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Zinc oxide nanoparticles as photo-catalytic and anti-bacterial pigment for alkyd resin based coating

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ABSTRACT

Purpose: Recently, there has been an upsurge among people around the world in maintaining a sustainable and hygienic environment. This is due to the over-exploitation of recourses causing environmental pollution and spreading bacterial infections. In this regard, scientists are motivated to develop smart coatings where environmental pollutants and bacterial cells are degraded when in contact with their surfaces.

Design/methodology/approach: In our previous report, ZnO nanoparticles (NPs) were prepared using the precipitation technique, showing good photocatalytic and antibacterial activity [1]. In this context, the present study details the use of ZnO NPs as pigment for the fabrication of alkyd resin-based self-cleaning coating. The coating was developed by mixing ZnO NPs and alkyd resin along with the additives using the ball milling technique. The developed coating was characterized using field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy, and water contact angle measurements.

Findings: To elucidate the self-cleaning and hygienic behaviour of the ZnO/alkyd resin coating, the dried coating was exposed to crystal violet (CV) solution as a model dye pollutant and bacterial strains to assess its photocatalytic and antibacterial activity. The droplets of CV solution placed over the coating almost degraded after 360 min of exposure to sunlight owing to the presence of ZnO NPs in the coating. Further, the coating exhibits reasonable antibacterial activity against *E. coli* and *P. aeruginosa* whereas it displays low antibacterial activity against *S. aureus*.

Research limitations/implications: Even though, the self-cleaning coating shows promising results, tuning the activity of the photo-catalytic pigment can improve the pollutant degradation efficiency and elevate bactericidal activity.

Originality/value: ZnO NPs-impregnated alkyd resin coating for self-cleaning applications is novel.

Keywords: ZnO NPs, Photocatalytic pigment, Anti-bacterial pigment, Alkyd resin coating, Self-cleaning surface

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PROPERTIES

1. Introduction

Nanotechnology has indefinitely many applications in the present decade, approximately in all the disciplines due to its attractive properties. Its crucial role in the coating industry, especially in self-cleaning, anti-fungal, anti-fouling, self-healing, scratch resistance, etc., is remarkable, and they all together come under the roof of smart coating technology [2,3]. Constructing a self-cleaning surface involves two major techniques; 1) fabricating the surface with roughness and functionalizing with low surface energy material so that the modified surface repels the water leading to a water-rolling phenomenon that tends to carry the dust on its way. This makes the surface clean, and also, the surface remains dry [4]; 2) the surface can be coated with hydrophilic material having photocatalytic activity so that the surface can break down organic contaminants into simple CO_2 and H_2O molecules [5]. Due to this process, the surface containing the contaminants is cleaned upon exposure to sunlight [6]. In the present research, the latter type of self-cleaning surface is focused on.

The ability of nanoparticles (NPs) that can be used as an active photocatalytic and antibacterial activity has been reported already. The antibacterial property observed in the paints that were incorporated with silver NPs embedded with $CaCO_3$ microspheres was reported by Sahoo et al. [7]. The effective reduction of bacterial growth using CuO NPs was reported by Ong et al. [8] in the comparative study between the alkyd resin and CuO NPs incorporated in alkyd resin. Silver vanadate decorated with silver NPs was also used as an antibacterial agent [9]. Much literature has discussed the photocatalytic properties and antibacterial activity of the paint separately, but fewer reports are available discussing both properties together.

One of the most utilized photocatalytic and antibacterial materials is the ZnO NPs [10]. Our previous report reported the preparation, characterization, photocatalytic and anti-bacterial activity of ZnO NPs prepared through the precipitation route [1]. Here, ZnO NPs were used as a photocatalytic and antibacterial pigment for alkyd-based coating for self-cleaning applications. Spectroscopic analyses were carried out for the characterization. Suitable methods were used to monitor the drying time, solid content, volatile organic emission, etc. The self-cleaning property was assessed using crystal violet dye (CV) as a model pollutant. It was observed that the dye degraded under the influence of sunlight in the presence of the self-cleaning coating. Further, the antibacterial property of the coating was assessed against various bacterial strains and displayed promising results.

2. Materials and methods

2.1. ZnO NPs preparation

The ZnO NPs were prepared using our previous report [1]. Briefly, ten mM of zinc acetate and ammonium oxalate were dissolved separately in 50 ml of distilled water. Under the continuous stirring condition, ammonium oxalate solution was added dropwise to the zinc acetate solution. The pH was increased to 10 by adding an appropriate quantity of ammonia. Then, a white precipitate was formed, which indicated the crystal growth of zinc oxalate. This precipitate was then collected and washed 2 to 3 times using distilled water. Then it was dried in a hot air oven and then calcinated at 700°C for three h. The zinc oxalate precipitate was decomposed to ZnO in the nanoscale range during calcination. The procedure is depicted in Figure 1.

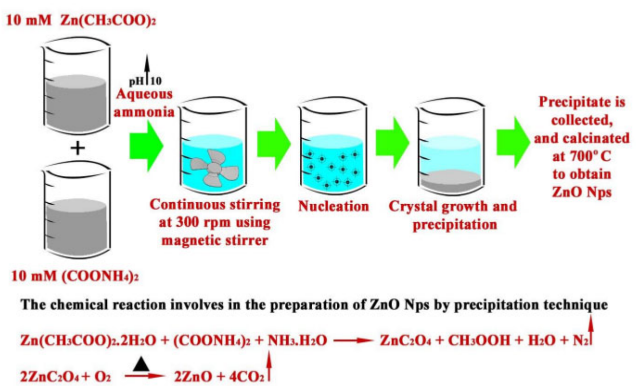

Fig. 1 Schematic representation and chemical reaction involved in the preparation of ZnO NPs

Table 1.
Additives present in the self-cleaning coating

Ingredients used	Additives	Purpose	Wt.%
Pigment	ZnO NPs	Provides self-cleaning property to the coating	15.0
Binder	Alkyd resin	Film forming component of the coating binds all the constituents together	65.0
Anti-settling agent	Aluminium stearate	Settling of pigment is prevented	0.5
Thickener	Polyvinyl alcohol	Maintains consistent viscosity	0.2
Wetting agent	Soya lecithin	The pigment is wetted for uniform distribution in the binder	0.6
Inner coat drier	Nano-sized ZrO_2	Chemical cross-linking agent of unsaturated fatty acids	0.6
Outer coat drier	Cobalt naphthenate	Catalyses the lipid auto-oxidation process	0.6
Thinner	Toluene	Solvent	17.5
Total			100

2.2. Fabrication of ZnO NPs impregnated alkyd resin coating

The high-energy planetary ball milling technique was used to impregnate the ZnO NPs into the alkyd resin matrix in a homogeneous manner. This mill is a type of grinder that blends the sample using mechanical balls as the medium for grinding. The pigment and binder, along with the required additives in appropriate wt.%, were taken in the grinding jar containing tungsten carbide balls (Tab. 1). The ratio of the ball to powder weight ratio was fixed at 10:1. For the homogeneous dispersion of the NPs in the alkyd resin medium; milling was performed for 5 h at 300 rpm. After milling, the mixture was collected and stored in a vacuum desiccator.

2.3. Coating characteristics: drying time, solid content, and a volatile organic compound

Drying time is required to dry paint completely after being coated over a suitable substrate. The solid content of the coating signifies the hiding power that describes the ratio of the weight of the solid phase component after drying to the total weight of the coating before drying [11],

$$Solid\ Content = \left(\frac{W2}{W1}\right) \times 100 \quad (1)$$

where W1 and W2 represent the weight of fabricated coating before and after drying, respectively. The remaining fraction contributes to the Volatile Organic Compound (VOC) of the fabricated coating. The Environmental Protection Agency has set a benchmark of 380 g/L for maximum VOC emission. Serious health issues will be caused if the VOC emission crosses the maximum allowable limit.

2.4. Surface morphology, roughness and hydrophilicity

The various physicochemical aspects influence the self-cleaning behaviour of the prepared coating over the surface. The physical properties like roughness, hydrophilicity, and surface morphology were studied using Atomic Force Microscope (AFM, XE-70, Park Systems, South Korea), goniometer (OCA15 Geottferd data physics, GmbH, Germany), and Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss EVO 18, Germany), respectively.

2.5. Adhesion studies

To check the adherence, an X-cut tape test was performed as per ASTM D 3359-97 standard [12]. Two cuts measuring 4 cm in length were done in the centre of the coating intersecting with an angle of 30° and 40°. An adhesive tape was pasted and then peeled off after a min at an inclination angle of 180°. The adherence activity was rated as

- No peeling/removal – 5A,
- Trace peeling/ removal near incisions or at the intersection – 4A,
- Spiked peeling near the incisions up to 1/16 in. (1.6 mm) on either side – 3A,
- Spiked removal near most of the incisions up to1/8 in. (3.2 mm) on either side – A,
- Removal from most of the area covered by X under the tape – 1A,
- Removal beyond the area covered by X – 0A.

2.6. Self-cleaning studies

The photocatalytic property of the NPs infused in the alkyd resin was the reason behind the self-cleaning behaviour. Consequently, a known concentration of CV solution was dropped over the coating, which faded upon sunlight exposure. The self-cleaning activity was recorded as a photograph periodically.

2.7. Anti-bacterial studies

The antibacterial activity of the NPs infused alkyd coating was also analysed. The coating was UV sterilized prior to the experiment, and their antibacterial property was studied using a modified literature procedure [13] for gram-negative as well as positive bacterial strains. 200 ml of the bacterial strain were swabbed, dried, and incubated at 37°C for different time intervals (24 h and 48 h). The specimen was then splashed with 2 ml nutrient broth three times after incubation. The splashed nutrient broth was collected, performed ten-fold dilution, and then swabbed on the agar plates, which were then incubated at 37°C. The number of colonies formed over the agar plate was calculated using the colony counter. Similarly, the antibacterial activity of the uncoated specimen was also evaluated by employing the same technique. The procedure was repeated three times, and the average was taken. The reduction in bacterial viable cells was computed using the expression,

$$Reduction\ in\ viability\ (\%) = \left(\frac{V_u - V_c}{V_u}\right) \times 100 \quad (2)$$

where V_u and V_c represent the number of colonies formed on uncoated and coated specimens.

3. Results and discussion

3.1. Characteristics of ZnO NPs impregnated alkyd resin coating

ZnO NPs were used as a pigment due to their photocatalytic and antibacterial properties for the alkyl resin-based self-cleaning coating preparation. The NPs were evenly distributed in the resin matrix using a high-energy ball milling technique. The additives and the wt.% of the constituents present in the coating are detailed in Table 1.

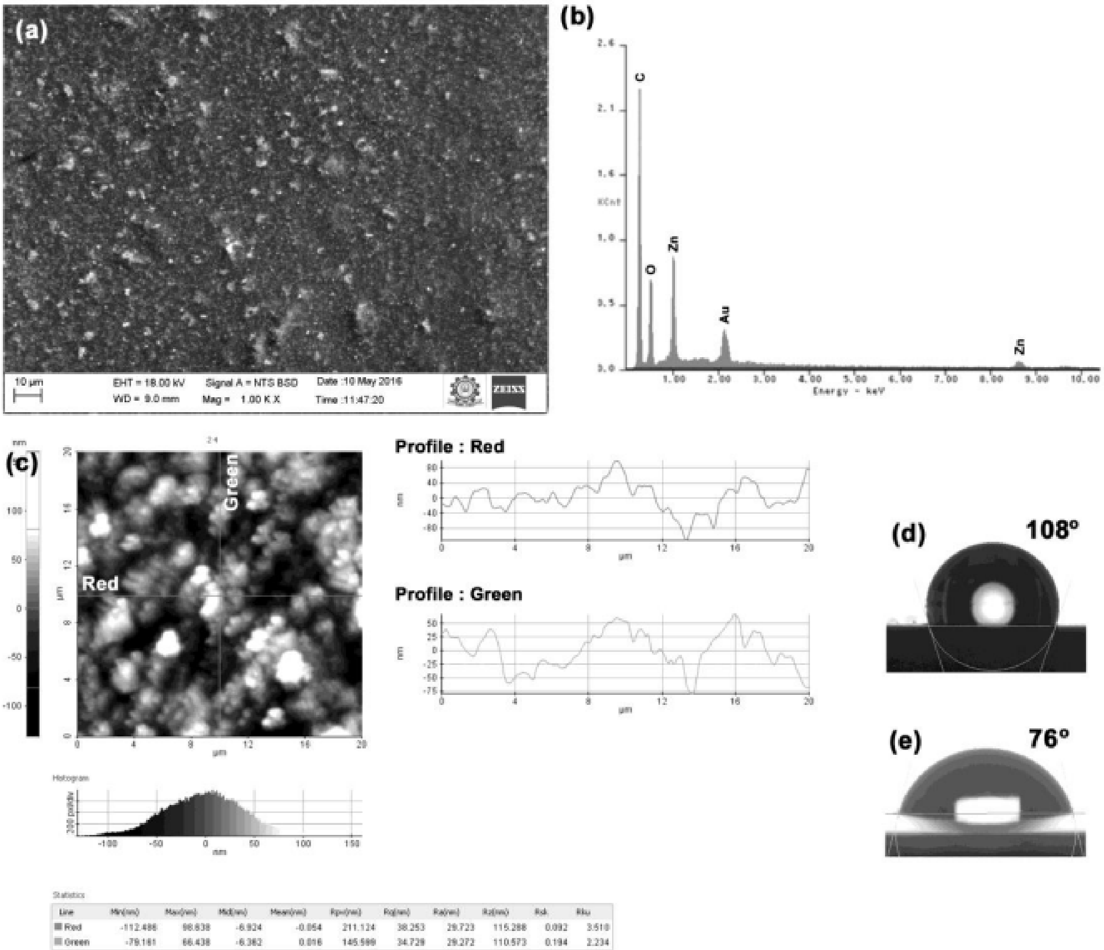

Fig. 2 (a) FESEM image, (b) EDX spectrum, and (c) 2D line profile analysis of ZnO NPs impregnated alkyd resin coating. WCA of alkyd resin coating without (d) and with ZnO NPs (e)

The homogeneous mixture containing ZnO NPs infused in the alkyd resin was coated over glass slides. The coating was done using the brush coating technique with a single coat and dried at room temperature. The drying time, solid content, and VOC content were elucidated as 7 h, 57.21%, and 310 g/L, respectively.

The coating had more solid content, i.e., it may decline the overcoating number to get perfect hiding of the underlying substrate. The VOC emission was within the allowable limit leading to negligible health problems. The thickness of the coating was found to be 120 µm evaluated using a screw gauge [14]. The adhesion test was carried out, and found that the coating was categorized on the scale of 5A.

Figure 2a shows the FESEM micrograph of ZnO-impregnated alkyd resin coating. The images were recorded with a magnification of 100x with backscattered electron detection mode. Before recording, the specimens were coated with Au through the sputtering technique to improve the image quality of FESEM. From the recorded images, it can be inferred that the NPs were uniformly suspended throughout the dried film validated by the difference in contrast. Following the confirmation of the distribution of NPs, EDX spectrum analysis was done. From the EDX spectrum, the peak value corresponding to the Zn (1.03 eV and 8.62 eV) and O (0.53 eV) confirmed the presence of ZnO NPs (Fig. 2b). Also, another peak corresponding to C was observed due to the presence of the alkyd resin. One more peak corresponding to Au was also seen as it was sputtered before FESEM analysis. Due to the less wt.%, elements like Zr, Co, Al, etc., added as additives for coating fabrication were not observed in the EDX spectrum.

AFM was used to study the roughness of the alkyd coating. 2D line profile analysis was obtained using XEI image processing software to analyse the surface (Fig. 2c). The profile shows a red and a green line, and both display a roughness of about 29 nm, which indicates the uniform distribution of ZnO NPs over the surface.

Figures 2d,e represent the WCA of alkyd resin coating without and with ZnO NPs. The WCA of alkyd resin display water repelling behaviour at 108°, which was then reduced to 76° after infusing ZnO NPs [15]. This was due to the capability of ZnO NPs to form hydrogen bonding with water molecules and increase the water-adsorbing behaviour or adherence of water molecules [16]. The hydrophilic nature of the coating highly influences the self-cleaning behaviour because of the firm interaction of the moisture. Since photocatalytic degradation activity can be activated in the presence of water molecules owing to the generation of active radicals, the moisture interaction is important for self-cleaning behaviour [17]. This property enables the CV molecules' adsorption and degradation of pollutants upon exposure to sunlight.

3.2. Self-cleaning studies

The self-cleaning behaviour of the ZnO NPs-impregnated alkyd resin coating was evaluated by placing 5 mL of 10 mg/L CV solution over the dried paint-coated surface (area = 2.5 cm × 7.5 cm) and exposed to sunlight (Fig. 3a-d). At t = 0 min, the solution was dark violet, while after 360 min, the colour faded to light violet. This was due to the degradation of CV [18] by the coating (Fig. 3d). This behaviour was due to the photocatalytic behaviour of ZnO NPs found over the surface of the dried coating. The CV molecules were adsorbed over ZnO NPs due to their hydrophilic nature while dropping the CV solution over the coating [19]. The adsorbed molecules were then degraded due to the photocatalytic nature of the ZnO NPs. Compared to the photo-catalytic degradation of ZnO NPs (80 min) [1], the ZnO-impregnated alkyd coating degraded the CV only after six h of exposure. This was because the ZnO NPs were almost blocked in the alkyd resin matrix [20] and allowed very trace active sites for the degradation of CV and, therefore, took a long duration for self-cleaning activity. As alkyd resin has no photocatalytic activity, the self-cleaning behaviour of the prepared paint was solely due to the presence of ZnO NPs used as a pigment.

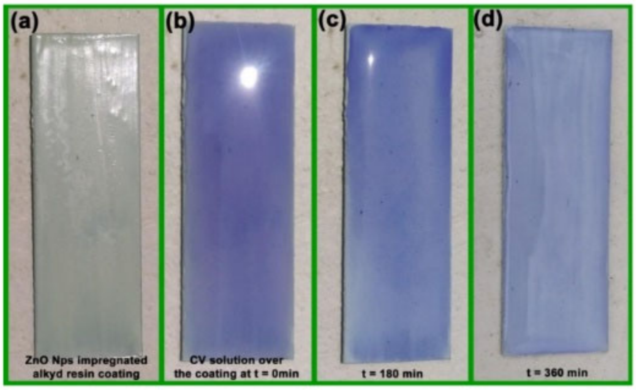

Fig. 3. (a) Optical image of ZnO NPs impregnated alkyd coating. Crystal violet solution dropped over the coating and exposed to sunlight at the time, t = 0 min (b), t = 180 min (c), and t = 360 min (d)

3.3. Anti-bacterial studies

The antibacterial test of ZnO NPs-based coating was performed against gram-negative bacteria (*E. coli* and *P. aeruginosa*) and gram-positive bacteria (*S. aureus*). Figure 4 shows the reduction in the viability of the bacterial cells with respect to the contact time with ZnO-alkyd resin coating. After 24 h of incubation, 17% and 21% reduction in cell viability was observed for *E. coli* and *P. aeruginosa*. After 48 h, the reduction in cell viability increases to 22% and 32% for *E. coli* and *P. aeruginosa,* respectively.

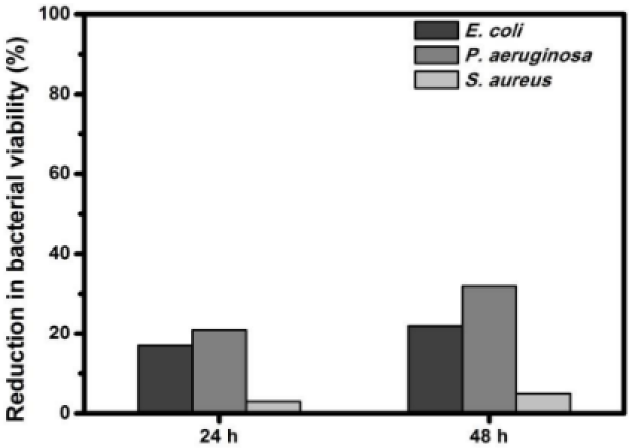

Fig. 4. Reduction in bacterial cell viability while exposed to the ZnO NPs-based coating for 24 h and 48 h

The antibacterial test results show that ZnO NPs displayed strong bactericidal activity against gram-negative bacteria but were limited against *S. aureus*. The other additives added to the coating had negligible effects on the antibacterial activity since their concentration was very lower. Thus, it can be inferred that the ZnO NPs contribute to the antibacterial activity as it was the only active constituent for the inhibition. From all these results, it was inferred that ZnO NPs impregnated alkyd resin coating displayed photocatalytic and antibacterial activity.

4. Conclusions

The ball milling technique prepared a coating comprising the alkyl resin matrix impregnated with ZnO NPs. The presence of ZnO NPs was observed from the characterization methods like FESEM and EDX. Good results were obtained from the paint properties like solid content, drying time, VOC emission, etc. Further, the modified coating displayed reasonable self-cleaning (against CV) and antibacterial activity (against *E. coli* and *P. aeruginosa*). Thus, the present multi-functional paint might be a highly useful candidate for self-cleaning coating applications.

Additional information

The work presented in this paper was presented in “Two Days Virtual National Meet on Nano Interface Science (NIS-2021)”, Chettinad Academy of Research & Education, Chennai, India, 2021.

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