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Research Article

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Green-synthesized TiO₂@Cu₂O hybrid nanoparticles for mechanically reinforced, antibacterial, and antifouling poly(vinyl chloride–vinyl isobutyl ether) coatings

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Abstract

The development of multifunctional coatings with antimicrobial, self-cleaning, and protective performance has intensified interest in nanostructured additives. Rutile TiO₂ offers strong light scattering, UV resistance, stability, and low cost, whereas Cu₂O provides intrinsic antibacterial activity via copper ion release and reactive oxygen species generation. Constructing TiO₂@Cu₂O core–shell heterostructures enhances charge separation, broadens visible-light absorption, and promotes synergistic antibacterial effects. Herein, TiO₂@Cu₂O nanopowders were green-synthesized with L-ascorbic acid being used as a reductant, polyethylene glycol and Tween 80 as surfactants. XRD, TEM, SEM, and EDS analyses confirmed the formation of Cu₂O crystals (4.17 wt.%) on rutile TiO₂ nanorods without altering the host crystal structure. The hybrid nanostructures extended optical absorption from 450 to 800 nm. Incorporation of 2 wt.% TiO₂@Cu₂O into poly(vinyl chloride–vinyl isobutyl ether) (PVE) coatings enhanced impact resistance, relative hardness, adhesion, and abrasion resistance by 28.6%, 51.4%, 12.5%, and 22.9%, respectively. The modified coatings exhibited strong antibacterial activity against *Pseudomonas stutzeri* B27, improved UV–humidity aging resistance, and reduced photodegradation and gloss loss. Controlled Cu ion release (23 µg/L) in seawater contributed to biofilm suppression and antifouling performance, highlighting the potential of TiO₂@Cu₂O as a multifunctional additive for durable PVE-based protective coatings.

Keywords: coating, $\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposite, antibacterial, antifouling, vinyl ether resin.

Highlights

- Green-synthesized rutile $\text{TiO}_2@\text{Cu}_2\text{O}$ core–shell nanoparticles
- First integration of $\text{TiO}_2@\text{Cu}_2\text{O}$ into PVE at 2 wt. %
- Hardness +51.4%, impact +28.6%, adhesion +12.5%
- 51.5% antibacterial inhibition via ROS and Cu^{2+} release
- Improved UV–humidity durability and bioadhesion resistance
- Promising marine and architectural protective coatings

1. Introduction

Surface coatings are widely used to protect materials from environmental degradation while imparting functional properties such as corrosion resistance, wear resistance, self-cleaning, and antimicrobial activity [1]. In practical applications including marine infrastructure, public transportation, food processing, and medical facilities, microbial adhesion and biofilm formation on coated surfaces can lead to cross-contamination, accelerated material deterioration, and increased maintenance costs. In humid or aqueous environments, biofouling further promotes corrosion and fouling-induced drag, underscoring the need for multifunctional coatings with durable antibacterial and antifouling performance. The integration of inorganic nanoparticles within polymer matrices is widely recognized as a promising approach to achieve such multifunctionality. Owing to its high chemical stability, low cost, minimal toxicity, and pronounced oxidative activity under UV light, titanium dioxide (TiO_2) is widely utilized as a photocatalytic additive [2–4]. Upon UV exposure, TiO_2 forms reactive oxygen species (ROS), including $\bullet\text{OH}$ and $\text{O}_2\bullet^-$ radicals, which play a key role in degrading organic contaminants and damaging microbial cells through oxidative processes. As a result, TiO_2 -containing coatings often exhibit measurable self-cleaning and antibacterial effects. Compared with other crystalline phases of TiO_2 , rutile exhibits properties that make it more suitable for polymer coatings, especially for outdoor and protective purposes, including a high refractive index (~ 2.7), strong light-scattering ability, and excellent weather resistance [5]. These characteristics contribute to enhance UV shielding and reduced photodegradation of polymer matrices compared with anatase-based systems [6–9]. However, rutile TiO_2

suffers from limited visible-light activity and rapid electron–hole recombination, resulting in relatively low antibacterial and antifouling efficiency under natural or indoor lighting conditions.

To overcome these intrinsic limitations, heterostructure engineering and semiconductor coupling have been extensively explored. Among various modifiers, copper(I) oxide (Cu_2O) has been widely investigated because of its narrow band gap (~ 2.17 eV), visible-light absorption (400–500 nm), and intrinsic antibacterial properties [10, 11]. When Cu_2O is coupled with TiO_2 to form $\text{TiO}_2@\text{Cu}_2\text{O}$ heterostructures, a p–n junction is established, leading to more efficient charge carrier separation and reduced electron–hole recombination. This synergistic effect has been quantitatively demonstrated in multiple studies [12–18]. For example, $\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposites showed approximately threefold higher degradation efficiency of Rhodamine B under visible light compared with pristine TiO_2 [19]. Similarly, degradation efficiencies exceeding 95% for benzene and 92–98% for toluene and chlorobenzene were achieved within 2 hours under visible-light irradiation using $\text{TiO}_2\text{--Cu}_2\text{O}$ systems, whereas TiO_2 alone exhibited substantially lower activity under the same conditions [20]. Beyond photocatalytic efficiency, $\text{TiO}_2@\text{Cu}_2\text{O}$ heterostructures exhibit enhanced antibacterial performance through dual mechanisms. Photocatalytically generated ROS induce oxidative stress, while released Cu^{2+} ions directly disrupt bacterial cell membranes and interfere with intracellular enzyme activity [10]. Asadinamin et al. demonstrated that optimized $\text{TiO}_2/\text{Cu}_2\text{O}$ interfaces promote directional electron transfer from Cu_2O to TiO_2 , leading to higher ROS yield and improved antimicrobial efficacy [16]. Experimentally, $\text{Cu}_2\text{O}/\text{TiO}_2$ -based systems have been shown to achieve >95% degradation of methylene blue within 3 hours under visible light, far exceeding the performance of either component alone [21]. Moreover, $\text{Cu}_2\text{O}/\text{TiO}_2$ nanocomposites simultaneously removed volatile organic compounds and achieved complete *E. coli* inactivation under simulated sunlight, maintaining stable performance over multiple reuse cycles [22, 23].

Given these quantitative advantages, $\text{TiO}_2@\text{Cu}_2\text{O}$ nanostructures are promising multifunctional additives for polymer-based coatings. Previous investigations have demonstrated the individual incorporation of TiO_2 or $\text{Cu}_2\text{O}/\text{CuO}$ nanoparticles into polymers such as vinyl ester, epoxy, PMMA, acrylics, PVA, polyurethane, and methacrylic–siloxane resins can improve mechanical properties and impart antibacterial activity [24–38]. However, in most of these systems, antibacterial performance is either

UV-dependent or significantly lowers under visible light, highlighting the advantage of heterostructured $\text{TiO}_2@\text{Cu}_2\text{O}$ additives. Despite their clear synergistic benefits, studies on coatings and polymer nanocomposites incorporating $\text{TiO}_2\text{--Cu}$ heterostructures remain limited. Pal et al. reported that CuO/TiO_2 coatings deposited on polypropylene (PP) achieved complete inactivation of *S. aureus* and *E. coli* within 24 h (log reduction $R > 6$), outperforming pure TiO_2 due to the combined effects of photocatalysis and copper toxicity [39]. Similarly, $\text{CuO}@\text{TiO}_2$ heterojunction coatings applied to PAA-grafted polyethersulfone (PES) membranes achieved 92% degradation of Acid Blue 260 within 60 min and exhibited significantly enhanced antifouling performance while maintaining stable photocatalytic activity over five consecutive cycles [40]. These findings confirm that $\text{TiO}_2\text{--Cu}$ heterostructures provide dual antibacterial mechanisms, improved charge separation, and durable photocatalytic performance, making them particularly attractive for multifunctional polymer coatings.

Poly(vinyl chloride–vinyl isobutyl ether) (PVC-VIBE, also referred to as PVE) represents a promising matrix for protective marine coatings, architectural paints, and specialty functional films due to its favorable balance of mechanical strength, chemical resistance, adhesion, and hydrophobicity derived from the PVC and VIBE segments [41, 42]. This structural combination enables the formation of tough, adherent films capable of embedding inorganic nanoparticles without compromising coating integrity. The incorporation of TiO_2 nanoparticles into PVE coatings has been shown to enhance UV resistance, gloss, and corrosion protection without sacrificing flexibility or adhesion [43]. Moreover, PVE-based nanocomposites containing oxide nanoparticles (TiO_2 , SiO_2) maintained 95% dispersion homogeneity after 30 days, indicating good compatibility between the polymer matrix and inorganic fillers [44]. Nevertheless, quantitative investigations into the antibacterial and antifouling performance of PVE coatings incorporating visible-light-active heterostructures such as $\text{TiO}_2@\text{Cu}_2\text{O}$ remain scarce. Therefore, integrating $\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposites into PVE coatings presents a clear opportunity to combine the established mechanical robustness of PVE with the enhanced visible-light-driven antibacterial and photocatalytic performance of $\text{TiO}_2@\text{Cu}_2\text{O}$. In this study, core–shell $\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposites are green-synthesized and incorporated into PVE-based coatings. The structure, dispersion behavior, mechanical properties, UV–thermal–humidity durability, and antibacterial and antifouling performance of the resulting coatings are systematically investigated.

2. Experimental

2.1. Materials and chemicals

Copper (II) sulfate pentahydrate ($\geq 98\%$), TiO_2 nanopowder (rutile, ≤ 100 nm, CAS No. 637262), L-ascorbic acid (99%), polysorbate 80 (Tween 80), and polyethylene glycol 600 (PEG) were purchased from Sigma–Aldrich. Ethanol (99.5%), acetone (99%), butyl acetate (99%), and xylene were supplied by Xilong (China). Vinyl chloride–vinyl isobutyl ether copolymer resin (MP35, CAS No. 25154-8-2), containing 75% vinyl chloride and 25% vinyl isobutyl ether with a viscosity of 35 cP, was obtained from Sino Sunman International (China) and denoted as PVE throughout this study.

2.2. Green synthesis of $\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposites

Cu or Cu_2O doping enhances the photocatalytic and antibacterial performance of TiO_2 only below a critical loading; excess dopant causes activity loss due to surface blocking. For antibacterial $\text{TiO}_2@\text{Cu}_2\text{O}$ heterojunctions, previous studies reported an optimal Cu_2O content of 5 wt.% [13,45], which was adopted in this work.

TiO_2 nanopowder (1 g) was dispersed in 50 mL ethanol/distilled water (70/30 v/v) by stirring (350 rpm, 15 min) and ultrasonication (40 kHz, 30 min). A $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution (0.174 g in 10 mL water) was added dropwise, then being magnetic stirred for 30 min. Subsequently, 10 mL of 0.625 N NaOH was added dropwise and the mixture stirred for 60 min. L-ascorbic acid was then introduced (LAA/ Cu^{2+} molar ratio = 2:1), followed by Tween 80 and PEG. The reaction was maintained at 60 °C and 600 rpm for 120 min. The resulting orange-yellow suspension was centrifuged (9,000 rpm), washed with ethanol/water (70/30) to neutral pH and acetone, and dried at 80 °C under vacuum to obtain $\text{TiO}_2@\text{Cu}_2\text{O}$ powder. Tween 80 and PEG acted as nonionic surfactants to control particle size, morphology, and dispersion.

2.3. Preparation of nanocomposite coatings

$\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposites (2 wt.% relative to resin) were dispersed in butyl acetate (1/10 g/mL) by stirring (1 h) and ultrasonication (40 kHz, 15 min). After further stirring, a PVE solution in xylene was added and mixed at 300–400 rpm for 3 h, followed by ultrasonication (30 min) and ball milling (24 h). Coatings were applied on steel and glass substrates using an Erichsen Film Applicator (wet thickness 150 μm ; dry thickness 30 ± 3 μm) and conditioned at 25 °C and 60% RH for 24 h.

2.4. Fabrication of three-layer coating systems

Three-layer coating systems with a PVE topcoat, with or without $\text{TiO}_2@\text{Cu}_2\text{O}$ additives, were prepared on C45 steel panels ($10 \times 15 \text{ cm}^2$). The primer and the intermediate layers were epoxy coatings containing organically modified ZnO and TiO_2 nanoparticles. The PVE topcoat containing $\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposites had a thickness of 120–130 μm .

2.5. Antibacterial activity test

Antibacterial performance was evaluated using the liquid culture method with *Pseudomonas stutzeri* B27. Single-layer PVE films (with and without $\text{TiO}_2@\text{Cu}_2\text{O}$) were cut (0.4 g) and immersed in 4 mL LB medium, followed by inoculation with 40 μL bacterial suspension. Samples were incubated at 37 °C and 200 rpm. Bacterial growth was quantified by OD_{600} at 0 and 24 h. Negative controls (no antibacterial agent), positive controls (ampicillin/cephalexin, 100 $\mu\text{g/mL}$), and material blanks (without bacteria) were prepared under identical conditions.

2.6. Accelerated UV–thermal–humidity aging

Accelerated aging was conducted on three-layer coating samples according to ASTM G154 [16] using a QUV device. Each cycle included under 8 h UV exposure at 60 °C and 4 h condensation at 50 °C. The total exposure time was 1080 h (90 cycles).

2.7. Natural seawater immersion test

Three-layer coating samples were immersed in natural seawater collected from Ha Long Bay using a dynamic flow tank ($44 \times 31 \times 21 \text{ cm}^3$), with a flow velocity of 4 m/s at 25–30 °C.

2.8. Characterization

FTIR measurements were carried out by using a Nicolet iS10 spectrometer (4,000–400 cm^{-1}). TEM images were obtained with a JEOL JEM1010 microscope. XRD patterns were obtained by a Siemens D5000 diffractometer with $\text{CuK}\alpha$ radiation. UV–Vis spectra were measured using a Jasco V770 spectrophotometer. SEM/EDS analyses were conducted on JEOL JSM–IT800 and JSM-6510LV microscopes.

Surface drying time was determined according to ISO 9117-3:2010 and ISO 9117-1:2009. Relative hardness was measured following ISO 1522. Adhesion strength was evaluated by pull-off testing according to ISO 4624. Impact resistance was measured according to ISO 6272-1. Abrasion resistance was determined by ASTM D968-15 using the falling sand method:

$$\text{Abrasion resistance (AR)} = \frac{\text{Volume of sand (L)}}{\text{Thickness of the abraded coating (mil)}} \times 25.4 \text{ (L/mil)} \text{ (Equation 1)}$$

The carbonyl index (CI) was determined as $CI = \frac{I_{1710}}{I_{1425}}$ (Equation 2), where I_{1710} and I_{1425} are the FTIR absorbance intensities at 1710 cm^{-1} and 1425 cm^{-1} , respectively. Contact angles were measured with an OCA 50 instrument (Dataphysics). Color variation was evaluated according to ASTM D6510, CIELAB AB 1.1.1, D1925, and E313, and total color difference (ΔE^*) was obtained from L^* , a^* , b^* values using Equation 3.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad \text{(Equation 3)}$$

Where, $\Delta L^* = L_t^* - L_0^*$; $\Delta a^* = a_t^* - a_0^*$; $\Delta b^* = b_t^* - b_0^*$ (t denotes the measurement time and 000 refers to the initial value of the unexposed sample)

Gloss was measured according to ISO 2813:2014. Copper ion release ($\text{Cu}^+/\text{Cu}^{2+}$) was quantified by AAS using an iCE 3500 spectrometer.

3. Results and Discussion

3.1. Synthesis of $\text{TiO}_2@\text{Cu}_2\text{O}$ nanopowder

a) FTIR spectra

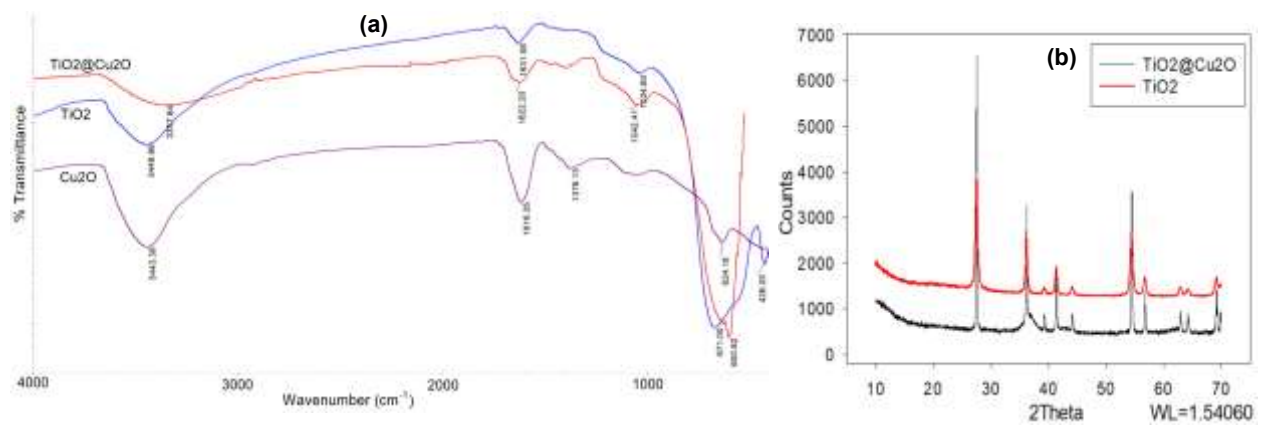


Figure 1. FTIR spectra (a) and XRD patterns (b) of Cu_2O , TiO_2 nanoparticles, and $\text{TiO}_2@\text{Cu}_2\text{O}$ hybrid nanocomposites.

Figure 1a represents the FTIR spectra of Cu_2O , TiO_2 , and $\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposites. The broad band appeared around 3400 cm^{-1} and the peak at 1600 cm^{-1} corresponding to the stretching and bending vibrations of surface $-\text{OH}$ groups in adsorbed water. Strong absorptions in the $400\text{--}800 \text{ cm}^{-1}$ region are attributed to metal–oxygen bonds, with characteristic $\text{Ti}\text{--}\text{O}$ and $\text{Cu}\text{--}\text{O}$ vibrations at 671 cm^{-1} and 634 cm^{-1} , respectively [46–48]. Compared to original TiO_2 , the $\text{TiO}_2@\text{Cu}_2\text{O}$ spectrum exhibits a broadened band with peaks at 600 cm^{-1} and 627 cm^{-1} , shifted to lower wavenumbers, indicating reduced photon adsorption energy. This shift suggests the $\text{Ti}\text{--}\text{O}\text{--}\text{Cu}$ bond formation by Cu_2O deposition on

TiO₂, leading to a heterojunction structure [48]. The O–H stretching band also becomes broader and shifts to lower wavenumbers, implying enhanced surface hydrophilicity. Weak peaks at 1376 cm⁻¹ and 2900 cm⁻¹ are assigned to residual C–H vibrations from Tween 80 and PEG, present only in trace amounts. The formation of Cu₂O proceeds according to the reaction [49, 50]:

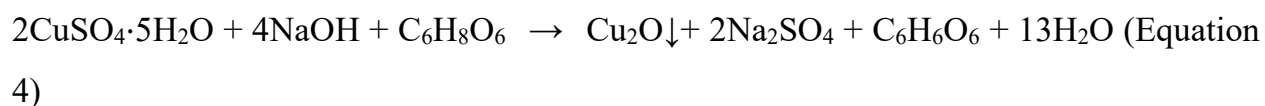


Figure 1b presents the XRD pattern of TiO₂, which is consistent with the rutile phase, exhibiting reflections at $2\theta = 27.4^\circ, 36.1^\circ, 41.2^\circ, 44.1^\circ, 54.4^\circ$, and 56.5° [31, 32, 51]. After being incorporated with Cu₂O, the rutile structure is preserved. Peak broadening and increased intensity near $2\theta \approx 36^\circ$ arise from overlap between TiO₂ (101) and cubic Cu₂O (111) reflections, confirming Cu₂O formation within the heterostructure [52]. No CuO or metallic Cu phases were detected, indicating successful synthesis of TiO₂@Cu₂O heterojunctions.

b) Structural morphology

TEM images (Figure 2a and b) show that both TiO₂ and TiO₂@Cu₂O nanocomposites possess a rod-like morphology. The TiO₂ nanorod core has a length of ~60–80 nm and a diameter of ~20–30 nm, consistent with supplier data (Figure 2a). Darker contrast shells of TiO₂@Cu₂O nanocomposites correspond to Cu₂O nanoparticles deposited on the TiO₂ surface, attributable to their higher electrical conductivity and electron absorption capability (Figure 2b) [14]. These proved a clear core–shell structure of obtained hybrid nanocomposites.

SEM images (Figure 2c) reveal uniform TiO₂@Cu₂O nanorods. Elemental analysis by EDX indicates the existence of Ti, O, and Cu, with no detectable carbon, implying a high level of purity. The elemental composition of O, Ti and Cu was respective to 50.58 wt.%, 46.54 wt.%, and 2.88 wt.% (Figure 2d), corresponding to a Cu₂O loading of ~4.17 wt.% and a doping efficiency of 83.4%. This value lies within the optimal Cu₂O range (≤ 5 wt.%) reported for antibacterial TiO₂@Cu₂O systems [13, 45]. EDX mapping (Figure 2e–h) shows homogeneous distribution of three above elements throughout the nanostructures, supporting the formation of uniform core–shell TiO₂@Cu₂O architecture.

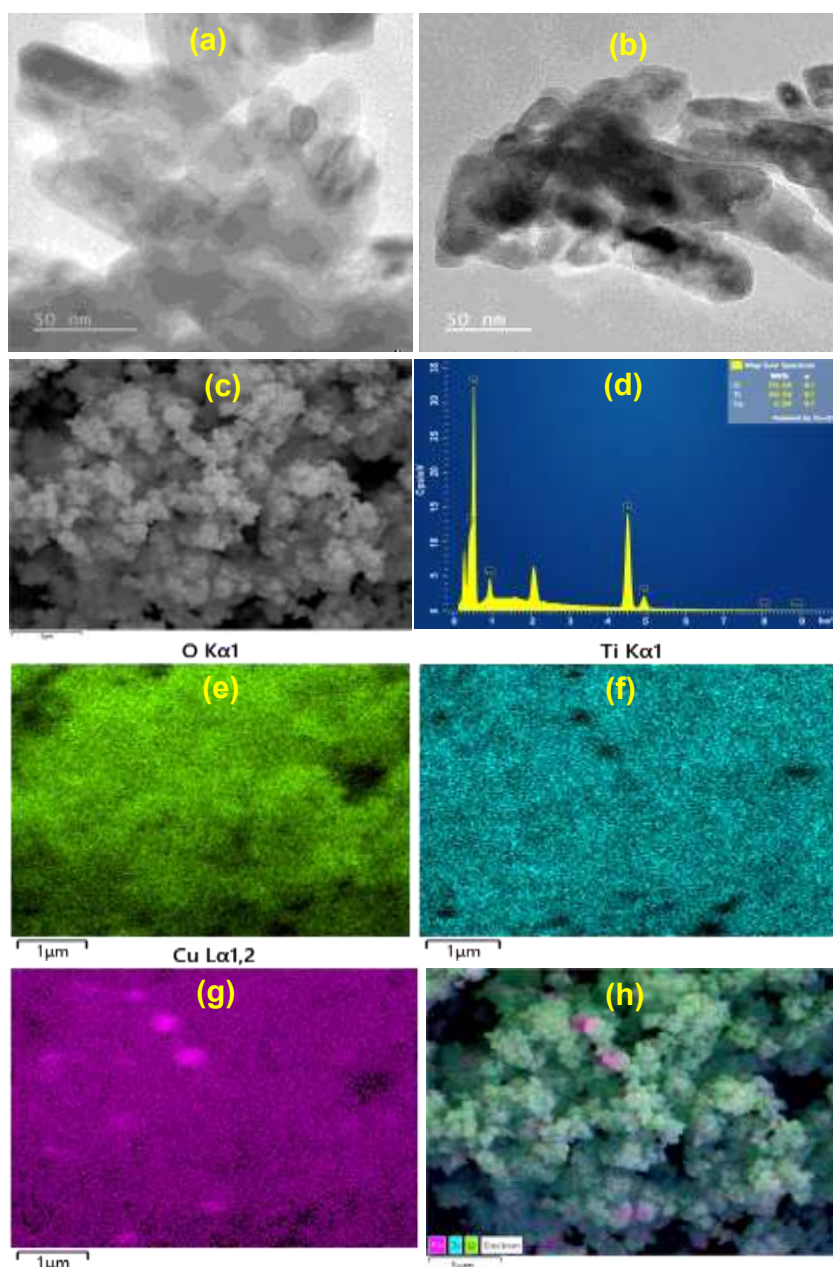


Figure 2. TEM images of (a) TiO₂ and (b) TiO₂@Cu₂O nanocomposites; (c) SEM image, (d) EDX spectrum, and (e–h) EDX elemental mappings of the TiO₂@Cu₂O nanocomposite.

d) UV–Vis analysis

Figure 3 shows that rutile TiO₂ exhibits a primary absorption edge at ~415 nm ($E_g \approx 3.0$ – 3.1 eV). After Cu₂O modification, this edge shifts slightly to ~425 nm, accompanied by an additional weak absorption at 450 nm and a broad band extending from 610 to 1100 nm. These features originate from Cu₂O ($E_g \approx 2.05$ eV), which enables visible-light absorption and promotes charge transfer across the TiO₂/Cu₂O heterojunction. Consequently, light absorption is extended from the UV into the visible region, confirming enhanced photocatalytic and antibacterial potential under sunlight [13, 53].

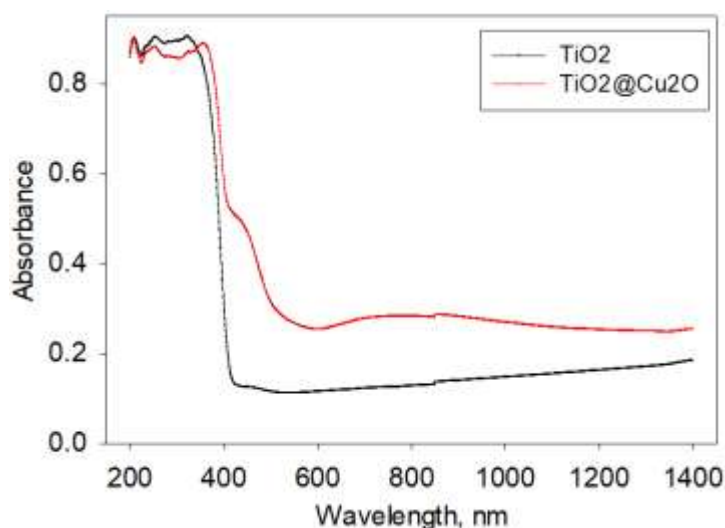


Figure 3. UV–Vis spectra of TiO₂ nanostructures and TiO₂@Cu₂O nanocomposites.

3.2. Some characteristics of single coatings based on PVE resin and hybrid TiO₂@Cu₂O nanoparticles

a) Surface drying time and morphology of coatings

Table 1 summarizes the surface drying time of PVE-based coatings. Incorporation of 1.0 wt.% TiO₂ reduced the drying time from 180 min (neat PVE) to 170 min, indicating that TiO₂ promotes the curing process. Replacing TiO₂ with TiO₂@Cu₂O further shortened the drying time. While the coating with 0.5 wt.% TiO₂@Cu₂O required 170 min, increasing the nanocomposite content to 1.0–2.0 wt.% reduced the drying time to 165 min, and to 160 min at 4.0 wt.%. These results demonstrate that TiO₂@Cu₂O nanocomposites are more effective curing promoters than pristine TiO₂. The accelerated drying might cause by the photocatalytic activity of TiO₂ under ambient light, which generates reactive oxygen species (ROS), enhances cross-linking, and facilitates solvent evaporation. TiO₂@Cu₂O exhibits stronger photocatalytic activity due to visible-light activation, producing more ROS and further accelerating film curing. After drying, all coatings showed high gloss; films on glass appeared lighter and more transparent, whereas those on steel were darker with minimal color variation.

Table 1. Surface drying time of PVE-based coatings with TiO₂@Cu₂O nanocomposites

Coded samples	Nano TiO ₂ @Cu ₂ O content (wt.%)	Nano TiO ₂ content (wt.%)	Surface drying time (minutes)
PVE	0	0	180
PVE 1.0TiO ₂	0	1.0	170
PVE 0.5 TiCu	0.5	0	170

PVE 1.0 TiCu	1.0	0	165
PVE 2.0 TiCu	2.0	0	165
PVE 4.0 TiCu	4.0	0	160

Cross-sectional SEM images indicated neat PVE films were homogeneous (Figure 4a), whereas PVE with 1.0 wt.% TiO₂ showed large clusters (Figure 4b). At the same loading, TiO₂@Cu₂O nanocomposites were more finely dispersed (Figure 4c). At 4.0 wt.% TiO₂@Cu₂O, microvoids appeared and fracture surfaces became smoother, likely due to accelerated curing and increased brittleness, which may adversely affect mechanical strength (Figure 4d).

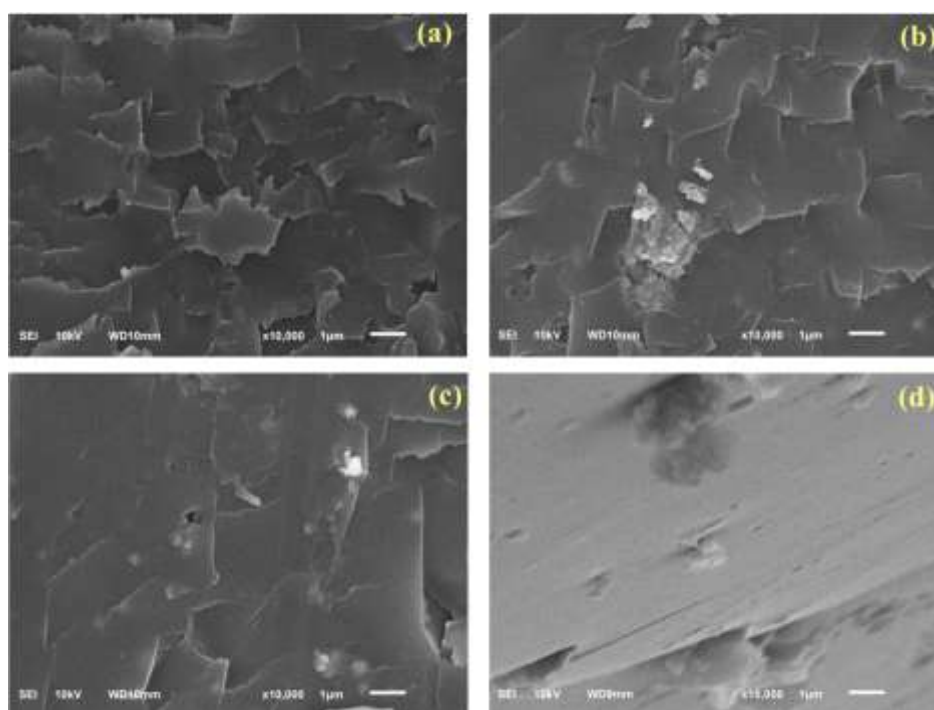


Figure 4. Cross-sectional SEM images (10×) of coating films: (a) neat PVE; (b) PVE with 1.0 wt.% TiO₂; and PVE with TiO₂@Cu₂O at (c) 1.0 wt.% and (d) 4.0 wt.%.

b) *Mechanical properties*

As summarized in Table 2, the nanoparticle incorporation generally enhanced the mechanical properties of PVE coatings. With 1.0 wt.% TiO₂, adhesion, abrasion resistance, impact resistance, and relative hardness of PVE increased by 1.5%, 3.7%, 8.6%, and 18.9% respectively. TiO₂@Cu₂O nanocomposites provided a more pronounced reinforcing effect. Even at 0.5 wt.%, improvements exceeded those achieved with TiO₂. Mechanical properties increased steadily with TiO₂@Cu₂O content up to 2.0 wt.%, where maximum enhancements were obtained (51.4% hardness, 28.6% impact resistance, 12.5% adhesion,

and 22.9% abrasion resistance relative to neat PVE). At higher loadings (4.0 wt.%), performance declined due to nanoparticle agglomeration and microvoid formation. These results highlight the critical role of microstructural uniformity in determining coating performance.

Table 2. Mechanical properties of PVE-based coatings containing $\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposites

Samples	Relative hardness	Impact resistance (kg/cm)	Adhesion strength (MPa)	Sand abrasion resistance (L/mil)
PVE	0.37 ± 0.04	35 ± 0.3	1.36 ± 0.02	101.7 ± 2.1
PVE 1.0 TiO_2	0.44 ± 0.05	38 ± 0.2	1.38 ± 0.03	105.5 ± 1.8
PVE 0.5 TiCu	0.50 ± 0.05	40 ± 0.2	1.49 ± 0.04	120.0 ± 3.5
PVE 1.0 TiCu	0.57 ± 0.03	43 ± 0.4	1.51 ± 0.05	123.2 ± 2.4
PVE 2.0 TiCu	0.56 ± 0.04	45 ± 0.4	1.53 ± 0.05	125.0 ± 3.3
PVE 3.0 TiCu	0.53 ± 0.06	41 ± 0.3	1.49 ± 0.02	120.4 ± 1.6
PVE 4.0 TiCu	0.52 ± 0.05	35 ± 0.5	1.46 ± 0.03	117.8 ± 2.7

c) *Antibacterial performance*

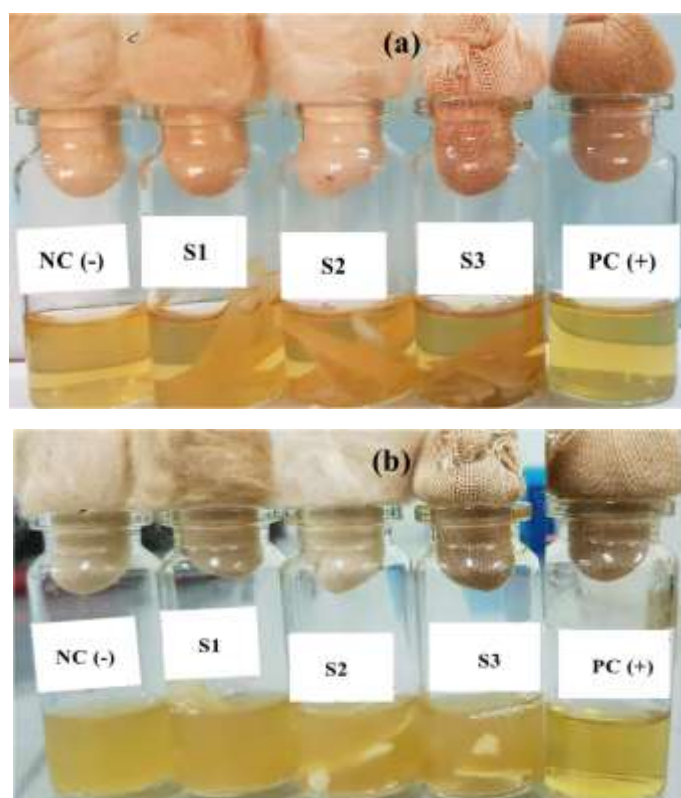


Figure 5. Growth of *Pseudomonas stutzeri* B27 at (a) 0 h and (b) after 24 h of incubation at 37 °C with shaking at 200 rpm.

Based on its superior mechanical properties, the PVE coating containing 2.0 wt.% TiO₂@Cu₂O (PVE-2.0TiCu) was selected for antibacterial evaluation. Neat PVE and PVE-2.0Ti coatings were used for comparison. Figure 5 illustrates the growth behavior of *Pseudomonas stutzeri* B27 after 0 and 24 h of incubation. Antibacterial efficiency was calculated according to Ref. [54].

$$\text{Antibacterial efficiency (\%)} = \frac{\text{OD}_{\text{negative control}} - \text{OD}_{\text{sample}}}{\text{OD}_{\text{negative control}}} \times 100\% \quad (\text{Equation 5})$$

$$\text{Corrected antibacterial efficiency (\%)} = \frac{\text{OD}_{\text{negative control}} - (\text{OD}_{\text{sample}} - \text{OD}_{\text{background}})}{\text{OD}_{\text{negative control}}} \times 100\%$$

(Equation 6)

Where, OD_{negative control}, OD_{sample}, and OD_{back ground} represent the optical density of the negative control, the tested sample and background, respectively, after incubation.

As shown in Table 3, the negative control exhibited normal bacterial growth, while the positive control (Cephalexin) showed strong inhibition. Neat PVE and PVE-TiO₂ coatings exhibited negligible antibacterial activity (3.55% and 6.51%, respectively). In contrast, PVE-TiO₂@Cu₂O achieved a significant reduction of 36.09%. This enhancement is believed to be related to the visible-light activity of the TiO₂@Cu₂O heterojunction, whereas TiO₂ remained largely inactive in the absence of UV irradiation.

Table 3. OD₆₀₀ values of *Pseudomonas stutzeri* B27 in PVE-based coating systems and corresponding antibacterial efficiency before and after background subtraction

Samples (Sample code and composition)	OD ₆₀₀		Background OD ₆₀₀ (24 h)	Antibacterial efficiency, %(a)	Corrected antibacterial efficiency (b)
	0 hour	24 hours			
S1: LB medium + PVE film + B27 bacteria	-	0.163	-	3.55	4.73
NC1: LB medium + PVE film	-	-	0.002	-	-
S2: LB medium + PVE 2.0Ti film + B27 bacteria	-	0.158	-	6.51	23.08
NC2: LB medium + PVE 2.0Ti film	-	-	0.028	-	-

S3: LB medium + PVE-2.0TiCu film + B27 bacteria	-	0.108		36.09	51.48
NC3: LB medium + PVE-2.0TiCu film	-	-	0.026	-	-
NC (Negative control): LB medium + B27 bacteria	0.038	0.169	-	-	-
PC (Positive control): LB medium + Cephalexin + B27 bacteria	0.014	0.016	-	-	-

Note: The values presented in panels (a) and (b) were determined based on Equations (5) and (6), respectively.

After correcting for background turbidity caused by nanoparticle scattering (Table 3), the antibacterial efficiencies were recalculated as 4.73% (PVE), 23.08% (PVE–TiO₂), and 51.48% (PVE–TiO₂@Cu₂O) via Equation 6. These results confirm that TiO₂@Cu₂O nanocomposites impart strong antibacterial functionality to PVE coatings even under ambient light conditions. The developed coatings are suitable for indoor protective applications. Under outdoor or marine conditions, antibacterial performance is expected to be further enhanced by broader light exposure. However, surface modification or the incorporation of light stabilizers will be necessary to mitigate potential photocatalytic degradation of the polymer matrix, which will be addressed in future studies.

3.3. Environmental durability and surface stability of triple-layer coatings with PVE topcoat

PVE is well suited for protective coatings on steel structures operating in marine environments, including ships, submarines, offshore platforms, industrial equipment, as well as composite materials and consumer products. Its performance can be further enhanced through the incorporation of nano-additives. As demonstrated in the preceding sections, TiO₂@Cu₂O nanoparticles significantly enhanced the mechanical strength and antimicrobial performance of the PVE coating. Accordingly, this modified PVE system was selected as the outermost layer

in a three-layer coating architecture designed for marine steel protection. The durability of the coatings was evaluated using UV–humidity accelerated aging and natural seawater immersion tests, while biofouling resistance and Cu ion release behavior were also investigated.

a) Effect of $\text{TiO}_2@\text{Cu}_2\text{O}$ nanoparticles on UV–humidity aging behavior of PVE topcoats

- Photochemical degradation and surface chemical variation*

ATR-FTIR spectroscopy was employed to investigate the chemical changes occurring in the PVE topcoat of the triple-layer coating system before and after accelerated UV–humidity aging (Figure 6). Prior to testing, both PVE and PVE containing $\text{TiO}_2@\text{Cu}_2\text{O}$ (PVE-TiCu) coatings exhibited characteristic absorption peaks and bands of the PVE matrix, including the stretching vibrations of $-\text{CH}_3$, $-\text{CH}_2-$, and $=\text{CH}-$ groups in the range of $2832\text{--}2945\text{ cm}^{-1}$, the bending vibrations of $-\text{CH}_3$ and $-\text{CH}_2-$ at 1322 and 1425 cm^{-1} , and the $\text{C}-\text{O}$ and $\text{C}-\text{O}-\text{C}$ vibrations at 1212 and 1085 cm^{-1} . In the PVE-TiCu sample, the characteristic $\text{C}-\text{Cl}$ absorption band at 601 cm^{-1} [55] was slightly shifted to 609 cm^{-1} due to overlap with $\text{Ti}-\text{O}$ and $\text{Cu}-\text{O}$ vibrations originating from the $\text{TiO}_2@\text{Cu}_2\text{O}$ nanoparticles. Overall, the FTIR spectra were dominated by the PVE polymer matrix.

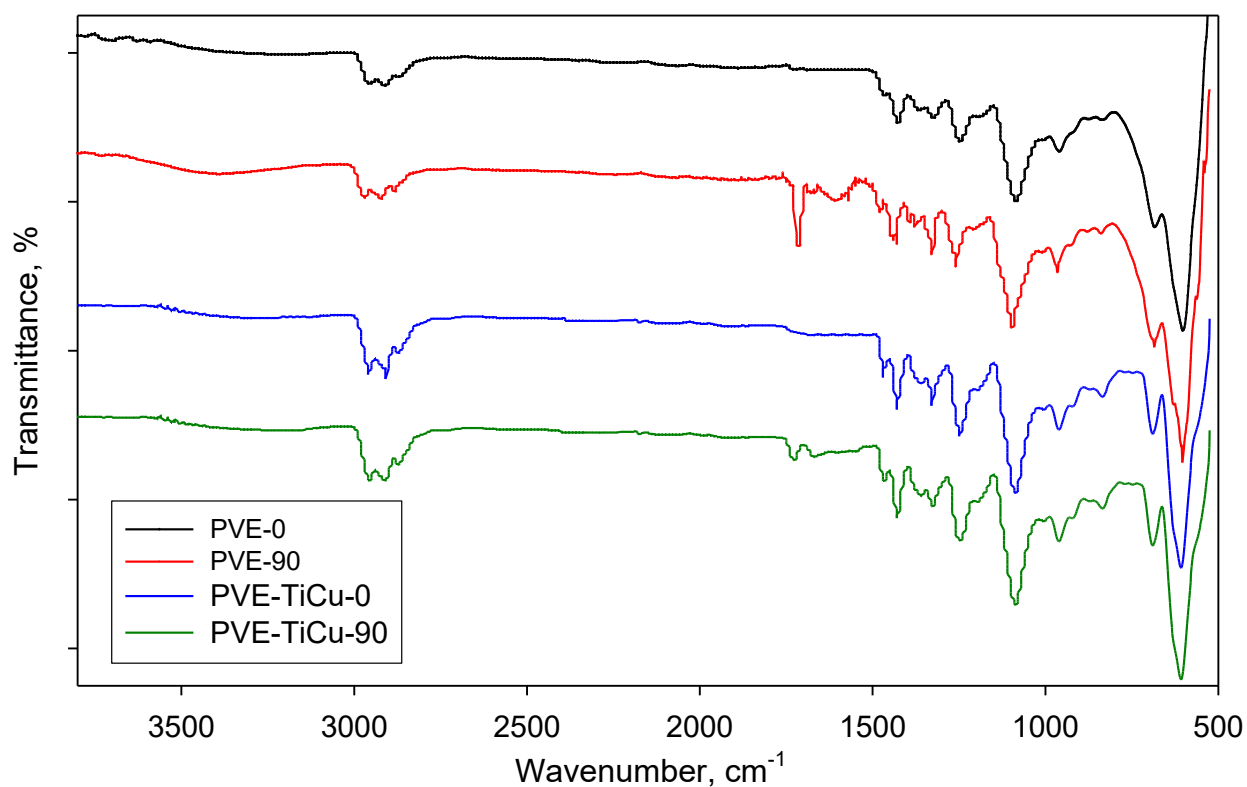


Figure 6. ATR-FTIR spectra of triple-layer coating systems with PVE topcoats, without and with $\text{TiO}_2@\text{Cu}_2\text{O}$ hybrid nanoparticles (PVE-TiCu), before and after 90 cycles of accelerated UV–humidity aging.

After 90 UV–humidity cycles, the positions of the main absorption bands showed negligible shifts; however, an increase in intensity and broadening in the 1080–1220 cm^{-1} region was observed, together with the appearance of a new band at approximately 1710 cm^{-1} corresponding to C=O stretching. This indicates the formation of photo-oxidation products during aging. The carbonyl band intensity was noticeably higher for the PVE coating than for the PVE-Ti coating. This trend is consistent with the carbonyl index (CI) values listed in Table 4, where the CI of PVE increased from 0 to 2.62, whereas that of PVE-Ti increased only to 0.69 after the same exposure duration. These results demonstrate that $\text{TiO}_2@\text{Cu}_2\text{O}$ nanoparticles, with TiO_2 in the rutile phase, act as effective inorganic UV stabilizers by shielding and scattering UV radiation, thereby suppressing photo-oxidative degradation of the polymer chains.

Table 4. Carbonyl index (CI) of the triple-layer coating system before and after different accelerated aging durations

Testing time (cycles)	PVE	PVE-TiCu
0	0	0
20	0.85	0.12
40	1.40	0.34
90	2.62	0.69

SEM images of the coating surfaces before and after UV–humidity aging are shown in Figure 7. Prior to exposure, both coatings exhibited relatively smooth and uniform surfaces. After 90 cycles, the PVE coating developed numerous crack-like grooves and surface voids, characteristic of photo-oxidative degradation. In contrast, the PVE-TiCu coating showed only minor microvoids, primarily localized at the polymer–nanoparticle interfaces. These observations clearly indicate that $\text{TiO}_2@\text{Cu}_2\text{O}$ nanoparticles effectively mitigate polymer degradation under the combined effects of UV radiation, humidity, and elevated temperature. The results are consistent with previous studies reporting the superior UV stability of rutile-phase TiO_2 [6–9], while the incorporation of Cu_2O does not alter the crystalline structure of TiO_2 .

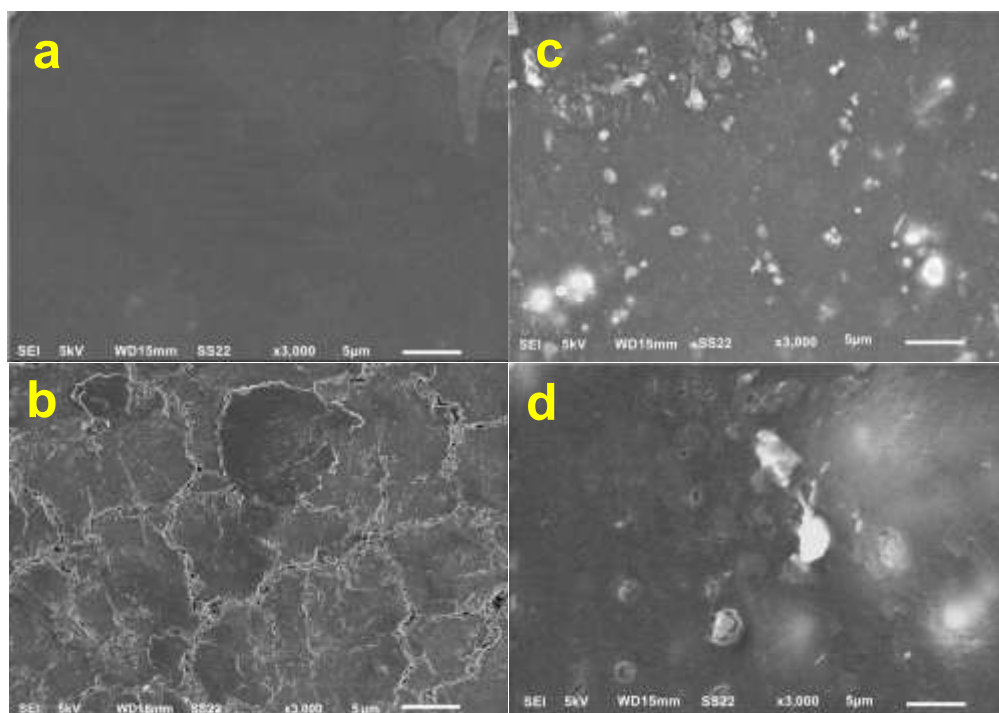


Figure 7. SEM surface images of PVE and PVE–TiCu coatings before (a, c) and after 40 cycles of accelerated UV–humidity aging (b, d).

- *Optical and surface appearance changes*

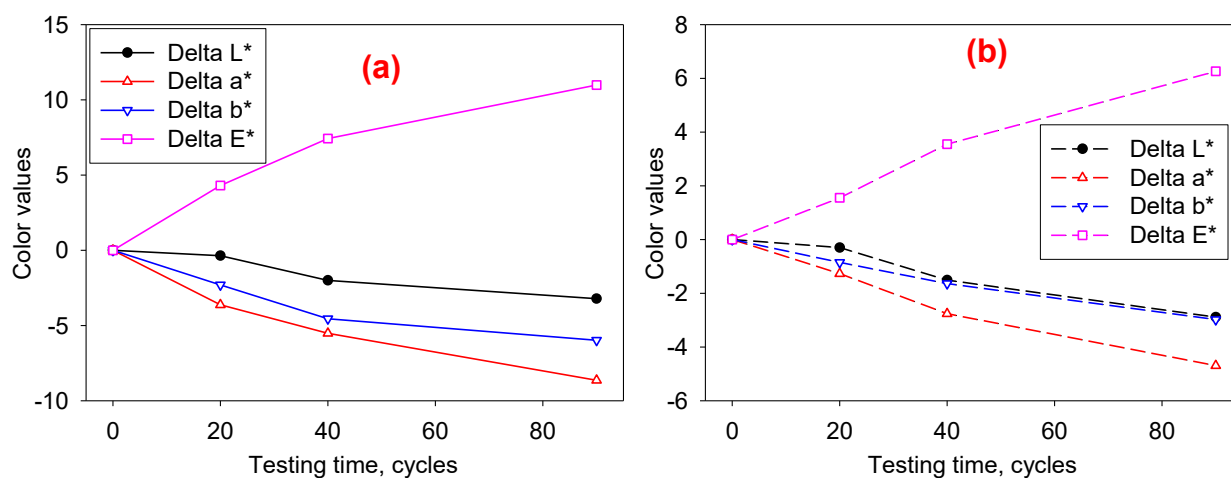


Figure 8. Evolution of color parameters (L^* , a^* , b^*) of the triple-layer coating system during accelerated UV–humidity aging, with PVE (a) and PVE–TiCu (b) as the topcoat.

Color changes of the triple-layer coatings before and after UV–humidity exposure was evaluated using the CIE Lab^* color system according to ISO 2470. As shown in Figure 8, the total color difference (ΔE^*) increased progressively with exposure time for both coating systems. The L^* , a^* , and b^* values decreased, indicating a gradual darkening of the coating surfaces. The color degradation of the PVE coating was significantly more pronounced than that of the PVE–TiCu coating. After 20, 40, and 90 cycles, the ΔE^* values of the PVE coating reached 4.31, 7.43, and 10.99, respectively, which were nearly twice

those of the PVE-TiCu coating (1.56, 3.55, and 6.27). Such color changes become visually perceptible when ΔE^* exceeds 3–5 [20], consistent with the surface appearance observed in the photographs after aging.

Gloss is inversely related to surface roughness. The gloss values of the triple-layer coatings measured at incident angles of 20°, 60°, and 85° are summarized in Table 5. A gradual decrease in gloss was observed with increasing exposure time for both coatings, indicating surface degradation induced by UV–humidity aging. At a 20° angle, the gloss of the PVE coating decreased sharply from 58.4 GU to 12.4 GU after 90 cycles, while similar trends were observed at 60° and 85°. The most pronounced gloss loss occurred within the first 20 cycles. In contrast, the PVE-Ti coating exhibited a much slower rate of gloss reduction, and its retained gloss values remained significantly higher than those of the PVE coating at corresponding exposure times (Figure 9). This result further confirms the stabilizing effect of $\text{TiO}_2@\text{Cu}_2\text{O}$ nanoparticles on the coating surface under UV–humidity conditions.

Table 5. Gloss values measured at different incidence angles of triple-layer coating systems with PVE and PVE- $\text{TiO}_2@\text{Cu}_2\text{O}$ as the topcoat before and after different cycles of accelerated UV–humidity aging.

Time. cycles	PVE			PVE-TiCu		
	20°	60°	85°	20°	60°	85°
0	58.4	77.8	96.8	58.3	77.6	96.4
20	32.6	48.2	68.5	53.6	67.4	79.8
40	20.7	31.2	54.2	47.7	54.8	67.4
90	12.4	17.3	21.6	34.1	42.9	49.1

- *Surface wettability changes*

Before aging, the water contact angles of the PVE and PVE-Ti coatings were 84.02° and 77.90°, respectively, indicating weak hydrophilicity. The incorporation of $\text{TiO}_2@\text{Cu}_2\text{O}$ nanoparticles slightly increased the hydrophobicity of the PVE-Ti coating. After UV–humidity exposure, the contact angles of both coatings decreased with time; however, the reduction was much more pronounced for the PVE coating. After 90 cycles, the contact angle of the PVE coating decreased by nearly 8°, whereas that of the PVE-Ti coating decreased by only ~1° (Figure 9). This decrease in contact angle is attributed to photo-oxidative degradation of the polymer, leading to the formation of oxygen-containing

functional groups on the surface. The slower and less pronounced changes observed for the PVE-TiCu coating demonstrate the protective role of $\text{TiO}_2@\text{Cu}_2\text{O}$ nanoparticles against environmental aging.

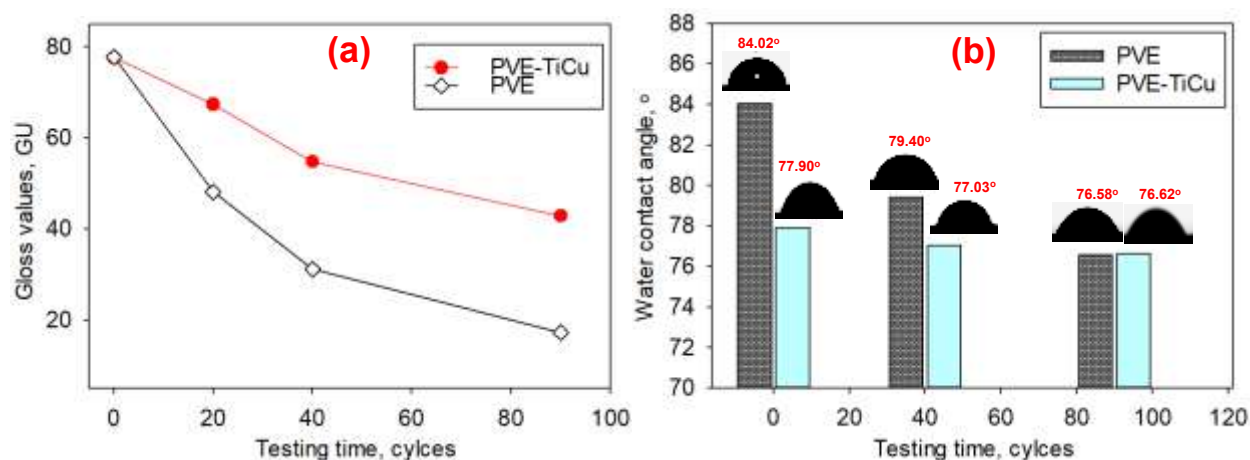


Figure 9. Evolution of (a) gloss values measured at 60° and (b) water contact angles of the triple-layer coating system during accelerated UV–humidity aging.

b) Surface stability and antifouling-related behavior during seawater immersion

- *Biofilm formation and surface property changes*

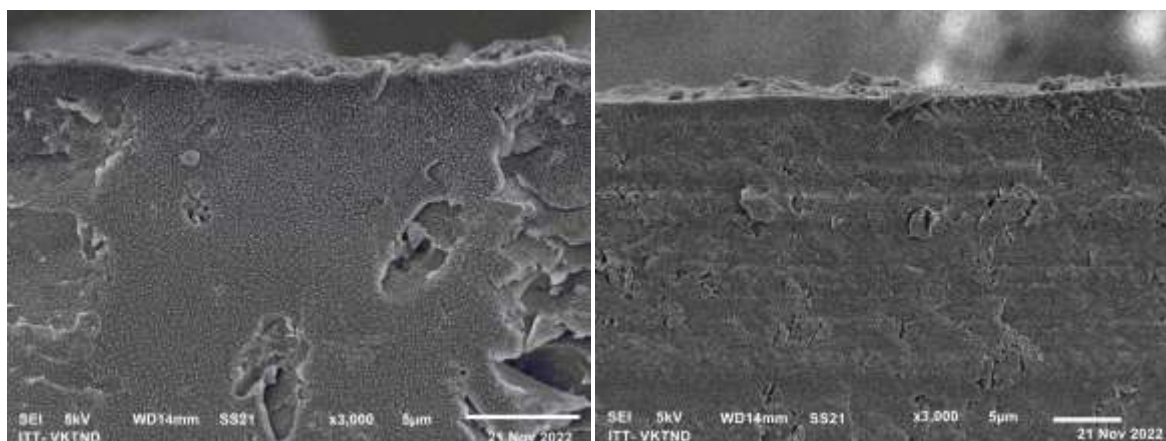


Figure 10. Cross-sectional SEM images of the PVE (left) and PVE–Ti (right) coatings.

Cross-sectional SEM images after 90 days of seawater immersion are presented in Figure 10. Both coatings remained generally homogeneous; however, the PVE coating contained a higher density of microdefects such as capillaries and pores, whereas the PVE-Ti coating exhibited a more compact and uniform structure. Notably, a porous biofilm layer formed on the outer surface of the coatings due to microbial activity in the seawater environment. The biofilm thickness was significantly greater on the PVE coating, with an average thickness of $1.03\ \mu\text{m}$ ($0.67\text{--}1.54\ \mu\text{m}$), compared to $0.69\ \mu\text{m}$ ($0.58\text{--}1.05\ \mu\text{m}$) for the PVE-Ti coating. The presence of $\text{TiO}_2@\text{Cu}_2\text{O}$ nanoparticles effectively reduced biofilm formation, thereby improving antifouling performance.

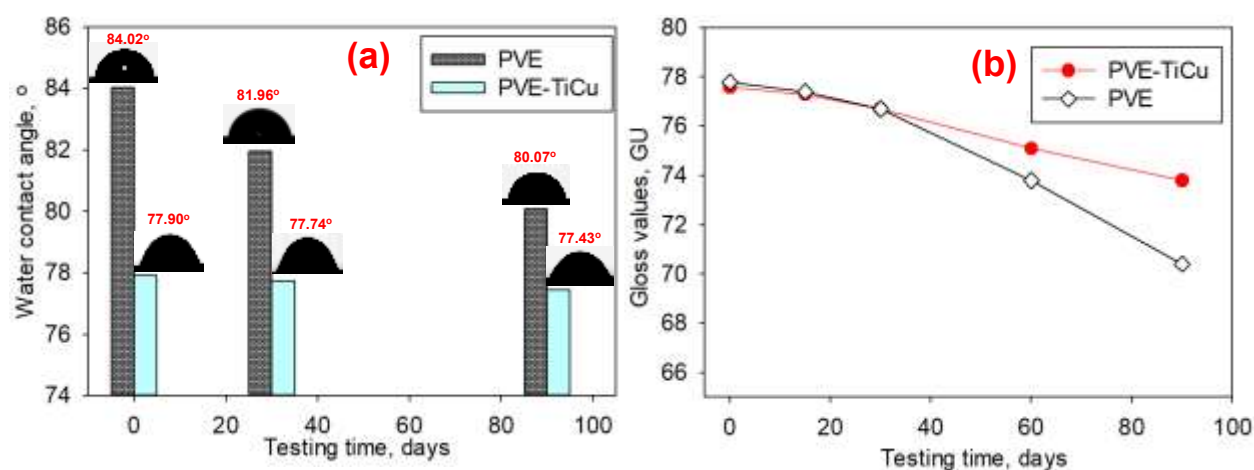


Figure 11. Time-dependent variation of water contact angles of the coating films during immersion in artificial seawater.

During immersion in natural seawater, the contact angles of the coatings exhibited only minor changes over time (Figure 11a). The PVE-Ti coating showed a negligible decrease of approximately 0.5° after 40 days, whereas the contact angle of the PVE coating decreased by nearly 4° , from 84.02° to 80.07° . This result indicates superior surface stability of the nanoparticle-modified coating in marine environments.

Table 6. Gloss values measured at different angles of PVE and PVE–TiCu coatings during immersion in natural seawater

Testing time (days)	PVE			PVE-TiCu		
	20°	60°	85°	20°	60°	85°
0	58.4	77.8	96.8	58.3	77.6	96.4
15	57.7	76.4	94.2	58.2	77.3	95.9
30	56.8	76.7	93.5	57.9	76.7	95.0
60	54.7	73.8	91.6	56.5	75.1	94.4
90	52.4	70.4	85.3	53.4	73.8	92.9

The gloss values of both coatings decreased gradually during seawater immersion (Table 6). However, the gloss loss of the PVE-Ti coating was minimal ($<5\%$), remaining within acceptable limits for surface quality evaluation. In contrast, the PVE coating exhibited a larger gloss reduction of approximately 10–11%, suggesting more pronounced surface deterioration (Figure 11b).

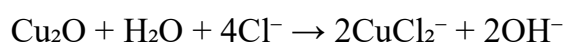
- *Controlled Cu ion release and antifouling mechanism*

Cumulative copper ion ($\text{Cu}^+/\text{Cu}^{2+}$) release from the PVE–Ti coating during immersion in natural seawater was quantified using atomic absorption spectroscopy (AAS), as presented in Table 7. The release profile clearly exhibits three distinct stages: (i) an initial rapid increase during approximately the first 21 days, (ii) a transition region, and (iii) a plateau corresponding to a quasi–steady-state release. This trend is also consistent with the Cu release kinetics illustrated in Figure 12.

Table 7. Cumulative release of Cu^+ as a function of immersion time in natural seawater

Immersing time (days)	Cumulative release of Cu^+ ($\mu\text{g/L}$)
0	0
1	5.2 ± 0.2
3	11.8 ± 0.4
7	13.7 ± 0.3
14	18.3 ± 0.3
21	21.0 ± 0.4
28	22.8 ± 0.4
56	23.4 ± 0.6
84	23.7 ± 0.3
112	24.3 ± 0.5

In the initial stage (burst release), rapid Cu liberation occurs due to direct exposure of $\text{TiO}_2@\text{Cu}_2\text{O}$ nanoparticles located at or near the coating surface to seawater. This phenomenon has been widely reported in conventional Cu_2O -based systems, where an “initial burst release” often leads to premature depletion of active species and reduced coating lifetime. Under chloride-rich seawater conditions, Cu^+ can be readily solubilized through complexation with Cl^- ions, forming CuCl_2^- according to the following reaction [56]:



In marine environments (high Cl^- concentration, $\text{pH} \approx 8$, and dissolved oxygen), Cu release is not governed solely by physical dissolution but is primarily controlled by coupled electrochemical and diffusion processes. Previous studies have demonstrated that Cu_2O -containing coatings can form micro-galvanic cells, where anodic–cathodic interactions accelerate Cu dissolution and ion release into the surrounding medium. Concurrently,

dissolved Cu predominantly exists as chloride complexes, facilitating its transport into seawater.

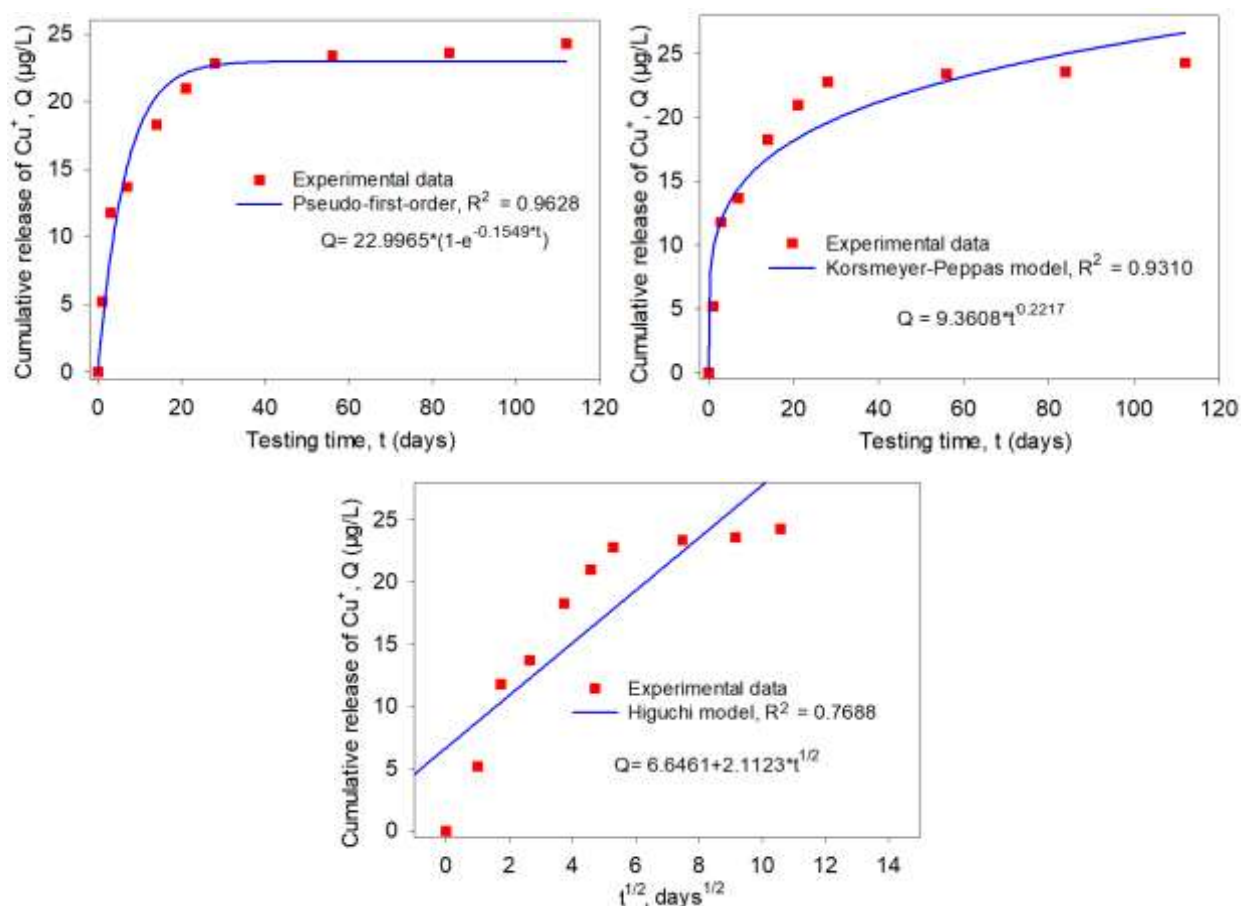


Figure 12. Kinetic models of Cu ion release from the PVE coating.

During the intermediate stage (diffusion-controlled regime), the formation of a leached layer and subsequent diffusion through this layer or the polymer matrix becomes the rate-limiting step. Recent studies confirm that Cu release from antifouling coatings is often governed by diffusion through corrosion products or polymer barriers [57]. In the final stage, the system approaches dynamic equilibrium, and the release rate significantly decreases, resulting in a plateau. This behavior aligns well with the multi-step release mechanism—electrochemical dissolution, chloride complexation, and diffusion—reported for Cu₂O-based antifouling systems [57–58].

Kinetic modeling further indicates that Cu release does not follow a simple linear (zero-order dissolution) or classical Higuchi diffusion model. The Higuchi model ($R^2 = 0.7688$) only adequately describes the initial stage ($t < 25$ days), corresponding to burst release. The Korsmeyer–Peppas model shows improved fitting ($R^2 = 0.931$), yet it fails to capture the plateau behavior observed at longer immersion times. In contrast, the pseudo-first-order kinetic model provides the best overall agreement with experimental data,

suggesting a combined dissolution–diffusion mechanism. This finding differs from conventional Cu₂O coatings, where diffusion-controlled models such as Higuchi or Korsmeyer–Peppas are typically more applicable [57].

Notably, traditional Cu₂O-based coatings often exhibit pronounced initial burst release followed by a rapid decline in release rate [58]. Since antifouling performance depends on maintaining an effective Cu concentration, excessive early-stage release may result in rapid depletion and increased environmental toxicity. The incorporation of TiO₂@Cu₂O nanostructures mitigates this issue through several mechanisms. First, the nanoscale architecture enhances Cu₂O dispersion within the coating matrix. Second, TiO₂ nanorods introduce a barrier effect, increasing tortuosity and hindering the penetration pathways of water and Cl[−] ions, thereby suppressing burst release. A similar reduction (>70%) in initial burst release has been reported in Cu₂O@bentonite nanocomposite coatings [59]. Furthermore, the heterojunction structure of TiO₂@Cu₂O nanocomposites may enhance micro-galvanic interactions, enabling controlled electrochemical dissolution of Cu. This mechanism is analogous to galvanic-assisted release systems and is particularly advantageous for antifouling applications. Transitioning from fast-release Cu₂O systems to controlled-release configurations allows for sustained Cu concentrations over time, thereby improving long-term antifouling performance.

The antifouling mechanism can be described by the formation of a “Cu-enriched interfacial layer” at the coating–seawater interface, which maintains a Cu concentration sufficiently high to inhibit the settlement of fouling organisms. This is consistent with the plateau observed in the experimental data, reflecting a balance between Cu release and outward diffusion. In this study, the Cu ion concentration stabilized at approximately 23 µg/L after 30 days, which lies within the effective antifouling range. Previous studies have reported inhibitory thresholds for barnacle and oyster larvae as low as 7 µg/L [60], with optimal performance typically observed at surface concentrations of 10–30 µg/L [61]. In addition, TiO₂@Cu₂O hybrid nanoparticles exhibit synergistic effects that enhance antibacterial and antifouling performance. Under light irradiation, these nanostructures can generate reactive oxygen species (ROS), which disrupt biofilms and damage microbial cells. Moreover, the hybrid structure improves the stability of Cu₂O and enables controlled, sustained release of Cu ions, thereby reducing excessive leaching and minimizing environmental toxicity. The nanoscale TiO₂ component also enhances dispersion and increases the biologically active surface area, allowing for reduced Cu loading while

maintaining effective antifouling performance. These mechanisms warrant further investigation using direct biological fouling models in future studies.

4. Conclusion

In this study, core-shell $\text{TiO}_2@\text{Cu}_2\text{O}$ nanopowders were successfully synthesized via a green route using L-ascorbic acid as a bio-reducing agent, with polyethylene glycol and Tween 80 as surfactants. The resulting nanocomposites exhibited a uniform morphology, with Cu_2O (4.17 wt.%) predominantly distributed in the outer shell. Notably, the incorporation of Cu_2O did not alter the rutile crystal structure of TiO_2 , thereby preserving its intrinsic photocatalytic stability while extending the optical absorption edge from 410 nm to approximately 800 nm in the visible-light region.

When incorporated into poly (vinyl chloride–vinyl isobutyl ether) (PVE) coatings, the $\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposites significantly enhanced the mechanical performance at an optimal loading of 2 wt.%, where the best dispersion was achieved. At this concentration, relative hardness, impact resistance, adhesion strength, and sand abrasion resistance increased by 51.4%, 28.6%, 12.5%, and 22.9%, respectively. In addition, under indoor conditions without UV or solar irradiation, PVE coatings containing $\text{TiO}_2@\text{Cu}_2\text{O}$ exhibited pronounced antibacterial activity against *Pseudomonas stutzeri* B27, achieving an inhibition efficiency of 51.5%.

Beyond mechanical reinforcement, the presence of $\text{TiO}_2@\text{Cu}_2\text{O}$ nanoparticles markedly improved the UV–humidity durability of PVE coatings and effectively suppressed bioadhesion during accelerated aging and seawater immersion tests. The controlled release of Cu ions from the coating reached approximately 23.3 $\mu\text{g/L}$ after 23 days of immersion, falling within the concentration range reported to inhibit the settlement of barnacle and oyster larvae. This controlled ion-release behavior provides a critical foundation for further investigations into the antifouling performance of $\text{TiO}_2@\text{Cu}_2\text{O}$ -based nanocomposite coatings under real marine conditions.

Overall, these results demonstrate that $\text{TiO}_2@\text{Cu}_2\text{O}$ nanocomposites are promising multifunctional additives for high-performance PVE-based coatings, offering a synergistic combination of mechanical reinforcement, UV durability, antibacterial activity, and antifouling potential. Such coatings show strong promise for applications in marine corrosion protection, architectural finishes, and hygienic or public health-related environments.

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Author contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Nguyen Thuy Chinh, Nguyen Xuan Thai, Nguyen Anh Hiep, Ly Ngoc Lien and Tran Thanh Thuy. The first draft of the manuscript was written by Do Van Cong and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Conceptualization: Thai Hoang, Nguyen Thuy Chinh; Methodology: Tran Thanh Thuy, Nguyen Anh Hiep, Nguyen Xuan Thai, Ly Ngoc Lien; Formal analysis and investigation: Do Van Cong, Nguyen Thuy Chinh, Tran Thanh Thuy, Nguyen Anh Hiep, Nguyen Xuan Thai, Ly Ngoc Lien; Writing - original draft preparation: Do Van Cong; Writing - review and editing: Do Van Cong, Thai Hoang; Funding acquisition: Thai Hoang; Supervision: Thai Hoang.

Conflicts of interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability: The data used to support the findings of this study are included within the article.

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