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High performance specialized coatings for applications in corrosive environments

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Abstract : In this paper a short review of various coatings developed based on facile as well as industrially scalable methods and the challenges encountered in enhancing the durability of the coatings in simulated service conditions are presented. These coatings include (i) development of noble metal (Pt/Pd) nanoparticle coated titanium electrodes for electrochemical processes employed in spent nuclear fuel reprocessing, and (ii) development of superhydrophobic (SHP) coatings on titanium, stainless steels, low-chromium steels and copper alloys to address corrosion and biofouling issues in chloride environments of condenser materials in nuclear power plants. Nanostructured noble metal (Pt, Pd) coatings on Titanium and titania nanotube for electrode applications were developed using a novel seed mediated coating technology involving electrodeposition assisted hydrothermal method. Studies demonstrated that by engineering the particle size of Pt, and nano-tubular self assembled arrays of TiO_2 (TiNT), the electrocatalytic activity for methanol oxidation could be enhanced ten times compared to polycrystalline Pt. By employing electrochemical cerium oxidation studies, excellent durability of this Pt nanoparticles coated TiNT electrode surpassing 1000 h in 11.5M nitric acid was also demonstrated. In the second part of the manuscript development of SHP coatings to address corrosion and biofouling issues in chloride medium of condenser materials such as titanium, stainless steels, low chromium steels and copper alloys is detailed. Inspired by the lotus effect two step techniques were adopted for creating a micro-nano roughness pattern, and reducing surface energy by coating with low surface energy material. Micro-nano texturing of different materials was achieved by various methods like polishing, pickling, anodization, sand blasting etc. Attempted different organic fatty acids and silica nanoparticles mixed silane, to enhance durability. Finally durable and stable SHP coatings were demonstrated with high water contact angle and corrosion resistance and reduced microbial attachment indicating superior bio corrosion resitance of the materials studied. Facile techniques were adopted for both coatings in order to support scaling up for real time applications in future.

Keywords: *superhydrophobic, coating, biofouling, corrosion, electrode, titanium, nanotubes, nanoparticles, platinum, silanes, anodization*

INTRODUCTION

Coatings are known to mankind for a long time and they are employed for protective or decorative puroposes or for both. The coatings may consist of organic or inorganic components depending on the application. Over the years, multifunctional coatings are preferred as they offer aesthetic appeal as well as protect the structure from corrosion which is one of the major degradation mechanisms. Electrocatalytic coatings, superhydrophobic (SHP) coatings, self healing coatings, antifouling coatings, oleophobic coatings, thermochromic coatings and so on are the new class of coatings developed for high performance. Depending upon a specific requirement or on identifying a gap area, a suitable coating or surface modification technology can be adapted and improvised to suit the application. In this review two different coatings (Scheme 1) developed for specific applications such as nano Pt/Pd coated electrodes for electro-oxidation of spent nuclear fuels and SHP coatings for corrosion and biofouling resistances are discussed.

Nano Pt/Pd coated electrodes for electrocatalytic applications

In India, a closed fuel cycle policy is followed to ensure long term energy security. Therefore, reprocessing of spent nuclear fuel is of paramount importance in Indian context. Various chemical and electrochemical methods have been employed for the reprocessing of spent nuclear fuel. The electrolyte used for these electrochemical methods is usually high concentrated nitric acid under boiling conditions. Normal electrode materials cannot

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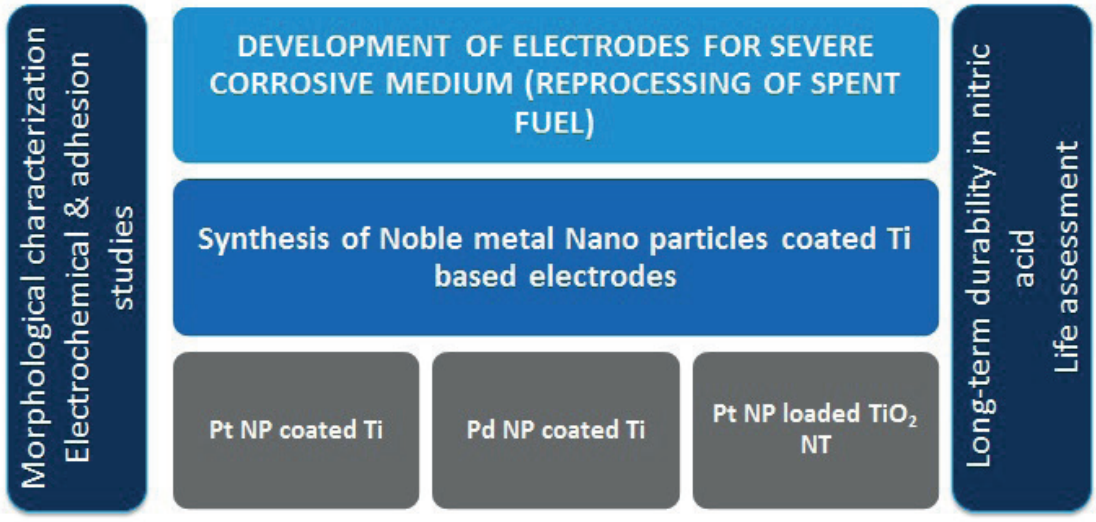
Scheme - 1

with stand this severe condition. Platinum is considered for electrode application as it exhibits good corrosion resistance, conductivity and electrocatalytic activity. But economic feasibility and severity of the corrosive environment titanium coated Pt electrodes are preferred when compared to bulk platinum as electrode. Due to the potential for new application and improving the established activities, intense research is going on to design novel platinum and platinum based nanomaterials with unique properties. Platinum being a precious metal, efforts are being made to synthesize Pt-based catalysts with increased catalytic efficiency and low platinum utilization by tailoring the size and shape of nano materials. Recent studies show that reduction in size to nanoscale improved the electrocatalytic activity of Pt. Hence it was decided to synthesize, characterize and study the electrochemical activity of nano Pt coated Ti for electrode application (Scheme 2). The present work deals with the development of Pt and Pd nano particle coated Ti electrode using electrodeposition assisted hydrothermal method. Attempts were also made to enhance the surface area of Ti by anodization leading to the formation of TiO_2 nanotube and coat nano Pt particle on this TiO_2 layer by similar method.

Scheme - 2

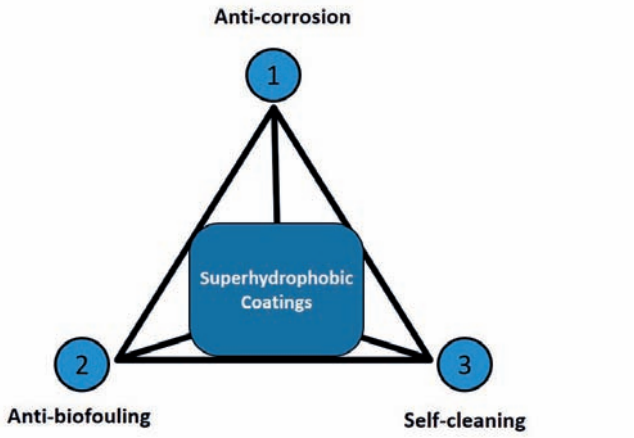


SHP coatings for corrosion and biofouling resistances

The cooling water systems in power plants are susceptible to fouling and corrosion which pose a big threat to achieve and maintain the highest possible electrical energy output. The microbes present in the natural sources of cooling water such as rivers, seawater etc., form a complex biofilm on the material surface which hamper the heat transfer property of the condensers. Biofilms also accelerate microbiologically influenced corrosion (MIC) beneath these deposits. The adhesion of microbes on the condenser pipe surface is the first step in biofilm formation leading to biofouling and corrosion. Hence it is beneficial to prevent bacterial attachment and biofilm formation. Environmental concerns drive antifouling technology towards more nonbiocidal or non-toxic approaches based on controlling the surface chemistry, topography and catalytic activity that have significant impacts on the interactions between microorganisms and the surface. Low-surface-energy materials, surface hydrophobicity, photocatalytic activity of certain materials such as titanium and micro-nano topography resist/ reduce the attachment of biofouling organisms.

Materials with superhydrophobic properties inspired by leaves, flowers, plants and insects are highly desirable for many potential applications. Thin film silane coating has been introduced as a chromium free multi metal surface pretreatment for corrosion protection, adhesion promotion and surface passivation of metals such as aluminium, steel, zinc, magnesium and others. Controlling the surface energy and the roughness is hence fundamental to achieve the superhydrophobicity. The fabrication methods that are simple, economical and scalable are preferred for preparing self-cleaning superhydrophobic coatings on various substrates such as glass, metal and composites. In this review, the superhydrophobic coatings developed on various materials for antibacterial as well as anticorrosion applications (Scheme 3) were discussed in the context of marine and sea water applications.

Scheme - 3



NOBLE METAL NANO PARTICLE BASED COATINGS FOR ELECTRODE APPLICATIONS

Nano platinum particle based coatings

Nanotechnology is considered as one of the key technologies of the 21st century, which has a huge impact on the society particularly in areas such as energy, environment, electronics and healthcare. The current focus in nanotechnology is to develop smart coatings with self cleaning and self healing ability, flexible electronics, targeted drug delivery, water purification and green energy. Thus the field of nanoscience and nanotechnology is ever expanding and there is broad scope to develop new materials and technologies that find real time applications.

Reprocessing of spent nuclear fuel forms the back end of the fuel cycle in nuclear industry. There are several industrial processes involved in the reprocessing of nuclear fuel. Electro-oxidative dissolution is one of the advanced techniques preferred for faster and complete dissolution of Pu-rich oxide/carbide fuels of fast

breeder reactors (FBR) over conventional method of refluxing in concentrated nitric acid. The efficiency of the electrochemical processes in the reprocessing plant highly depends on the endurance of the anode in radio-toxic environment. Noble metals especially metallic Pt/Pd based electrodes are considered as outstanding candidates for the electro oxidative dissolution technique. Accordingly, dimensionally stable anodes (DSA) such as mixed oxide coated titanium anodes (MOCTA) [1] and mixed oxide coated titanium anodes-glazed (MOCTAG) [2, 3] were developed in early 90s for employing them as anodes in the dissolution and purification processes of the spent (U, Pu) C fuel of fast breeder test reactor (FBTR) in India.

In order to overcome the limitations due to cost, uniformity and adherence of the coating on the base titanium substrate, nanotechnology based seed mediated hydrothermal method was employed to develop Pt and Pd nanoparticle coated titanium electrodes [4,5] for nitric acid applications. Initially Pt nanoparticle coated titanium substrate was fabricated and the performance was analyzed in severe corrosive environments. There are two steps [6] involved in the fabrication of nano platinum coated Ti electrodes (NPCT): (i) electrodeposition of Pt nuclei on titanium substrate and (ii) hydrothermal reduction to ensure uniform and complete coverage of the base substrate. The optimized experimental conditions for electrodeposition of Pt nanoparticle on titanium were 1 mM chloroplatinic acid with 0.5 M sulphuric acid as supporting electrolyte for a duration of 60 s at a voltage of -0.08 V [7]. Field Emission Scanning Electron microscope (FESEM) images showed the deposition of Pt seeds of average size 130 nm on the titanium surface, the higher magnification images revealed the flower shaped morphology of Pt seeds. Further Pt seed deposited Ti substrate was subjected to hydrothermal reduction in a teflon lined stainless steel (SS) autoclave containing chloroplatinic acid, foramaldehyde and hydrochloric acid at 100°C for 10 h. The electrodeposited Pt nuclei acted as seed and enhanced further growth and coverage during hydrothermal reduction. The thickness of the Pt nanoparticle coating on titanium substrate was estimated to be around 10 µm. NPCT electrode was subjected to cross hatch tape test to evaluate the adhesion of the Pt coating on the titanium substrate. The electrodes showed a perfect 5B as per ASTM D 3359 [8]. X-ray Photoelectron Spectroscopy (XPS) and X-ray diffraction (XRD) analysis confirmed the presence of metallic Pt in the coating. The complete coverage of the electrode surface and the adherent coating are essential for industrial applications and the NPCT electrode was found to satisfy both these requirements.

The electrocatalytic activity of the NPCT electrode was evaluated by calculating the electrochemically active surface area by conducting hydrogen adsorption - desorption studies in 1 M H_2SO_4 at the scan rate of 100 mVs^{-1} and the charge associated is calculated from the cyclic voltammogram. The active surface area for NPCT substrate was found to be 108 times higher than that for polycrystalline platinum. It is worthy to note here that the geometrical area is the same for both the electrodes. Similarly, NPCT electrodes performed better than the polycrystalline Pt in oxygen reduction reactions which further confirmed the electrocatalytic activity of the NPCT electrode. The electrocatalytic activity of the NPCT electrode was further validated for methanol oxidation [8] and the relative intensity ratio of the forward and reverse anodic peak currents, I_f / I_b was found to be 1.55 which was comparable to Pt based catalysts reported in literature and commercially available Pt/Carbon [9-11].

Ce (III) / Ce (IV) is chosen as the mediated redox catalyst for the electro oxidative dissolution of Pu-rich spent mixed carbide fuel discharged from the Fast Breeder Test Reactor (FBTR) at Kalpakkam. Therefore the efficiency of the synthesized NPCT electrode was evaluated by employing it as anode in the electro oxidation of cerous ions in 11.5 M nitric acid at 0.1 A constant current supplied to the cell [8]. Since the active surface area of NPCT was 108 times higher than the polycrystalline platinum electrode, complete cerium oxidation was accomplished within 55 % of the time required for the oxidation with polycrystalline Pt electrode. Scanning Electron Microscopy (SEM) analyis revealed that there was no significant damage to the Pt coating on the titanium surface after this experiment. To further evaluate the long term performance of NPCT electrode, the electrode was tested in 11.5 M nitric acid at 9 mA/cm^2 current density for about 1000 h. The conversion percentage of Ce(III) in 11.5 M nitric acid was found to be better compared to that of polycrystalline Pt. No delamination was observed even after 1000 h

of operation in severe corrosive nitric acid condition at high current density. Stability of the NPCT electrode was evaluated using an advanced characterization technique such as in situ electrochemical atomic force microscopy (ECAFM) in 1 M nitric acid. The morphology and rms roughness of the coating were continuously monitored with applied voltage. The electrode surface was found to be intact upto 4 V applied voltage while in continuous immersion in nitric acid.

Though the NPCT electrode was robust upto 1000 h in extreme conditions, it was felt that the performance could be further enhanced by anodizing the titanium substrate thereby facilitating the formation of titania nanotubes. These nanotubes offer many advantages such as high specific area, corrosion resistance, thermal stability and non-toxicity to name a few. Moreover, vertically aligned TiO_2 nanotubes ensure more dispersion of platinum nanoparticles and serve as better electrode material [12-15]. Anodization was chosen for the fabrication of vertically aligned titania nanotubes on titanium [16,17]. Commercially pure titanium foil was anodized in ammonium fluoride and ethylene glycol at a voltage of 30 for 1 h. Then the anodized titanium substrate was annealed at 450 °C for 3 h to retain crystallinity of the titania nanotubes. FESEM studies showed that the inner diameter of the nanotubes was 85 ± 5 nm and the vertical length was approx. 1 µm [18]. Similar to NPCT electrode, anodized titania nanotubes were subjected to electrodeposition and then hydrothermal reduction for the deposition of Pt nanoparticles (Figure 1). Cross section FESEM and transmission electron microscopy (TEM) analysis confirmed the loading of Pt nanoparticles of size 46 to 200 nm both inside and outside the titania nanotubes. The electrochemically active surface area (ECSA) of Pt nanoparticle coated Ti was found to be more than Pt nanoparticle loaded TiNT because more number of Pt nanoparticles are present on the titanium surface than Pt nanoparticle loaded TiNT. XPS results showed that there is an interaction between the TiNT surface and the Pt nanoparticles whereas similar interaction was absent in the case of NPCT electrode. This interaction is assumed to be responsible for the enhanced electrocatalytic activity of the Pt nanoparticle loaded TiNT electrode for methanol electro oxidation and oxygen reduction reaction. The electrocatalytic activity of Pt deposited on TiO_2 nanotube was found to be ten times more than that of NPCT. In the earlier reports also similar results [19] were discussed highlighting the better contact area between the TiNT support and the Pt nanoparticles resulting in better catalytic activity and stability.

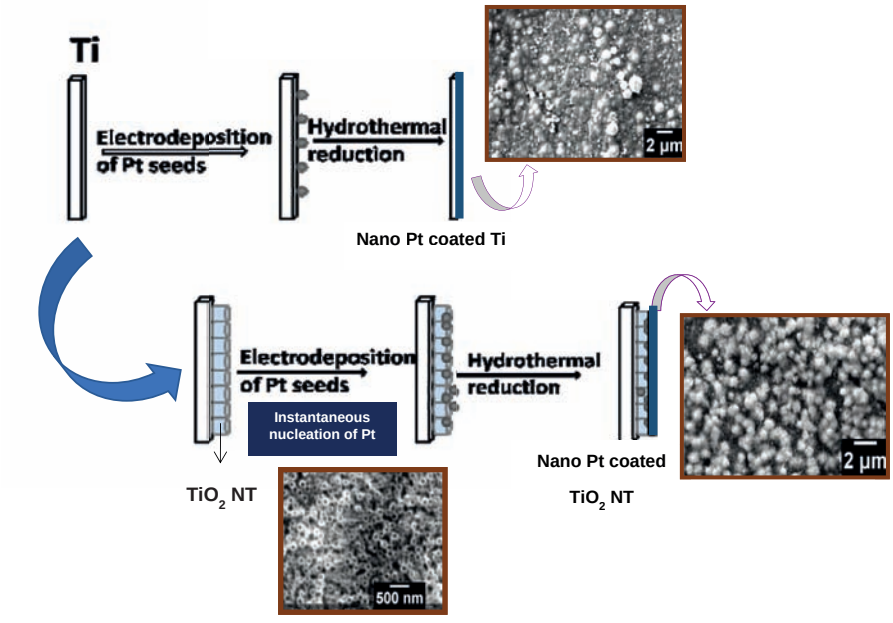


Fig. 1. Seed mediated hydrothermal reduction of Pt nanoparticles on titanium substrate and titania nanotubes.

Nano palladium particle based coatings

Another noble metal that could be an alternative to Pt is Pd. It is an ideal candidate possessing good electrocatalytic activity and it is one of the highly active catalysts after Pt in acidic and alkaline media[20-23]. Several attempts were made to enhance the electrocatalytic activity of Pd by a simple and effective approach of dispersing smaller nanostructures of Pd on suitable support, since the electrocatalytic activity highly depends on dispersion and size/ shape of metal nanoparticles. Similarly, support material should possess good surface area, excellent conductivity, high corrosion resistance and so on in the process medium and the most widely used supporting materials for dispersing Pd nanoparticles are CNT[24], Ti [25], TiO_2 [26] and graphene oxide [27]. Most notable support material is Ti with its chemical stability and excellent corrosion resistance in high acidic medium make Ti and Ti based supports more suitable for the dispersion of Pt and Pd nanoparticles for electrode application. There are several methods reported in the literature for the synthesis of supported Pd nanoparticles which include chemical reduction of Pd complex, vapor-liquid-solid (VLS) growth techniques, ion exchange method, hydrothermal reduction and electrochemical synthesis. However, chemical reduction of metal salt precursor in the presence of template or seed mediated growth method [28-30] are preferred due to simplicity, low cost and high dispersion of uniform sized nanoparticles. The experience gained from the development of Pt nanoparticle coated Ti / TiNT surfaces assured that seed mediated hydrothermal reduction method was effective for uniform and better surface coverage of metal nanoparticle. Development of Pd nanoparticle via a seeding approach is quite new and very less literatures are available so far.

Palladium seed particles were deposited chronoamperometrically from 1 mM Palladium chloride in 0.5 M H_2SO_4 for 20 s at 0.40 V. The Ti substrate with electrodeposited Pd seeds was then transferred to a Teflon lined stainless steel autoclave for hydrothermal reduction in 5 mM $PdCl_2$ solution along with 0.5 % formaldehyde reducing agent for 10 h at 180ºC. FESEM and high resolution transmission electron microscopy (HRTEM) images confirmed the presence of solid, sharp edged cubic, triangular, truncated triangular, octahedron shaped Pd nanoparticles with an average size ranging from 20 to 80 nm in the coating. It is worthy to note here that the Pd nanoparticles coating was not as uniform as the Pt coating and the base titanium substrate remained uncovered in many spots. Nevertheless, the electrocatalytic activity of Pd nanoparticle on titanium substrate in acidic medium was confirmed by hydrogen adsorption-desorption studies [31].

Performance evaluation of electrode coatings

The stability and durability of these three electrodes namely Pt nanoparticle coated Ti, Pt nanoparticle coated TiO_2 nanotubes and Pd nanoparticle coated Ti synthesized via seed mediated hydrothermal reduction method were evaluated. The comparison of electrode properties like adhesion of coating to substrate, ease of synthesis, stability of coating and electrocatalytic activity for Ce oxidation were studied. As described in ASTM D 3559-09, both Pt nanoparticles coated Ti and TiNT were ranked as 5B and Pd nanoparticles coated Ti as 1B. Pt nanoparticles possessed excellent adhesion to Ti and TiNT substrates whereas, Pd nanoparticles were loosely coated over Ti substrate. The performance of Pt nanoparticles coated TiNT, Pt and Pd nanoparticle coated Ti electrodes were investigated by employing it as anode in the oxidation of cerous ions under an applied current of 0.1 A in 11.5 N nitric acid. Pt nanoparticle coated TiNT electrode accomplished 100 % conversion of Ce^{3+} to Ce^{4+} within 2h 15 min and Pt nanoparticles coated Ti electrode completed in 2h 30 min (Figure 2), whereas both polycrystalline Pt and commercially available Pt plated titanium anodes could complete the conversion after 4.5 h. In the case of Pd nanoparticle coated Ti electrode initially electrode was found to be electrochemically active but after 30 min of the experiment the loosely adhered Pd nanoparticles detached from the Ti substrate resulting in reduced reaction rate and subsequent electrode failure.

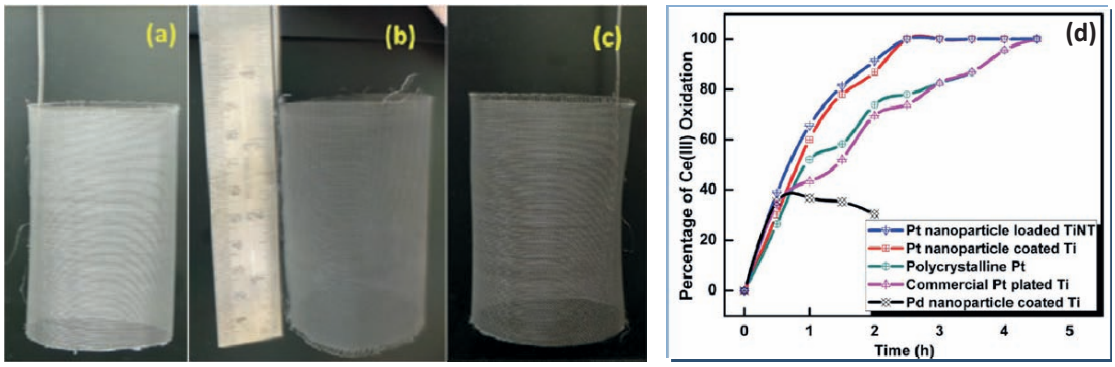


Fig. 2. Photographs of the Ti mesh (5 cm diameter and 8 cm length) electrode (a) without coating, (b) Pt nanoparticle coated Ti mesh, (c) Anodized and Pt loaded Ti mesh and (d) the performance of electrodes for the electro-oxidation of Ce in 11.5 N nitric acid (Reprinted from ref [31] K.R. Rasmi, Ph. D thesis, Active and noble nanostructured coatings to enhance corrosion resistance of electrode materials, HBNI University, Kalpakkam, India, 2016; Figure 2a&b Reprinted with permission from ref [8] Copyright Springer 2017)

Finally Pt nanoparticle coated Ti and TiNT electrodes were chosen for life assessment studies as anode for electro-oxidation of Ce in 11.5M nitric acid under an applied operational current density of 9 mA/cm^2 which is similar to reprocessing plant conditions [8]. The life of Pt nanoparticle coated TiNT electrode was 1728 h and the coating was still intact whereas the life of Pt nanoparticle coated Ti was 1152 h and cracks were noticed in the coating after the experiment as evident from FESEM studies [32]. Since Pt coated TiNT electrode showed excellent durability it was exposed in the simulated reprocessing solution containing a representative fraction of low-activity actinides and fission products in 11.5 N nitric acid in a mock-up of the service dissolver vessel [33] for about 1185 h at 110°C. The morphology, chemical composition and electrocatalytic activity of the Pt nanoparticle coated TiNT electrode was evaluated after exposure. The morphological and compositional studies confirmed the presence of metallic Pt nanoparticles on the electrode surface with some localised cracking after exposure and the electrochemically active surface area of the Pt nanoparticle coated TiNT electrode after exposure was found to be twice that of polycrystalline platinum thus establishing its durability and efficiency.

Thus the development and systematic evaluation of the durability of the electrodes would pave the way to develop many binary alloys of noble metal nanoparticles like Pt-Pd, Pt-Ir alloys to generate an electrode surface with improved catalytic activity than individual noble metals. There is also scope for exploring the possibility of employing Pt nanoparticle coated Ti/TiNT electrode for other electrochemical processes in reprocessing related applications such as electrochemical reduction of uranium, destruction of soluble organic waste and electrolytic destruction of nitric acid before waste disposal.

SUPERHYDROPHOBIC COATINGS WITH CORROSION AND BIOFOULING RESISTANCES

A close observation of nature provides inspiration to poets as well as scientists; the nature is an open source and anybody can adapt its ideas. This study has drawn its motivation from the self-cleaning and superhydrophobic surface of lotus leaf. Extreme water repellent superhydrophobic coating with water contact angle more than 150° has caught the attention of corrosion researchers in the recent decade and attempts are being made to explore the possibility of using them to protect metals and alloys against corrosion.

A detailed microscopic observation of the lotus leaves in SEM and AFM showed micro-nano features namely papillae and a wax-like coating (Figure 3). Motivated by the lotus effect in which water droplets falling on the leaves bead up and roll off, superhydrophobic surface modification (Scheme 4) was carried out on engineering materials such as titanium [34-36], chrome-moly steels [37,38], marine steel [39] and copper alloys [40,41] for corrosion and biofouling resistance in aqueous environments by providing suitable surface roughness and micro chemistry. Tailor-made experimental approaches were employed depending on the material chosen. The long term stability and durability of the as developed materials were studied in detail [42].

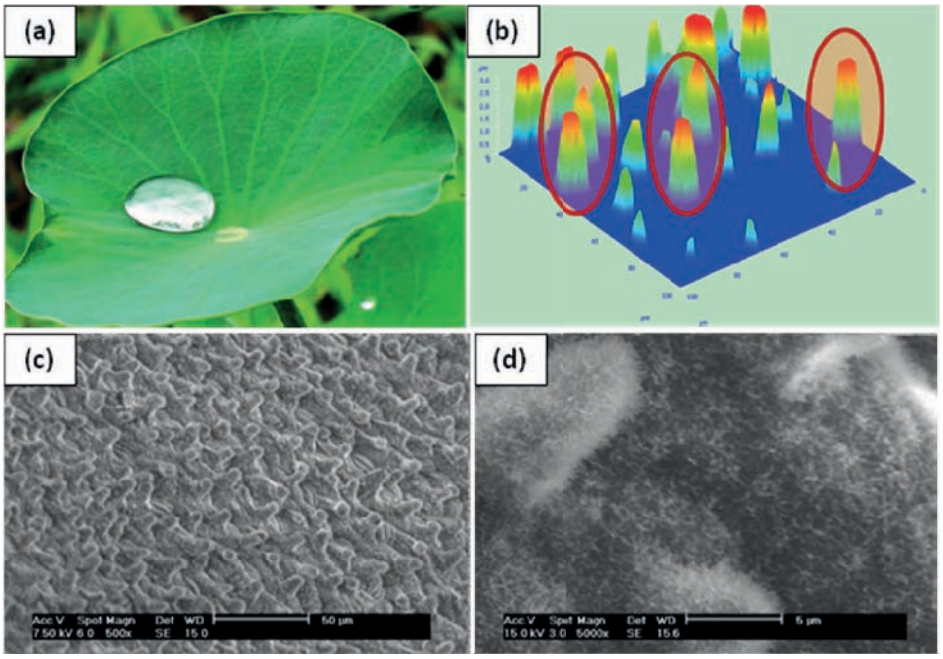
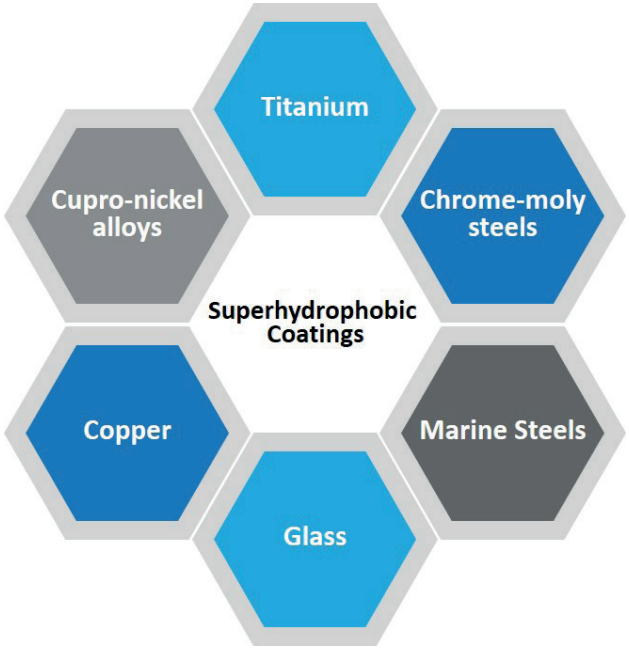


Fig. 3. (a) Photograph of water droplet on lotus leaf, (b) AFM image of lotus leaf indicating two different scale papillae, (c&d) SEM micrographs showing the distribution of the papillae and the nanocrystal wax pins on the papillae.

Scheme - 4



Titanium

SHP surface modification of titanium (Figure 4) was attempted to address the corrosion and biofouling problems of titanium which is used as condenser tubes in the seawater-cooled nuclear power plants. The main objective was to carry out a systematic study on the stability and durability of SHP coating on titanium for long term practical applications [42]. The SHP Ti samples were prepared by abrading, pickling, anodization, dip coating in silane and heat treatment. The as-prepared SHP samples showed heterogeneous lotus leaf-like morphology on the surface with an average water contact angle of 150°. Attenuated total reflectance – infrared spectroscopy (ATR-IR)

confirmed the presence of silanol groups on the anodized titanium surface. The adhesion strength and scratch resistance of the coatings on Ti was confirmed by cross hatch tape test. The samples scored a perfect 5B as per ASTM D3359-09. In addition, the mechanical stability of the coatings was ascertained by ultrasonication, water impact tests and flowing water conditions. SHP titanium showed excellent chemical stability in chloride medium for a period of 60 days. There was minimal reduction in WCA after UV exposure for 3 h and no reduction in WCA after low temperature heat treatment at 50°C for 6 h. The bacterial adhesion studies showed one order reduction in bacterial density in the case of SHP Ti samples compared to control samples over a period of 60 days, with the SHP surfaces still maintaining minimal antibacterial activity. The shelf life of the SHP coatings on Ti was evaluated to be around 2 years in ambient conditions. SHP Ti samples were exposed in sea water kept in a flat cell and the impedance data was recorded in 15, 30, 45 and 60 days. SHP property was retained in the samples after exposing them for 60 days in sea water. The feasibility of scaling up the SHP modification procedure developed for Ti coupons to Ti with any geometry including tubes was also demonstrated. SHP modification was carried out with Ti (CP Grade 2) tubes of 4 cm length, 19 mm ID and 0.7 mm thickness. SHP Ti tubes showed a water contact angle of 147°±2° on the outer side of the tube and the water rolled off the tube surface with a slight disturbance.

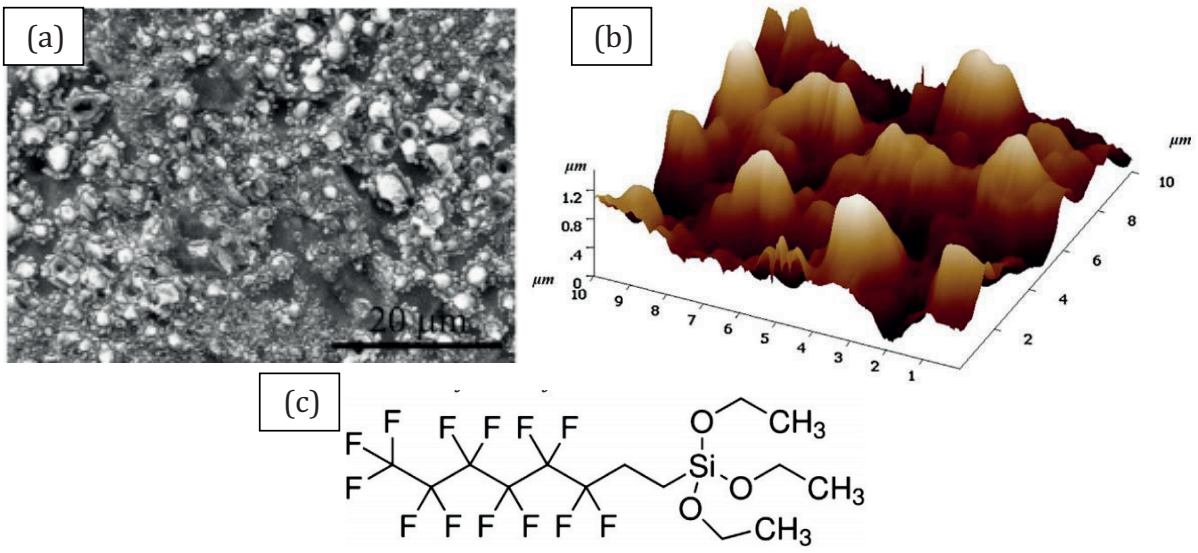


Fig.4. (a) SEM micrograph and (b) AFM image of a superhydrophobic titanium surface and (c) Molecular formual for the silane used in the surface modification of Titanium (1H, 1H, 2H, 2H Perfluorooctyltriethoxysilane, PFOTES). (Reprinted with permission from ref [36] Copyright Elsevier 2014)

Subsequent to these tests, the stability and / or coating durability of SHP silane coating on anodized Ti substrate in different environmental conditions was assessed by employing atomic force microscope (AFM) in Kelvin Probe Force mode (KPFM)[43]. AFM topography images and surface potential images of the SHP samples before and after exposure were recorded and corroborated with the surface roughness and water contact angle values. The SKPFM mapping results (surface potential measurements) revealed that only partial removal of the SHP silane coatings from anodized Ti surface after exposure to the UV light and flowing water system. The results succinctly showed that the SHP silane coated Ti is exceptionally stable in the aggressive environments.

Chrome-Moly steels

With the successful superhydrophobic surface modification of titanium, SHP coatings were fabricated by incorporating hydrophilic silica (HS) nanoparticles in ethanolic perfluoro octyl triethoxy silane (PFOTES) solution on mod. 9Cr-1Mo substrate [37,38]. 9Cr-1Mo ferritic steel and its modified versions are the favored steam generator tubing material in fast reactors. Even though these classes of steels have far excellent mechanical properties, high temperature corrosion resistance and high resistance to chloride induced stress corrosion cracking in water-

steam systems, they are susceptible to localized and general corrosion. Prolonged time lag was found from storage, fabrication stages to commissioning and installation stage. Hence modifying the surface to get a SHP coating that can reduce chloride ions condensation leading to general and localized corrosion in the humid coastal environments during transit, storage and installation in the coastal power plant is a need of the hour. Therefore, a SHP coating may impart good corrosion resistance to retain the integrity of the 9Cr-1Mo steel during storage period. In this regard, coatings containing optimum amounts of PFOTES and HS exhibited superhydrophobic property with high water contact angle (WCA) of 150º ± 1° and low sliding angle of 2°. AFM and SEM studies have shown micro-nano features on the surface. The synergistic effect of these micro-nano features and the low surface energy silane coating was responsible for the observed superhydrophobicity of the samples. The surface topographic structure is an important factor that influences the surface wettability [44]. As described by Cassie–Baxter equation [45,46],

$$\cos\theta^* = f_s \cos\theta_s + f_v \cos\theta_v \quad (1)$$

where θ* is the apparent WCA value of rough surfaces, θ_s and θ_v are the intrinsic WCA values of smooth flat surfaces of solid and air respectively. f_s and f_v are the fraction of the projecting solid and air on the surface respectively. If θ_v is considered to be the surface fraction area of air (θ_v = 180°) and $f_s + f_v = 1$ $f_s + f_v = 1$, then eq (1) can be written as

$$\cos\theta^* = f_s(\cos\theta_s + 1) - 1 \quad (2)$$

By using equation (2), the f_s value was calculated as 0.17, where θ* = 150° and θ_s = 102°. From this fs value, it can be concluded that the small fraction of contact area between the liquid droplet and solid surface allows the droplet to roll off easily over the surface [47–49]. The large fraction of air gaps trapped within the interstices of microtextured surface increased the air/water interface, which in turn effectively prevented the penetration of water droplets into the grooves.

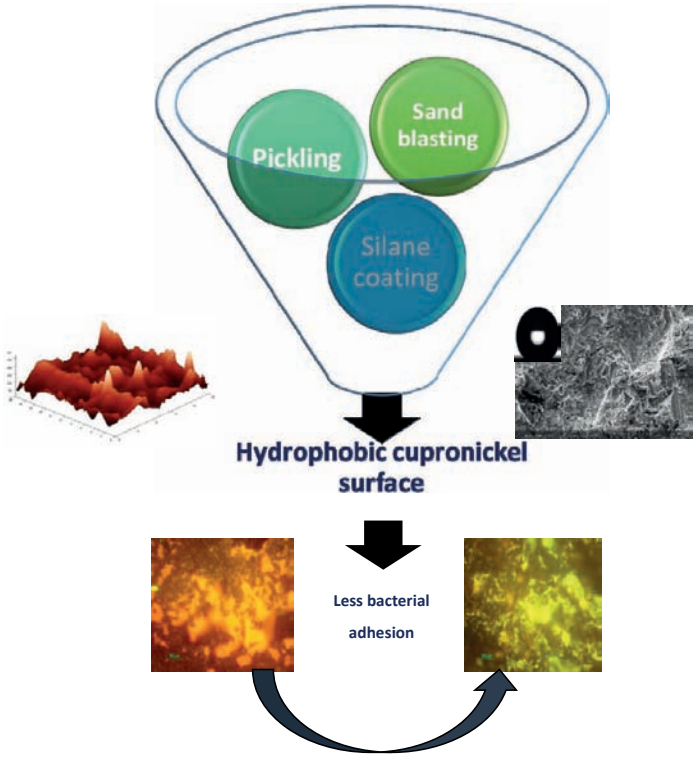


Fig. 5. Superhydrophobic surface modification of cupro-nickel alloys (Reprinted with permission from ref [40] Copyright Elsevier 2018)

The self-cleaning characteristics of the SHP mod. 9Cr-1Mo substrate surface were also examined. Coatings were contaminated by spreading saw dust on the SHP mod. 9Cr-1Mo substrate surfaces randomly. The contaminated substrate was then secured on a tilting stage (2° tilt) and water droplets (total volume 5 µL) were dropped onto the surface from a specified height. The removal of saw dust particles by the water droplets for SHP mod. 9Cr-1Mo substrate was imaged using Goniometer with a CCD camera. As discussed earlier, superhydrophobicity is a novel strategy that has been widely employed as antibacterial coating in recent times. Superhydrophobicity reduces the adhesion force between bacteria and a solid surface which enable the relatively easy removal of bacteria by conventional cleaning methods before a thick and adherent biofilm is formed on the surface. The antibacterial activity of the SHP mod. 9Cr-1Mo substrate was enhanced by an order compared to uncoated mod. 9Cr-1Mo substrate when exposed to Pseudomonas sp. culture. Open circuit potential (OCP) and EIS studies were carried out to evaluate the enhancement of corrosion resistance properties of SHP 9Cr-1Mo steel surfaces in 0.005M chloride environment. The OCP shifted to nobler direction indicating the good passive behavior of the SHP coating [50,51] and the impedance values are one order more than the control samples. These results are mainly attributed to the SHP coatings which prevent the accumulation of corrosive species or water on their surface, resulting in superior anticorrosion property.

Marine steels

Lotus effect based superhydrophobic coatings were developed on marine steels [39] to inhibit biofouling. The aim of this work is to develop superhydrophobic coatings on alloys that are used in marine environment. In this regard, DMR 249A was modified using mechanical methods such as polishing and shot / grit / glass bead blasting and finally dip coated with a low-surface energy material such as silane. The surface modification resulted in water contact angles of about 150° and tilting angles less than 5°. The surface treatment directly influenced the morphology and surface roughness of the samples, for example, glass bead blasted samples exhibited the maximum water repelling property and showed the least bacterial adhesion compared to shot blasted and grit blasted samples. The bacterial adhesion on the glass bead blasted and silane coated DMR steel samples was five orders of magnitude less than that of the as-received samples when exposed to Pseudomonas sp. culture. The aim of this work is to stress the unconventional use of superhydrophobic coatings based on silanes to inhibit biofouling on marine steels.

Copper alloys

Cupronickel alloys are used as condenser materials in the seawater cooled systems owing to copper toxicity towards microbes. However, there is also a possibility of copper resistant microbes forming biofilms on these alloys leading to microbiologically influenced corrosion (MIC) during prolonged service in seawater. In order to address these issues, hydrophobic cupronickel alloys were prepared by using a combination of chemical and mechanical methods such as polishing, acid pickling, sand blasting and a low surface energy silane coating [40]. The surface profile, morphology, roughness and the water contact angle of the two different surface pretreated samples were analyzed. The bacterial adhesion studies in gram negative Pseudomonas sp. culture revealed that the sandblasted, pickled and silane coated cupronickel samples (WCA~ 140°) exhibited better resistance to bacterial adhesion compared to the polished, pickled and silane coated (WCA~ 135°) cupronickel samples. In comparison with the as-received samples, a significant reduction of the bacterial density on surface modified samples was observed.

Superdrophobic coating on copper was made by employing a facile and economic synthesis procedure including annealing and coating the surface with silica nanoparticles dispersed in silane solution [41]. The annealed Cu surface was uniformly covered with spherical micron-sized copper oxide particles and significantly enhanced

surface roughness as evident from morphology studies. The composition analysis showed that an outer layer of CuO and inner layer containing mixture of CuO and Cu_2O phases have formed on the annealed Cu surface. This surface was further dip coated in silica nanoparticles dispersed silane solution resulting in dense agglomerates of silanized silica nanoparticles uniformly distributed on the surface. The as developed copper surface exhibited a superhydrophobic behavior with water contact angle (WCA) of 147°± 0.1° and tilting angle of 5° with the critical surface energy of 17.72 mN/m as calculated from Zisman plot. SHP Cu was immersed in de-mineralized (DM) water in ambient conditions for about 8 months and no significant reduction in water contact angles was noticed. Electrochemical studies carried out in aqueous chloride environments demonstrated the corrosion resistance of superhydrophobic copper surface as evident from the shift in open-circuit potential (OCP) values towards the nobler direction, increase in the charge transfer resistance and lower anodic current as compared with the fresh copper foil. The evaluation of the short term durability of the SHP Cu foil in aqueous chloride environments using EIS technique showed that the corrosion resistance improved with time indicating the self-healing nature of the copper oxide layers formed on the SHP Cu foil.

Glass

As a spin-off from the superhyrophobic surface modification of metals and alloys for anticorrosion and antibiofouling applications, attempts were made to synthesize one dimensional ZnO nanorods on glass substrates [52] using solution based techniques such as successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD). The glass substrates were finally coated with a low surface energy PFOTES silane. The surfaces with water contact angle greater than or equal to 150° are called superhydrophobic surfaces and if such surfaces have contact angle hysteresis less than or equal to 10°, they are said to possess self cleaning property. The surfaces with self cleaning properties play an important role in various technical and practical applications such as self cleaning windows, antireflective and protective coatings for solar panels, water repellent textiles and low friction surfaces for fluid flow. The as developed SHP glass slides were proposed for solar panel applications. The effect of air pockets in increasing contact angle was demonstrated by measuring sliding angle and contact angle hysteresis. The fraction of solid to liquid contact area according to modified Cassie's equation was theoretically calculated to be 4%. The water repellent silane coated one-dimensional ZnO nanostructures showed a water contact angle of 148° with a sliding angle of 1° and the contact angle hysteresis of 2°. This study clearly brought out the significance of the underlying mechanism of superhydrophobic self cleaning coatings on glass substrates based on one dimensional ZnO nanorods.

SUMMARY

Electrocatalytically active Pt/Pd nano particle coated Ti electrodes with excellent corrosion resistance and high catalytic activity were developed which could be employed in reprocessing plants as anodes for electro-oxidative dissolution of spent nuclear fuel in severely corrosive boiling 11.5 M nitric acid medium.

Pt nanoparticles were deposited over titanium substrate and also loaded into titania nano tubes for electrode applications. A seed mediated hydrothermal reduction method was developed and customized to fabricate such electrodes. The electrocatalytic activity of the electrode as well as the stability and durability of the electrodes were excellent in lab as well as simulated plant conditions.

Superhydrophobic coatings were developed on titanium, chrome-moly steels, marine steels, copper alloys with reduced bacterial attachment and enhanced corrosion resistance for applications in marine environments. Superhydrophobic coatings were also developed on glass slides with self cleaning property for solar panel related applications.

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