Fabrication of nano core-shell aided multifunctional robust polymeric coating for steel protection

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Abstract

In this study, we have developed a highly efficient and low-cost multifunctional robust polymeric surface coating which are super-hydrophobic, antimicrobial as well as mechanically-strengthened super protective nanocoating. To achieve this development, polyurethane (PU) coating formulations were successfully developed with $SiO_2@TiO_2$ core–shell nanoparticles prepared via peptization synthesis on mild steel substrate. Easy synthesis steps and low processing temperature is major achievement of this synthesis technique. The idea behind the synthesis of $SiO_2@ TiO_2$ core–shell nanoparticles was to utilize the mechanical strength of silica and the hydrophobicity, antimicrobial property of the TiO_2 together. In this coating development nanoparticle concentration was varied from 1% (wt) to 6% (wt) in the coating formulation. Used nanoparticles was modified by using methyl trimethoxy-silane (MTMS) for betterment of the surface. Further investigation on this nanocoating has been carried out by analysing the mechanical behaviour, antimicrobial property, and contact angle measurement. Developed $SiO_2@ TiO_2$ based polymeric nanocoating has shown improved corrosion/erosion resistance, antimicrobial property, and super-hydrophobic nature (~146 degree) with good anti-scratch property up-to 20N load.

Keywords: core-shell nanoparticles, polyurethane, nanocoating, surface wettability, antimicrobial property, mechanical behaviour

1. Introduction

Degradation of steels due to relative motion among several structural components, erosion, thermal degradation, and failure by chemical attack is reported very frequently by different studies [1,2]. To counter such surface and subsurface related degradations, surface modification by the application of protective hard multifunctional coatings is one of the relevant solutions. Multifunctional coatings are coatings that respond well to the external environment for protecting the coated material on demand. They respond to one or more triggers such as temperature, pH, moisture, active ions, or mechanical damage. These responses protect the material from chemical as well as physical damage via on-demand release of stored or embedded corrosion-inhibitor agents. The development of multifunctional surfaces is an area of significant academic and industrial interest, due to the wide range of applications that can be impacted by the development of such surfaces such as self-cleaning, anti-icing, separation of liquids, corrosion resistance, drag reduction, [1, 2] oil-repellent, anti-bacterial, adhesion architecture coatings, antifouling paints for marine industry etc. [3, 4]. These surfaces also display thermal stability and excellent long-term stability under atmospheric conditions. In addition to the broad range of applications, there are many other advantages including a reduction in maintenance costs and elimination of monotonous manual effort. The anti-contamination properties of these type of surfaces in solar cell prevents reductions in their efficiency. So, development of this type of coatings are gaining great interest for various research fields [5,6], By creating new properties using suitable fillers and matrix as well as suitable surface treatment methods, the functional and multifunctional coatings can meet the most difficult standards of users, especially in high-tech industries but these smart coatings are less explored. As reported by literatures, previously developed multifunctional coatings using iron, magnesium, nickel nanoparticles had issues of long-term chemical stability for corrosion resistant superhydrophobic surface with low mechanical stability [7-10]. To resolve these issues, we successfully developed $SiO_2@TiO_2$ core-shell nanoparticles to prevent the steel from corrosion, erosion, scratch, microbial side-effects with superhydrophobicity.

2. Nano core-shell based coating development and surface characterization

In this work, we followed peptization process for the synthesis of silica-titania ($SiO_2@TiO_2$) core-shell nanoparticles. Peptization is the organic synthesis approach used for converting a fresh precipitate into colloidal particle by shaking it in the dispersion medium in the presence of small amount of electrolyte. Generally, electrolyte is added whose one ion is common with one ion of precipitate. The particles of precipitate absorb common ion of electrolyte. Then they get dispersed due to electrostatic repulsion. Low processing temperature is major achievement of this synthesis technique for nano core-shell development. This method not only avoids complicated processes such as the layer-by-layer technique and polymer/surfactant grafting methods. It also reduces costs due to its short reaction time and the use of inexpensive reactants. For preparation of this core-shell, titanium tetra-isopropoxide (2 mL) was used as a precursor and added in to 50 mL of distilled water under stirring condition in presence of 1 g of silica nanoparticle prepared through sol-gel process. In the next step, 1mL of 70% nitric acid was added in this solution (when acid concentration maintained in the reaction media became about 0.20M) and stirred for 4 h at 70°C. After this whole material was

centrifuged at 8000 rpm for 10-15 min and dried at 70°C for overnight. Developed nanoparticle size was measured through TEM and it was around 100 nm and confirmation of prepared core-shell structure was justified by XPS. Further, multifunctional coating has been developed with SiO_2@TiO_2 nano core-shell in polyurethane (PU) on mild steel substrate at different concentration (1-6wt%) of the nanoparticles after surface modification using functionalizing agent methyl trimethoxy-silane (Figure 1). A primary benefit of using polyurethane coatings is the protection, it provides the surface itself. When applied, the coating creates what is essentially an impermeable barrier between the elements and the object it's covering. Developed coating thickness was measured around 40μm. Further multi-functionality of developed PU coatings has been investigated by testing its antimicrobial properties (against fungus, bacteria, and algae), surface wettability, scratch resistance, corrosion, and erosion behaviour. This SiO_2-TiO_2 core-shell based coating enhanced different properties in three ways; (i) core silica will improve strength of the coating due to its high mechanical stability, (ii) shell TiO_2 will improve the hydrophobicity as well as antimicrobial property of the coating surface and (iii) this layer can serve as a protective coating to prevent any further oxidation of the metals.
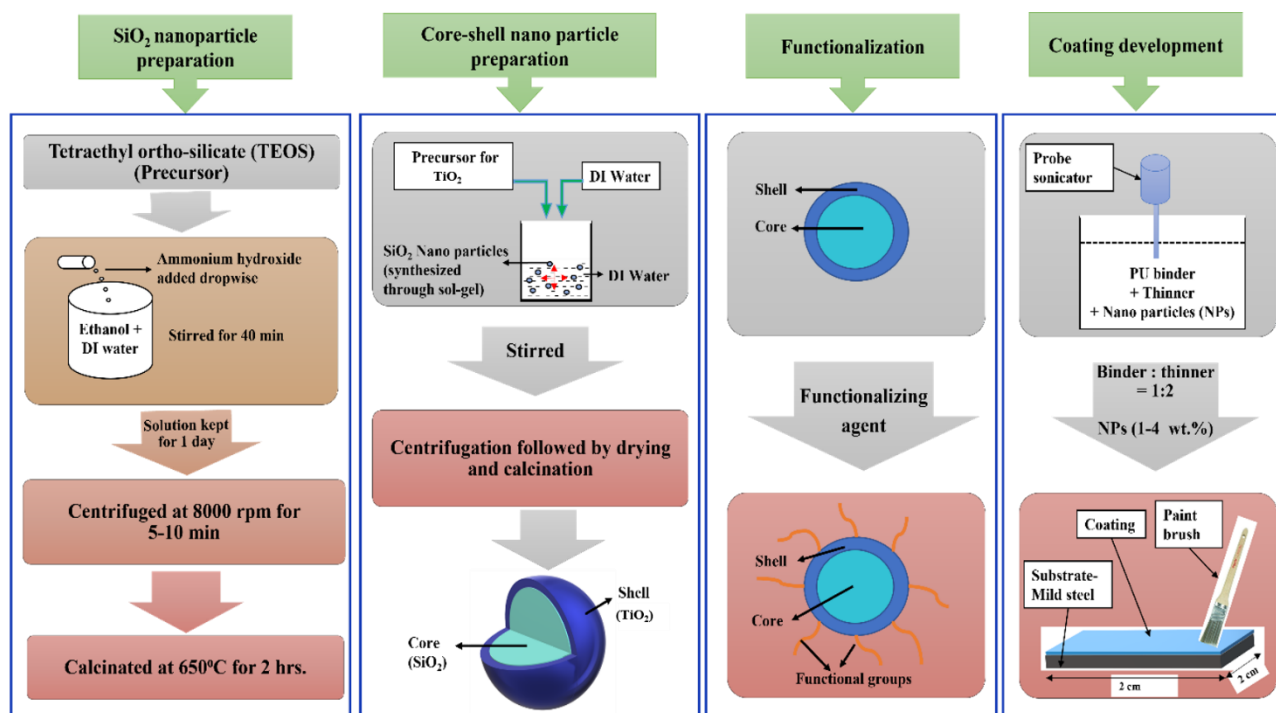

Figure 1. Development of nano core-shell aided polyurethane coating

3. Results

3.1 Antimicrobial property against fungus

Anti-fungal testing of prepared nanoparticles was carried out against *fusarium solani* which are shown in Figure 2. The presence of nanoparticles reduced the growth of fungus. The growth diameter of fungus in petriplate for control is considered as 100%. The coating formulation with core-shell nanoparticles killed this fungus completely (0% fungus growth) and it was most effective at 1% (wt) core-shell nanoparticle in the coating only as shown in Figure 2.
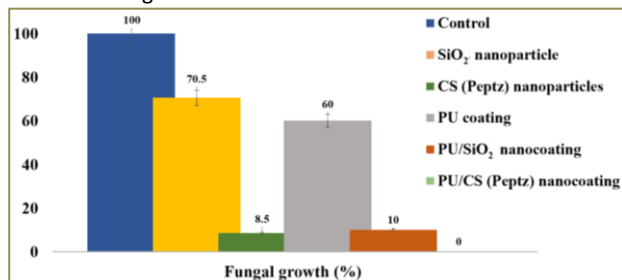

Figure 2. Antifungal effect of the coated samples

3.2 Antimicrobial property against bacteria

In the present study antibacterial testing were performed against *Escherichia coli (E.coli)* and *Bacillus*. *E. Coli* bacterium is a rod-shaped, gram-negative bacteria and it can cause food poisoning, breathing problems, diarrhea, abdominal pain, dehydration, urinary tract infections, get pneumonia, and kidney failure also. Optical density of all coated samples was checked at 600 nm at 6 hrs interval up-to 24 hours and found best antibacterial effect in nanocoating developed with core-shell particles at 4% (wt) concentration as shown in Figure 3.
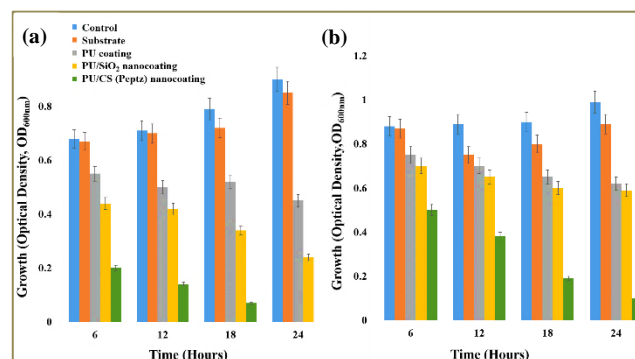

Figure 3. Antibacterial effect: optical density of the coated samples (a) *E. coli* (b) *Bacillus*

3.3 Antimicrobial property against algae

A culture (5 % of algal biomass) of blue green algae named

Cyanobacteria was grown photo autotrophically in sterile Fogg's media. The algal growth was measured at 665 nm (A665nm) using UV–vis spectrophotometer with the nanoparticle concentration from 1% (wt) to 6 % (wt) in coating formulations. Optical density of culture media containing free nanoparticles and coating samples were measured at 665 nm up-to 120 hours at 24-hour interval (Figure 4). Algal mass dry weight and chlorophyll content were also measured to confirm the anti-algal effect of these coatings for quantitative analysis After analysing all the samples, best anti-algal effect was observed in polyurethane coating developed with core-shell nanoparticles at 4% (wt) concentration.
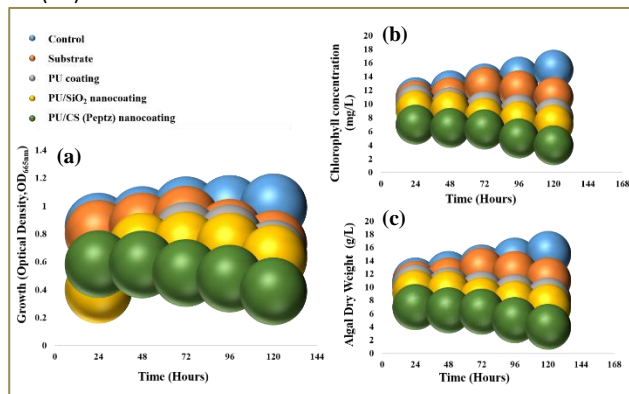

Figure 4. Anti-algal effect against blue green algae for all the coating samples (a) optical density (b) chlorophyll concentration (c) algal dry weight

3.4 Anti-scratch performance

Coating formulation of these functionalized nanoparticles were developed with polyurethane at 4% (wt) concentration on mild steel substrate because this concentration has shown best results for antimicrobial effect as well as in development of superhydrophobic surface. As we know, PU is a polymer composed of organic units joined by carbamate links and we prepared nano core-shell (CS) through peptization process for this study have shown better dispersion as we can see in the SEM image (Figure 5) because peptization is also organic synthesis approach and made this coating useful for multipurpose uses. Even its dispersion was better than silica. For the anti-scratch study of these coatings were analysed by Universal Materials Tester (CETR UMT-3) up to 21 N load. Analysis was done with scanning electron microscopy and found the successful anti-scratch performance up-to 20N load with this nano core-shell-PU coating and failed after higher load than 20N which was tested at 21N.
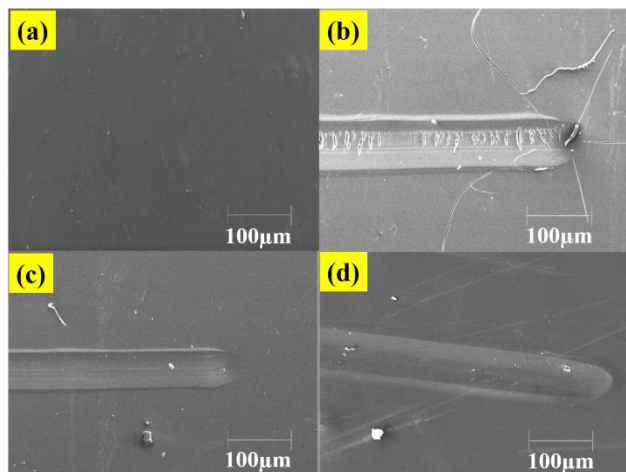

Figure 5. SEM image of scratched coating surface at 20 N load (a) coated substrate before scratch (b) PU coating after scratch (c) PU-SiO$_2$ nanocoating after scratch (d) PU-CS nanocoating after scratch

3.5 Analysis on surface wettability

Wettability is the ability of liquids to keep in contact with solid surfaces. It is a direct result of intermolecular interactions, which occur when two media (liquid and solid) are brought together. Surface wettability were investigated by measuring water contact angle and it was ~146.4° ± 2° i.e., almost superhydrophobic surface coating as shown in Figure 6 also showed oleophilic properties, with an oil contact angle of 51.3°±2°, which is tested with rapeseed oil.
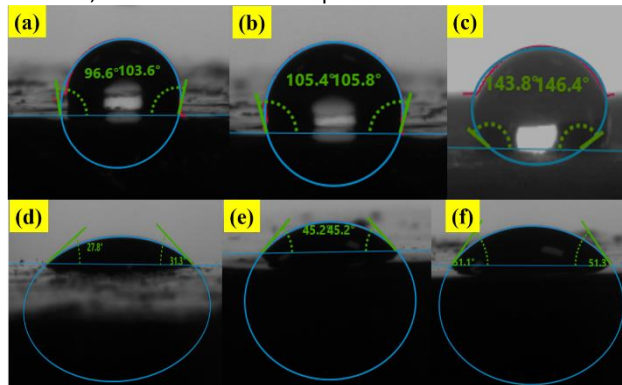

Figure 6. Contact angle measurement with water (a) PU coating (b) PU/SiO$_2$ nanocoating (c) PU/core-shell nanocoating, with oil (d) PU coating (e) PU/SiO$_2$ nanocoating (f) PU/core-shell nanocoating

3.6 Analysis on the erosive and corrosive behaviour of the coating

Figure 7a and 7b show the variation of scratch hardness and erosive wear rate of the coatings. Three noteworthy observations were made: (i) PU/CS showed the highest scratch hardness value and the least erosive wear rate, (ii) coating with harder reinforcement (PU/SiO$_2$), showed lesser scratch hardness value and higher erosive wear rate than the coating with less hard reinforcement (PU/CS); and (iii) The trend among the coatings for erosive wear rate remained similar for both the erosion angles (30° and 90°).
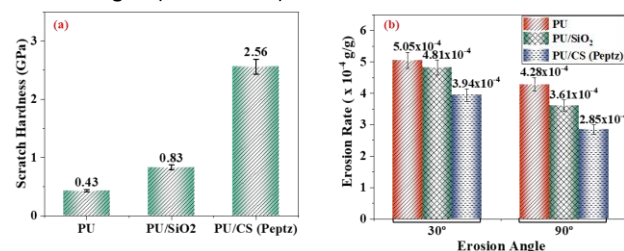

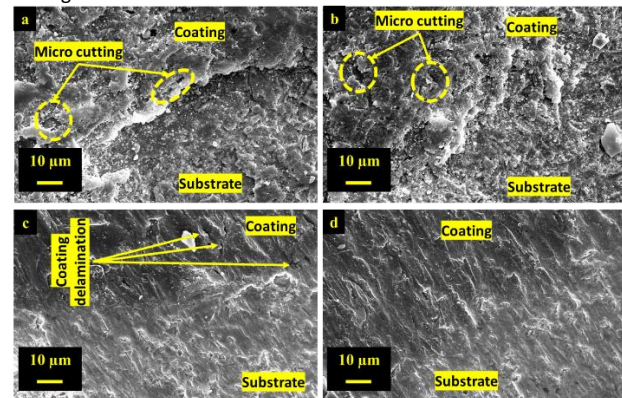**Figure 7** (a) Variation of scratch hardness and (b) erosion rate; for the coatings

Figure 8. SEM micrographs post erosive wear studies of PU (a-90° and c-30°), and PU/CS (b-90° and d- 30°)

Regardless of higher hardness of SiO$_2$ than TiO$_2$, PU/CS showed higher scratch hardness value than PU/SiO$_2$ which is attributed to more effective and higher degree of dispersion of the

reinforcement in the latter than in the former (a) High dispersion strengthening and high hardness further allowed PU/CS to exhibit the least erosive wear rate among all the coatings. Further, all the coatings showed higher wear rate at 30° erosion angle than at 90°. This behaviour of the coatings is in accordance with that of the soft and ductile materials that tend to flow more than hard and brittle materials (b) PU being a polymer is less hard in nature than other class of materials like metals and ceramics in general, hence showing higher wear rate at oblique erodent impact than at right angle.

SEM micrographs (Figure 8) indicate the wear mechanisms and features involved with PU and PU/CS after the erosion studies. It could be clearly seen that the coating volume left at the coating substrate interface is significantly lesser in Figure 8c and 8d than that in Figure 8a and 8b, thus indicating the higher erosive wear of coatings at 30° than at 90° respectively. At 30° erosion angle, both the coatings (Figure 8c and 8d respectively) showed ploughing marks with indistinct coating delamination interface. For PU, a sharp coating-substrate interface (Figure 8a) indicates the wear of less hard coating, whereas indistinct coating-substrate interface (Figure 8b) shows the wear of harder coating (PU/CS) at 90° erosion angle.

Table 1: Corrosion current and corrosion potential for the coatings and the substrate

	Substrate	PU	PU/SiO$_2$	PU/CS
Corrosion current, i_{corr} (A)	6.85 X 10^{-6}	5.62 X 10^{-7}	3.03 X 10^{-7}	3.36 X 10^{-8}
Corrosion potential, V_{corr} (V)	-0.67	-0.56	-0.54	-0.49

Table 1 shows the values of corrosion current and corrosion potential for the substrate and the coatings. PU/CS was found to be the most effective against corrosion among all the specimens that were tested. It showed the least value of corrosion current (3.36 X 10^{-8} A) and highest value of corrosion potential (-0.49 V) (Table 1 and Figure 9b). It also exhibited least corrosion rate (1.65 X 10^{-5} mm/year) (Figure 9a). High inertness of TiO$_2$ towards corrosion and its highest degree of dispersion in PU matrix explains its (PU/CS) significantly better corrosion performance than other coatings. Mild steel on the other hand being highly susceptible to corrosion performed the poorest in the test.
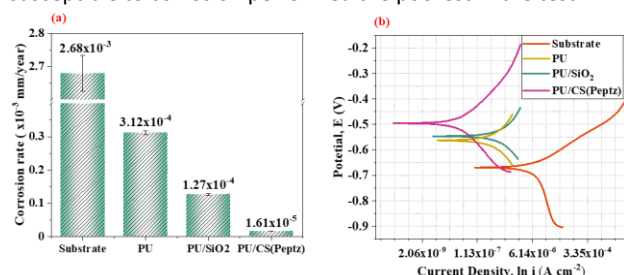
Figure 9. (a) Variation of corrosion rate and (b) Tafel plots; for the substrate and the coatings

Summarizing all the results, this research relates to an improved method for the preparation of multi-functional silica particles which comprises preparing a composite nanostructured, multifunctional material in the core-shell morphology by attaching ultra-fine TiO$_2$ nanoparticles on the silica particle surface. The TiO$_2$ nanoparticles are bonded on silica particles throughout the surface via silanol groups and properly adhere on the steel surface after functionalizing with a coupling agent (adhesion promotor) MTMS during PU coating development.

These coupling agents are mainly bi-functional reactive additives, designed such that one part of the molecules form covalent bonds with the substrate and another part participates in the crosslinking of the binder system of the paint during film formation to create strong substrate-coating adhesion. Previously many methods have been applied by researchers for fabrication the super-hydrophobic coating using various types of nanoparticles such as iron, nickel, but most of the proposed methods suffer from many constraints such as time-consuming, being complicated, requiring special equipment as well as the raw materials and being expensive including low chemical and mechanical stability. So, with this nano SiO$_2$@ TiO$_2$ core-shell based PU coating development, we were successful to provide long term protection of steel surfaces from corrosion, erosion, scratch, microbial side-effects with superhydrophobicity. Developed core-shell materials are non-toxic itself and completely environment-friendly in nature. So, there is no harmful environmental impact of the developed coating.

4. Conclusion and future directions

The present research work on development of multifunctional polyurethane coating with silica-titania (SiO$_2$@TiO$_2$) core-shell nanoparticles has been successfully carried out and invested findings are as follows:

- Superhydrophobic (Water contact angle= 146.4° ± 2°) and oleophilic surface (oil contact angle=51.3° ± 2°) was achieved by polyurethane coating with the concentration of 4wt % core-shell nanoparticles.
- Antimicrobial testing of the developed PU-core shell coatings was performed against bacteria, algae, and fungus. Best antimicrobial results were obtained at 4wt% concentration of core-shell nanoparticles in the coating formulation against bacteria & algae and at 1wt % against fungus.
- Anti-scratch testing was performed up-to load 21 N and coating developed in polyurethane containing core-shell nanoparticles at 4wt% allowed to pass load up to 20N successfully.
- Apart from above properties, high dispersion strengthening, and high hardness further allowed PU/core-shell to exhibit the least erosive wear rate among all the coatings at 4wt % concentration with good anti-corrosion performance.

So, concluding all the data from this research, we can say, this is a multifunctional coating and can be useful for various field of applications in near future like self-cleaning, separation of liquids, corrosion resistance, anti-bacterial, adhesion architecture coatings, antifouling paints etc.

References

[1] Esmeryan KD 2021 *Coatings* **11**, 339
[2] Iynoon S A J, Ravichandran K and Sankara Narayanan T S N 2021 *J. Alloys & Comp.* **185** 157290.
[3] Zhang L, Zhou A G and Sun B R, 2021 *Nat Commun.* **12** 1-7.
[4] Kavalenka M N and Vüllers F 2017 *Sci Rep.* **7** 1-10.
[5] Ali A and Andriyana A 2020 *RSC Adv.* **10**, 16390.
[6] Bagheri H, Aliofkhazraei M, Mojiri H Forooshani H, Sabour Rouhaghdam A 2018 *App. Surf. Sci.* **436** 1134.
[7] Nguyen P, and Nguyen T A, 2018 *Int. J. corros.* **4749501** 1687.
[8] Conradi M and Kocijan 2017 *Materiali in tehnologije* **51** 1043.
[9] Mirco F and Lorenzo B, 2021 *App. Sci.* **11** 1-18.
[10] Christopher S, Kenneth N, Mark N, 2016 *Coatings* **2** 221-234.