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STUDY OF THE INFLUENCE OF NANOPARTICLES ON THE HYDROPHOBIC PROPERTIES OF COATINGS

Лі Че,

аспірант

КПІ ім. Ігоря Сікорського

liche1kpi@gmail.com

Анна Білоусова,

аспірант

КПІ ім. Ігоря Сікорського

a.bilousova@kpi.ua

Анотація. Для створення супергідрофобних поверхонь часто використовують дорогі фторовмісні або силанові сполуки, а багато методів потребують спеціального обладнання, суворих умов і тривалих процесів, що ускладнює їх застосування на широкій основі. В статті представлено одностадійний метод синтезу наночастинок ZnO та ZnO-SiO₂, який є екологічно чистим і безпечним, забезпечуючи практичний підхід до широкомасштабного виробництва супергідрофобних поверхонь. Метою дослідження було проаналізувати вплив різного вмісту синтезованих частинок ZnO та ZnO-SiO₂ та частинок TiO₂, SiO₂ на гідрофобні властивості покриттів. Виявлено, що покриття з додаванням лише частинок ZnO демонструє кут змочування лише 74,8°, що не відповідає критерію гідрофобності. Водночас, кут змочування в покриттів з наночастинками ZnO-SiO₂ досягає 152,5°, що свідчить про супергідрофобність покриття.

Ключові слова: гідрофобні покриття, композиційні матеріали, ZnO, кут змочування, супергідрофобність

Abstract. To create superhydrophobic surfaces, expensive fluorine or silane compounds are often used, and many methods require special equipment, harsh conditions and lengthy processes, making them difficult to apply on a large scale. This paper presents a one-step method for the synthesis of ZnO and ZnO-SiO₂ nanoparticles, which is environmentally friendly and safe, providing a practical approach to the large-scale production of superhydrophobic surfaces. The aim of the study was to analyse the effect of different contents of synthesised ZnO and ZnO-SiO₂ particles and TiO₂ and SiO₂ particles on the hydrophobic properties of the coatings. The study revealed that the coating with the addition of only ZnO particles shows a contact angle of only 74,8°, which does not meet the hydrophobicity criterion. At the same time, the contact angle of the coatings with ZnO-SiO₂ nanoparticles reaches 152,5°, which indicates that the coating is superhydrophobic.

Keywords: hydrophobic coatings, ZnO, composite materials, contact angle, superhydrophobicity

In contemporary urban settings, the phenomenon of dust aggregation on various surfaces, notably walls and glass structures, has emerged as a notable concern.

Traditional approaches to mitigating this issue, such as manual cleaning, are plagued by inefficiencies including elevated labor demands and associated costs. Consequently, there has been a surge of interest in the development of coatings endowed with self-cleaning capabilities, prompting extensive research endeavors.

German scientists Barthlott et al. [1] first utilized scanning electron microscopy in 1997 to study the superhydrophobic surface of lotus leaves. They proposed that the surface hydrophobicity is caused by a combination of rough microstructures formed by trichomes, epidermal folds, and waxy crystals of the epidermal wax. The rough/waxy surface of lotus leaves not only exhibits water-repellent properties but also shows low adhesion to particulate pollutants. Further research on the microstructure of lotus and rice leaf surfaces has suggested that micron/nanometer-scale composite structures are key to obtaining artificial superhydrophobic surfaces [2].

To comprehend the principles of superhydrophobic surfaces, one must first understand the concept of wetting. Wetting refers to the process of forming a new interface when a liquid contacting solid (or liquid) surface, which is ubiquitous in daily life, industry, agriculture, and other fields [3]. Surface wettability is one of the most important characteristics of solid surfaces. Since the introduction of Young's equation in 1805, research on wetting and wettability has continued for over two hundred years. Non-wetting surfaces (also known as superhydrophobic surfaces) have emerged as an important branch of wetting research, attracting significant interest from academia and industry.

The static contact angle θ is a criterion for judging the degree of surface wetting, with contact angles divided into four stages: $0^\circ < \theta < 10^\circ$ for superhydrophilicity, $10^\circ < \theta < 90^\circ$ for hydrophilicity, $90^\circ < \theta < 150^\circ$ for hydrophobicity, and $150^\circ < \theta < 180^\circ$ for superhydrophobicity. This experiment primarily explores the properties of materials within the range of hydrophobicity and superhydrophobicity.

The main filler studied in this article is ZnO. It is a type of direct bandgap wide-bandgap semiconductor material. With a bandgap of 3.37 eV and an exciton binding energy of 60 meV at room temperature, it becomes an excellent optoelectronic material in the ultraviolet to visible region. However, the inherent hydrophilicity of ZnO

significantly limits its applications in waterproofing, self-cleaning, and other aspects. Therefore, the preparation of superhydrophobic surfaces through surface modification of nano ZnO has become a hot topic in recent years.

Wu et al. [4] placed clean carrier substrates in a mixed solution of zinc nitrate, ammonium chloride, urea, and ammonia water, and grew columnar zinc oxide on the carrier substrate surface. The surface can achieve superhydrophobicity after modification with octanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, and octadecanoic acid. However, the wetting mechanisms of carboxylic acids with different carbon chain lengths vary greatly. It was found that when the carbon chain length of the carboxylic acid is greater than 16, the superhydrophobic mechanism of its surface conforms to the Cassie model, while with a carboxylic acid length of 8-14, it tends toward the Wenzel model. This method can be applied to various substrates, such as silicon wafers, glass substrates, polymer surfaces, and even some irregular and curved surfaces. The advantage of superhydrophobic surfaces can find practical applications in aircraft, ships, and certain special decorations.

Chen et al. [5] prepared low-adhesion copper-based superhydrophobic CeO₂/ZnO nanotube arrays (NTAs) using a two-step chemical bath deposition method and improved them through modification with low surface energy silane. Initially, ZnO nanotube arrays were uniformly prepared on copper plates using chemical bath deposition, and then they were immersed in a solution of Ce(NO₃)₃ to obtain CeO₂/ZnO nanotube arrays. After (FAS) modification, this composite material exhibited excellent superhydrophobicity, with a high contact angle of 157,3° and low adhesion force of 14μN. This type of superhydrophobic nanocoating can be applied in catalysis, fuel cells, self-cleaning, and enhanced condensation heat transfer fields.

Experimental Section

Zinc oxide (ZnO) particles were synthesized using a streamlined one-step method. Initially, zinc nitrate (Zn(NO₃)₂) was dissolved in deionized water within a beaker. The solution was then subjected to magnetic stirring for 30 minutes, with the gradual addition of a predetermined quantity of sodium citrate. Stirring continued for

an additional 30 minutes until the sodium citrate was fully dissolved, resulting in the formation of solution A.

Subsequently, a specific mass of sodium hydroxide (NaOH) was weighed and completely dissolved in deionized water, forming solution B. Solution B was then slowly added dropwise to solution A while stirring continuously for 2 hours. Following the reaction, the beaker containing the mixture was placed in a thermostat set to 80°C for 5 hours to facilitate aging.

The resulting suspension was subjected to centrifugation to collect a precipitate, which was subsequently washed three times with deionized water and absolute ethanol. The washed precipitate was then transferred to an oven set at 80°C for 5 hours to ensure thorough drying. Finally, the dried particles were subjected to calcination in a muffle furnace at 500°C for 2 hours. The resulting ZnO particles were obtained after grinding.

0,05 grams of polyvinylpyrrolidone (PVP) and 0,5 grams of zinc oxide (ZnO) were used to synthesise ZnO-SiO₂ particles. PVP and ZnO combined in 30 milliliters of isopropyl alcohol (IPA) and stirred for 30 minutes, denoted as solution A. In a separate vessel, 2,5 grams of tetraethyl orthosilicate (TEOS) were mixed with 20 milliliters of IPA, designated as solution B. Solution B was slowly introduced into solution A while simultaneously adding ammonia solution to maintain the pH within the range of 8,5-9,5. Stirring continued for 1 hour, followed by aging at 80°C for 6 hours.

The resultant solid was separated via filtration, washed thrice with deionized water and IPA, and subsequently dried. Finally, the material underwent processing in a muffle furnace at 500°C. Upon grinding the obtained product, composite particles of zinc oxide-silicon dioxide (ZnO-SiO₂) were obtained.

To prepare the coating, acrylic polymer and xylene were combined in a mass ratio of 1:5 and thoroughly mixed with stirring until complete dissolution occurred. Subsequently, specific mass ratios of silica dioxide (SiO₂), titanium dioxide (TiO₂), zinc oxide (ZnO), and zinc oxide-silica dioxide (ZnO-SiO₂) particles were added to the solution and stirred. The mass ratios ranged as follows: SiO₂ wt% = 0-40%, TiO₂ wt% = 20-95%, ZnO wt% = 20-80%, and ZnO-SiO₂ wt% = 20-80%.

A glass slide measuring $2.5\text{cm}\times 1\text{cm}\times 0.02\text{cm}$ served as the substrate for coating. Once the paint mixture achieved homogeneity, it was evenly applied onto the surface of the glass slide and subsequently dried in an environment maintained at 55°C for 10 minutes.

The sessile drop method was employed to determine the static water contact angle on the surfaces of the coated glass slides. Measurements were taken at 3-5 distinct locations on each slide, and the average angle was calculated to yield the final result.

Surface wetting performance analysis was conducted to investigate the influence of varying particle content ratios on the hydrophobic characteristics of coatings comprising zinc oxide (ZnO), titanium dioxide (TiO_2), silica dioxide (SiO_2), and zinc oxide-silica dioxide (ZnO- SiO_2) particles. These coatings were designed to create micro-rough structures and utilized acrylic polymer as a low-surface-energy material to achieve superhydrophobic properties. Following drying at 55°C for 10 minutes, the coatings were subjected to contact angle testing.

Experimental data obtained from the four materials were plotted on a histogram. Analysis of the data, as depicted in Figure 1, reveals a discernible trend in the contact angle between water droplets and the surface coating of glass. Initially, with changes in the mass ratio of the four materials, there is an observed increase followed by a subsequent decrease in the contact angle. The inherent hydrophobic angle of the acrylic polymer is noted to be $73,8^{\circ}$. Upon amalgamation with the sample, the coating's hydrophobic performance improves due to heightened surface roughness. Furthermore, the inclusion of acrylic polymer contributes low surface energy constituents essential for constructing superhydrophobic coatings. However, when the mass ratio of the sample surpasses a certain threshold, the hydrophobic angle tends to decrease. This phenomenon arises from an excessive quantity of the sample, which exposes more hydroxyl groups on the coating surface, thereby augmenting its hydrophilicity.

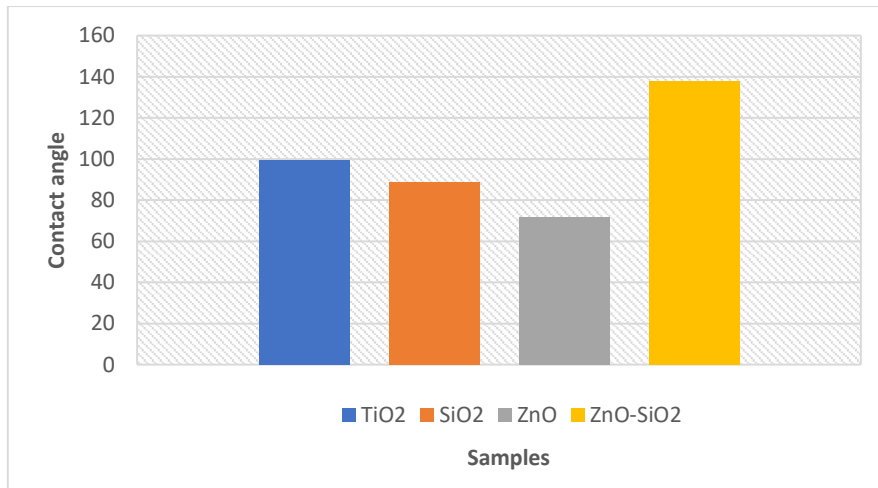


Fig. 1 - Contact angles of different samples

Figure 2 presents electron microscope images labeled as (a), (b), (c), (d), and (e), illustrating the maximum contact angles attained by coatings composed of acrylic polymer and those doped with TiO₂, SiO₂, ZnO, and ZnO-SiO₂ particles, respectively. The images distinctly indicate that the incorporation of the aforementioned samples notably enhances the hydrophobic performance of the coatings. Notably, when the mass ratios are TiO₂-80%, SiO₂-30%, ZnO-60%, and ZnO-SiO₂-60%, the contact angle reaches its maximum value.

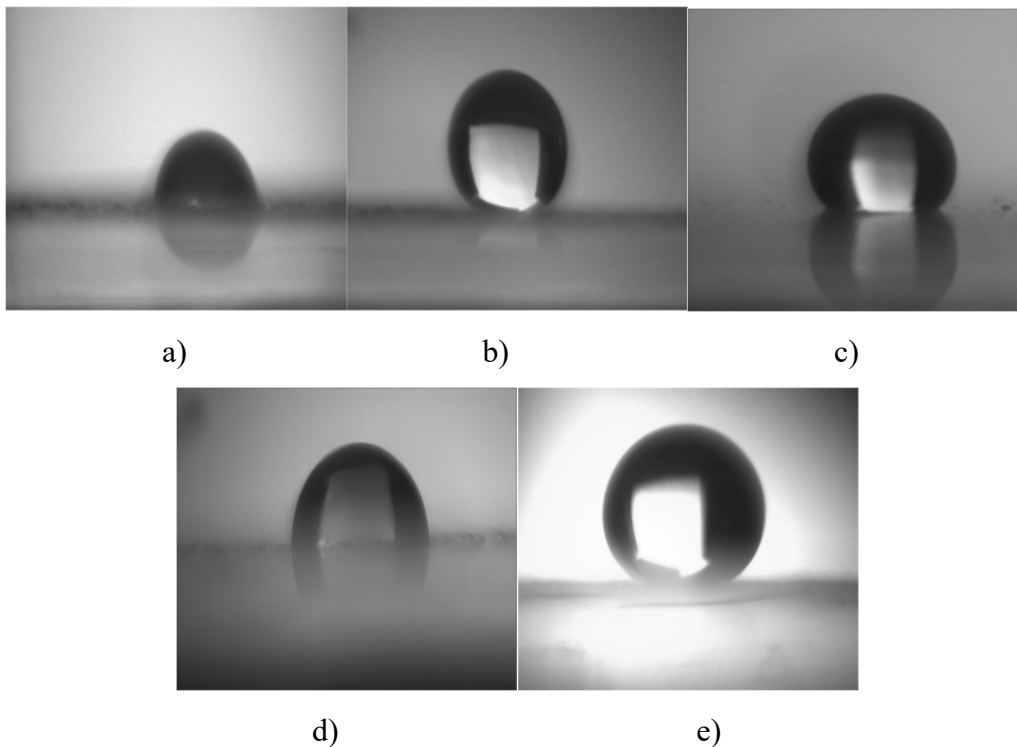


Fig. 2 – Coating contact angle for different fillers: a) without acrylic polymer; b) TiO₂; c) SiO₂; d) ZnO e) ZnO-SiO₂

CONCLUSION

The study found that the addition of nanoparticles improves the hydrophobic properties of the coating by increasing the surface roughness. However, when a certain threshold value of the sample mass fraction is exceeded, the hydrophobic angle decreases. This phenomenon is due to the excess of the sample, which leads to the exposure of more hydroxyl groups on the surface of the coating, which in turn increases its hydrophilicity. It was also found that a hydrophobic coating containing only ZnO nanoparticles reaches a contact angle of $74,8^\circ$ without showing a significant improvement in hydrophobic performance. At the same time, the hydrophobic coatings obtained using ZnO-SiO₂ particles demonstrate a contact angle of $152,5^\circ$, which meets the criteria of superhydrophobicity.

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