages include the capacity to monitor and prevent corrosion, as well as the availability of corrosion inhibitors on demand and environmental protection. A smart coating on the other hand, is the most advanced and is defined as a functional coating that responds to stimuli produced by intrinsic and external events [4].

Surfaces coated with superhydrophobic coatings are difficult to wet or repelled water. As a result, water droplets are unable to flatten and instead roll off. To be superhydrophobic, a water droplet's contact angle on a surface must be more than 150° [7]. Surprisingly, superhydrophobic coatings can successfully resist corrosion due to the existence of air pockets between the surface and the corrosive solution, and these pockets function as a barrier, preventing corrosion ions diffusion and protecting the substrates [11]. Superhydrophobicity is inspired by nature which is the "lotus effect". The "lotus effect" is a natural inspiration for superhydrophobicity. The lotus effect refers to the self-cleaning capabilities of the leaves of the "lotus flower" as a result of superhydrophobicity [8]. Water droplets pick up dirt particles owing to the surface's micro- and nanoscopic architecture, which reduces the droplet's adherence to that surface [12]. Furthermore, superhydrophobicity of coatings used to protect metallic materials, such as marine vessels, offshore platforms and wind turbines, often require additional features to enhance other related properties. For instance, additional nanotechnology and nanomaterials presence in the coating enhances the ability to prolong the service of life of metal substrates. The rise in nanotechnology and nanomaterials has encouraged an explosion of new functional coatings in recent years, and this trend will continue to expand in the coming years [4].

Coating nanoscale particles onto substrate surfaces to produce micro/nanoscale structures, followed by low-energy alteration of the hierarchical structure, is one way to create a hydrophobic surface [3]. It has been shown that covering different substrates with nanoparticles and adhesion agents can enhance the durability of superhydrophobic surfaces by increasing interfacial adhesion between coated particles and substrates [10]. As a significant eco-friendly move intended to offer satisfaction with the toughness and reliability of the coating, the concept of nanoparticles inside a polymer resin has been well-received [5]. For reasons, polymeric nanocomposite coatings have been

engineered to combine water repellence and elasticity effects. The permeability and hardness of the coatings have been achieved for both organic polymers and inorganic nanomaterials [10].

Several conventional procedures may be used to repair visible or exterior damage to coatings, but these processes are difficult, costly and time-consuming, making them unsuitable for industrial usage, and their ability to cope with internal and concealed or invisible damage is critical [5]. Fabricating nanocomposite superhydrophobic coatings containing nanoparticles is the most cost-effective way [11]. Smart superhydrophobic coatings are capable of repelling water and preventing corrosion from external stimuli on metallic surfaces. In recent years, an easy-to-apply superhydrophobic coating has attracted a lot of attention and is extensively utilised in a variety of sectors, such as anti-corrosion and oil/water separation. It also reduces drag and is self-cleaning and anti-icing [2]. The superhydrophobic coating has high demand in the market, especially in the automotive industry. Not only have the automotive industry, textile and footwear industries also been involved with the superhydrophobic coating application. There are expected to be possibilities for the industry as a result of recent advances in underwater electronics and wearable electronic devices. Food packaging has a few uses for superhydrophobic coatings, which might possibly create prospects for the future industry ("Superhydrophobic Coatings Market, Growth, Trends and Forecast (2020 - 2025)"). A new and low-cost superhydrophobic coating with outstanding corrosion resistance and protective performance that can be manufactured is therefore essential.

Antibacterial properties of zinc oxide nanoparticles have attracted a great deal of attention because to the ease with which they may be produced from low-cost natural sources and are thus relevant to useable materials [11]. As anticorrosive coatings for metals, coatings containing zinc oxide powder have long been used. They are particularly effective in the case of galvanized steel. Steel is hard to protect because its organic coating reactivity leads to brittleness and lack of adhesion. For many years, zinc oxide paints have retained flexibility and adherence to such surfaces. Zinc oxide is biologically stable and almost harmless to humans with strong bioactivity against many microorganisms [9]. Zinc oxide is used both for indoor and outdoor coatings and for protective metal coatings. Due to its interesting properties, zinc oxide is a very important technological substance. Technological benefits and enhancements in a variety of processes are possible by using nanoparticles created specifically for the automobile sector, textile and footwear industries and other industries that have used superhydrophobic coatings for corrosion prevention applications. Method to fabricate smart superhydrophobic coating need to use inexpensive composition and involving simplest procedures. Therefore, the aim of this study is to fabricate smart superhydrophobic coating based on zinc oxide/epoxy nanocomposite.

2. Methodology

2.1 Materials

S50C medium-sized carbon steel substrates were utilised, with dimensions of 2 cm by 2 cm by 0.3 cm. Less than 50 nm zinc oxide nanoparticles were employed in this work as nanocomposites. In a ratio of 2:1, Sky Tech Malaysia Sdn Bhd provided epoxy resin and hardener. This experiment utilised deionized water and absolute ethanol. Figure 1 shows the schematic diagram of the developed fabrication technique to form the smart superhydrophobic coating.

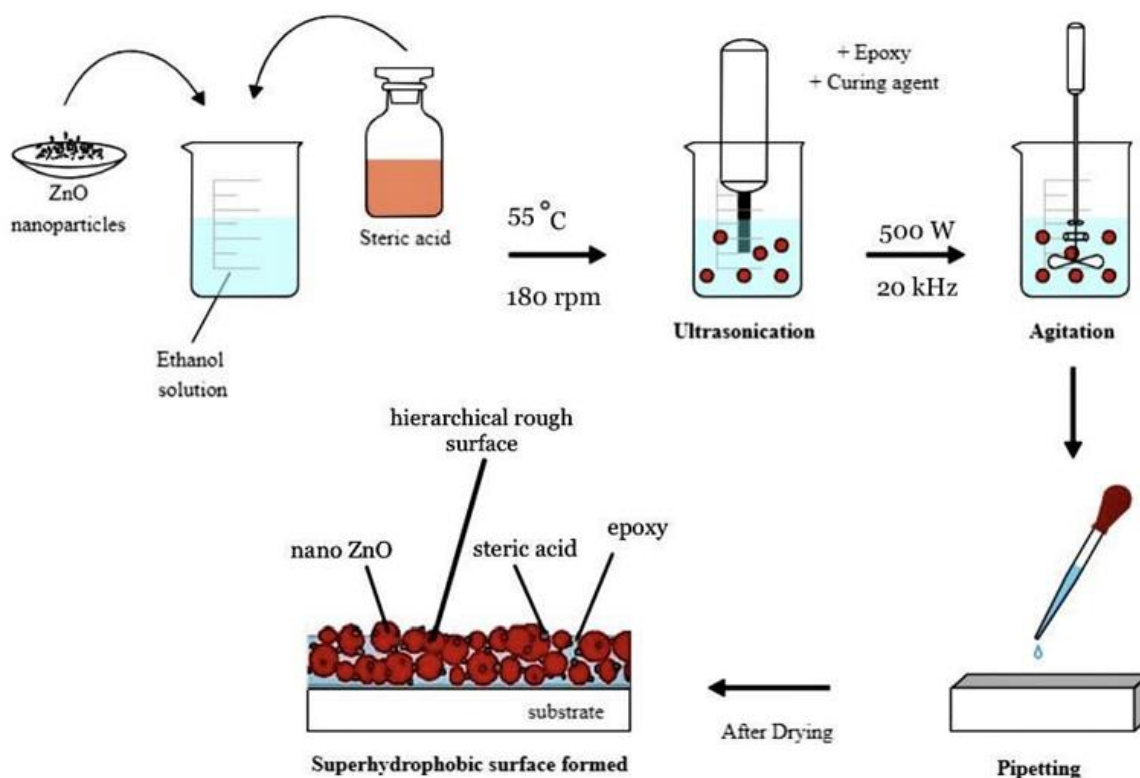


Fig. 1. Schematic diagram of the developed fabrication technique to form the smart superhydrophobic coating

2.2 Fabrication of Superhydrophobic ZnO Nano-coating

The smart superhydrophobic coating with water-repellency and corrosion resistance will develop by mixing the epoxy resin and stearic acid solution which acts as the host component of this experiment with low-cost types of nanoparticles composition which is zinc oxide. The metal substrates to be used in this study is carbon steel graded S50C medium which is commonly used as a building's structure and bridges, axles, gears, shafts, rails, pipelines and couplings, vehicles, fridges and washing machine. Carbon steel also has high tensile strength. By using carbon steel as a testing material, it is enough to prove that this coating can be applied to all other metal substrates. The carbon steel (2 cm x 2 cm x 0.3 cm) undergoes surface grinding to achieve a perfectly flat and level surface and to make sure that no dirt and rust on the metal surface to avoid any error in collecting the data. A generous amount of ethanol solution will be applying on to the surface to clean the carbon steel. It effectively removes dirt, grease and staining from the metal which allows better application of coating onto the surface. The ethanol solution will dry under normal conditions at room temperature at 27°C for 10 mins. Meanwhile, 2.4 g zinc oxide nano-particles and 2.5 % weight-to-volume (w/v) of stearic acid were dispersed in 10 ml of absolute ethanol solution with constant agitation of 180 rpm at 55°C for 5 mins. The stearic acid is used to improve the hydrophobicity of the solution and the ethanol solution is a medium for the reaction of other materials to bind with each other. Then, the mixture solution undergoes ultrasonication for 5 mins using an ultrasonicator probe at 500 W and 20 kHz. Afterwards, 0.6 g of epoxy resin and hardener were added into the suspension and mechanically stirred for 10 mins. The resulted coatings were applied to the carbon steel (2 cm x 2 cm x 0.3 cm) surface with a thickness layer, not more than 1 mm by using the pipetting method. Pipetting technique is the simplest and least expensive. Since this project requires a small production batch, pipetting provides a comparatively simple method of conformal application with the

additional benefits of cost-effectiveness. By adding hardener, the coating layer becomes more durable. Another requirement was a 20-minute time limit for applying superhydrophobic coating. Otherwise, it would lose its effectiveness and will cause an error in the result. The carbon steels with the coating will undergo a drying process for 24 hours at room temperature at 27°C. The method of wettability testing will be used to measure the water contact angle and contact angle hysteresis of the superhydrophobic coatings.

2.2.1 Pre-treatment of carbon steel

First, in order to remove the oxide layer and the hydroxide layer, the carbon steel substrate will undergo surface grinding with a surface speed of 25-45 ms^{-1} , respectively. The carbon steel will be cleansed with a generous amount of ethanol solution and rinsed with deionized water. The carbon steels will dry under normal conditions at room temperature at 27°C for 10 mins.

2.2.2 Preparation of superhydrophobic with zinc oxide nanoparticles coating

2.4 g zinc oxide nano-particles and 2.5% w/v of stearic acid were dispersed in 10 ml of absolute ethanol solution with constant agitation of 180 rpm at 55°C for 5 mins. Then, the mixture solution underwent ultrasonication for 5 mins using an ultrasonicator probe at 500 W and 20 kHz. Then, mechanical stirring for 10 mins with 0.6 g of epoxy resin/hardener was undergone. Figure 2 shows the flowchart of the smart superhydrophobic coating via zinc oxide nanocomposite.

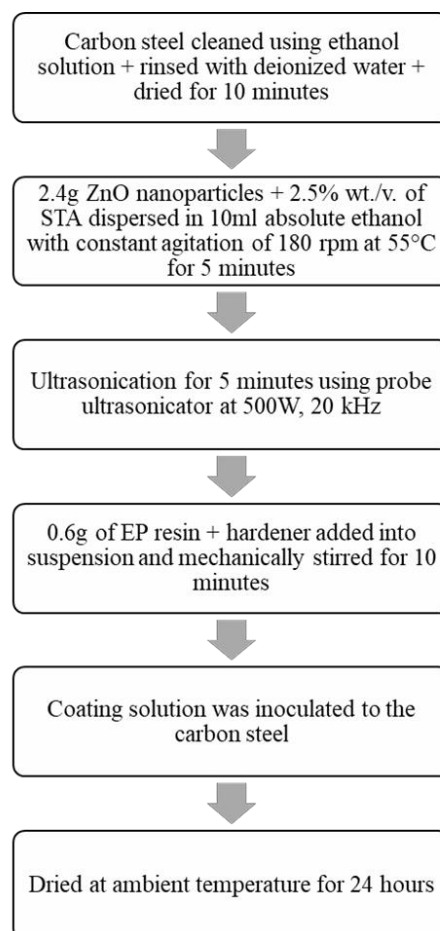


Fig. 2. The flowchart of smart superhydrophobic coating

3. Results and Discussion

3.1 Fabrication of Smart Superhydrophobic Zinc Oxide Nano-coating

The smart superhydrophobic coating was fabricated with zinc oxide nanoparticles, epoxy resin (EP), stearic acid (SA) and absolute ethanol. SA is composed of a polar tail and a non-polar hydrophobic head. It is a surface energy modifier because zinc oxide nanoparticles contain a large hydroxyl group on their surface, the carboxyl groups of SA were easily esterified with the hydroxyl groups on the surface of nano zinc oxide and grafted onto the nano zinc oxide to form a monolayer, which resulted in the formation of a hydrophobic layer on nanoparticles. Thus, the zinc oxide nanoparticles scatter effectively in ethanol and prevent agglomeration. SA was utilised to alter both zinc oxide nanoparticles and epoxy polymer, which aids in surface energy reduction. As a result, the EP matrix inhibits zinc oxide from overlaying and allows surface roughness to develop. EP acts as a binding agent and gives the structure with great mechanical stability, making it an important "anchoring agent" for keeping the zinc oxide nanoparticles together to form a strong hierarchical structure. As a result, the zinc oxide nanoparticles embedded and firmly attached themselves in the epoxy layer, revealing a hierarchical structure with nano-level surface roughness. On the other hand, if the surface lacks a "anchoring structure," it may lose hydrophobicity. Therefore, a superhydrophobic surface can be developed through a simple/one-step process when EP is used as a matrix.

3.2 Morphology of Smart Superhydrophobic Zinc Oxide Nano-coating

The surface morphology of the coating samples was assessed by FESEM images with different magnifications as shown in Figure 3 below. Figure 3 (a) shows the blank carbon steel surface with a water CA of 76.09°. Figure 3 (b) shows the surface of EP coating surface. With a water CA of 104.14°, the EP coating surface was smooth and demonstrated hydrophilic wettability. The hydrophilicity of the EP coating demonstrated that the coating lacked low surface energy and had surface roughness. To attain superhydrophobicity, a coated surface must have low surface energy and surface roughness. A comparison can be made with superhydrophobic zinc oxide nano-coating displayed in Figure 3 (c) that give a result of water CA of 166.60° which exhibits microscale roughness. The aggregation of zinc oxide nanoparticles is responsible for the increase in hydrophobicity of the zinc oxide surface over the EP layer. In contrast, the addition of SA to the zinc oxide coating formulation increased the water CA to higher than 160° and the SLA to less than 10°, as shown in Figure 3 (d), demonstrating the superhydrophobicity feature. The low surface energy of zinc oxide and EP resin modified by SA efficiently prevents the nanoparticles from being covered by the EP resin. The aggregation of zinc oxide nanocrystals in irregular forms grouped in skeletal form, as display in Figure 3 (c) and (d). A micro-level protuberance on the EP layer was shown using a high-resolution FESEM (Figure 3 (c)), which increased the roughness of the surface. Figure 3 (d) is the close-up micrograph of zinc oxide nano superhydrophobic which display the faceted-crystal form in the structure of zinc oxide nanoparticles.

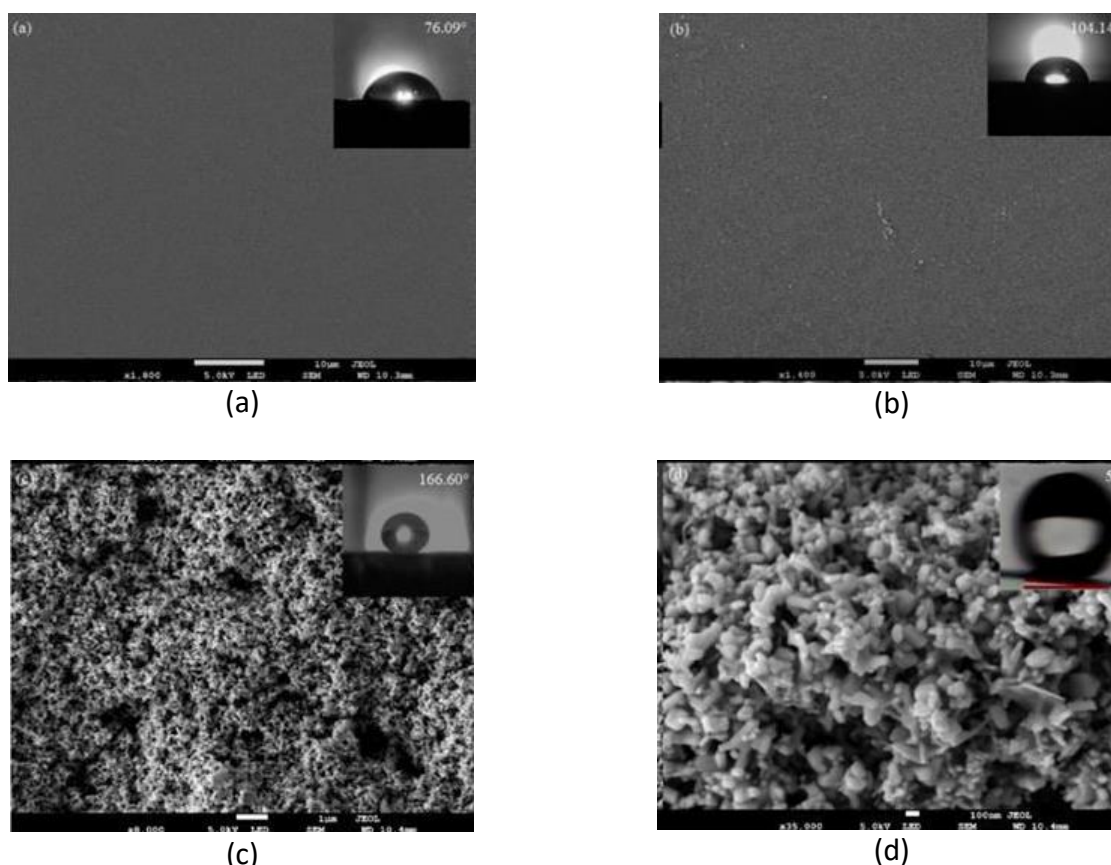


Fig. 3. Collage of FESEM images and CA results of (a) blank carbon steel, (b) EP resin coating and (c) zinc oxide superhydrophobic coating at low magnification (8000x) and (d) at high magnification (35,000x)

Laser scanning confocal microscopy (LSCM) was used to assess the average surface roughness and 3D profile of the coated samples. The LSCM topological scans together with average surface roughness results of EP and zinc oxide nano superhydrophobic coating were shown in Figure 4. The average roughness of the EP resin surface is $2.46 \mu\text{m}$, as shown in Figure 4 (a), which is most likely due to the coarse structures produced on its surface. However, as shown in Figure 4 (b), the average roughness of the zinc oxide nano superhydrophobic surface has increased to $3.77 \mu\text{m}$. The increment average roughness was because of the addition of SA to the coating which owing to the creation of richer topography induced by SA modification. As a result of the air trapped within the rough surface's interspace, the surface can successfully achieve superhydrophobicity. Nonetheless, the micrographs can only reveal the roughness of the coated surface, which is inadequate evidence that the rough surface was changed by SA. EDS and FTIR analyses were used to further the investigation.

FTIR and EDS analysis can confirm the existence of SA absorbed on the zinc oxide nano-coated surface. Figure 5, shows the element nature of the coating's surfaces as revealed by the EDS elemental spectrum. The presence of a strong zinc signal in the spectra indicated that zinc oxide was the primary component present in the coating. In addition, the peak intensity of elemental C was 68.5% as indicated in the table index of Figure 5 (a), demonstrating that SA modified the zinc oxide nano-coating. For the sake of simplicity, only FTIR spectra of EP and zinc oxide nano superhydrophobic coating samples was examined, as shown in Figure 5 (b). FTIR analysis confirmed that the superhydrophobic layer of EP resin containing zinc oxide nanoparticles on the zinc oxide/epoxy-coated surface. The peaks at 2851 cm^{-1} and 2916 cm^{-1} in the spectra of zinc oxide nano superhydrophobic matched to symmetric and asymmetric CH_2 vibrations of the SA alkyl group,

which demonstrate that the surface of zinc oxide nanoparticles has been linked to the SA alkyl group. This implies that SA has been modified on the zinc oxide nanoparticles matrix.



Fig. 4. 3D topographical images and average roughness results of (a) EP resin and (b) zinc oxide nano superhydrophobic coating samples

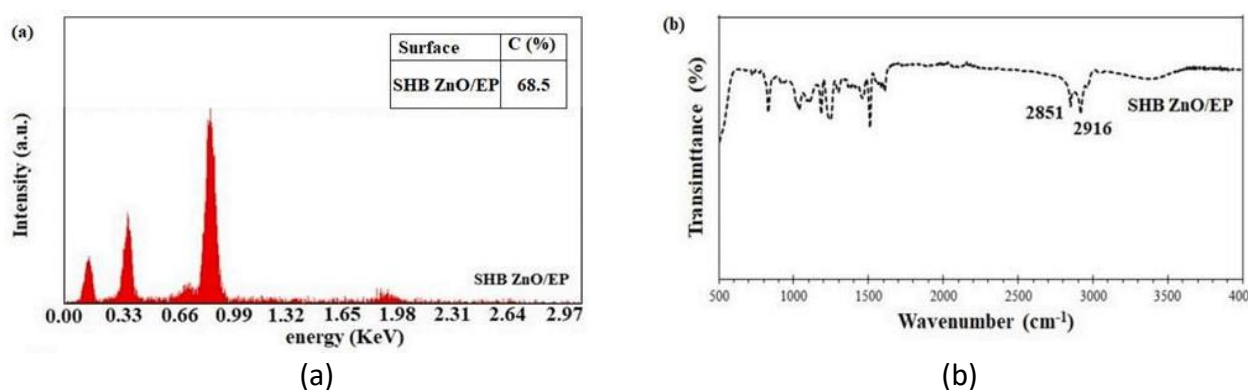


Fig. 5. (a) EDS and (b) FTIR spectra of the superhydrophobic zinc oxide/EP coating

4. Conclusion

This study successfully fabricated smart superhydrophobic coating via zinc oxide nanoparticles with a simple strategy that focuses on a one-step solution coating deposition procedure. The process of fabricating the coating only involved simple equipment and drying process at ambient temperature without the need for surface treatment. Zinc oxide nanoparticles are the main component that plays an important role to create a multiscale rough structure, while EP is added to increase coating adhesion and SA is included as a hydrophobic agent to reduce the surface energy of the coating. The smart superhydrophobic coating exhibited excellent water repellency and self-cleaning properties with WCA = 166.60° and SLA = 5° respectively.

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