

STUDY ON THE FACTORS AFFECTING PHOTOCATALYTIC BEHAVIOR OF TITANIA COATINGS USING DIFFERENT PLASMA SPRAY PROCESS

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Abstract— Titanium Dioxide (TiO₂) coatings deposited using Plasma Spray Process has wide range of application in recent years. The feed stocks used for spraying can be in form of powders, suspensions or solutions. Titania is used as photocatalyst for many industrial applications. The coating photocatalytic activity was evaluated for their performance. There are discussions on the factors affecting the performance of the catalytic activity. The use of Methylene blue (MB) dye as aqueous solution was used for evaluating the photocatalytic performances of the coatings. The phase analyses were discussed with X-ray diffraction (XRD) and Raman spectroscopic techniques.

Index Terms— TiO₂ ; Solution precursor plasma spraying; Photocatalytic activity

I. INTRODUCTION

The heterogeneous photocatalytic oxidation of organic pollutants has been a promising and emerging process for purification of water. Extensive researches have been examined on the ability of semiconductor photocatalyst promoting the degradation and mineralization of various pollutants [1-7].

Titania has received considerable attention in recent years because of its wide application such as solar cells [8], photocatalysts [9, 10], gas sensors [11] and microelectronics [12]. TiO₂ coatings are considered due to its in vivo corrosion behaviour, as a chemical barrier against the release of metal ions from biomedical implant, corrosion resistance [13, 14].

Titania is the most important photocatalyst having the potential applications in purification and treatment of water and air, concerning to environmental protection [15, 16]. For photocatalytic applications, titanium dioxides can be either used in the form of powders or coatings.

However the use of conventional powder catalysts has the disadvantage of stirring during the reaction and the separation of the powders from the liquid state will be used in water treatment [17, 18]. In order to overcome these disadvantages extending the industrial application the catalyst are coated as thin films or coatings [18].

Photocatalytic activity of TiO₂ depends on the phase structure and porosity of the thin film or coating. There are various techniques for the deposition of the Titania coatings such as sol-gel, hydrothermal, physical vapor deposition, chemical vapor deposition, spray pyrolysis and plasma-spray deposition etc. Plasma spraying process is a thermal spraying process, where the materials are propelled towards the substrate, by introducing the materials to the plasma jet [19-22].

The plasma spraying can be of different forms based on the type of feed stocks in the form of powders, suspensions or precursor solutions. In plasma spraying the nano/submicron sized powder feedstocks are used for spraying. In suspension plasma sprayings the stable suspensions are prepared using the powders of smaller particle size. The precursor solutions are prepared for solution precursor plasma spraying. In atmospheric plasma spraying the feedstock powder or the suspensions are sprayed to the plasma flame to provide the coating.

Suspension plasma spraying (SPS) process involves dispersing ceramic feedstock in a liquid suspension which is injected to the plasma jet. Suspensions of nanosized particles and agglomerates are sprayed in the plasma jet. The use of finer powder as suspension allows the deposition of finer micro structured coatings Fig. 1.1. SPS are used to achieve both dense and thin coatings. Suspensions prepared from the fine powder are injected to the direct current plasma jet. Due

to the action of plasma jet the suspension drops are sheared, as long before they start vaporizing. The solvents present in the suspension are then evaporated and decomposed in the plasma jet. Solid particles in the droplets of the suspension are then accelerated and melted before deposition on the surface of the substrate. This allows the coating formed in a granular microstructure [23].

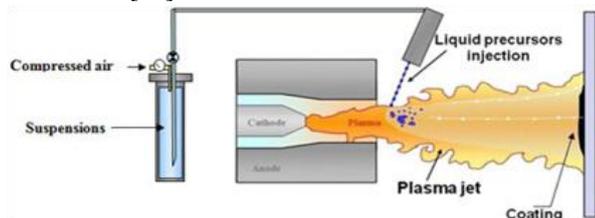


Figure 1.1: Schematic representation of SPS process
[<http://uses.encs.concordia.ca/~dolat/Research-TS-Processes.html>]

The benefits of SPS process are it enables multilayer deposition gradient properties (such as composition, porosity) using one or more suspensions. By adjusting the experimental parameters coating porosity may be controlled and the working environment in ambient air with some of modifications of conventional plasma spraying system [21].

The disadvantages of SPS process are the substrates of complex alloys containing 5 - 10 components, results the deposition with amorphous coatings which occur due to the lowered critical cooling rates of these complex alloys. Devitrification occurs when these amorphous coatings are heated above crystallization temperature. This is because at transformation temperature there will be a very low rate of diffusion in the solid state. The range for iron alloys is 0.4–0.7 T_m , where T_m is the melting temperature which results microstructures in nanometer range and the deposition of nanosized structures limits the safety which is overcome by the SPPS process [21].

The coating technology using solution precursor was first reported by Karthikeyan et.al. [24], in their work use of solution were feasible, lacking good adhesion coatings. In 2001, they reported another work refining the process producing thermal barrier coatings and silicon ceramic coating at University of Connecticut and Inframat Corporation [24].

SPPS is a thermal spray process. SPPS is a type of plasma spraying where the liquid- precursor solutions are directly injected into the plasma jet. The precursor solutions were prepared by dissolving the salts. The commonly used salts for the formulation of thermal barrier coatings were yttrium and zirconium. The dissolved solutions were injected via feed system which was pressurized. As other thermal spraying process, feedstock materials are melted and the deposition takes place on the surface of the substrate. The

materials are injected directly to the plasma plume. Several physical and chemical changes occur to the droplets when solution is injected that include evaporation, crystallization, pyrolysis where in a single step the coating will be formed. Finally on the substrate, coating will be formed in several different states like fully melted or unpyrolyzed Fig. 1.2. In order to control the properties of the coating such as strength, thickness, density and many more the spray parameters can be used. In recent years, importance of the SPPS process has increased where the nitrates and chlorides species in the precursor solution are being deposited forming a coating. Fabricating various functional coatings such as thermal barrier coatings, coatings for medical implants the precursor solution will be atomized through a nozzle front of the spray torch and the sequential deposition on the substrate surfaces in SPPS process [25]. The potential of the SPPS method to deposit wide range of ceramics (oxides and non oxides) make them attractive [26].

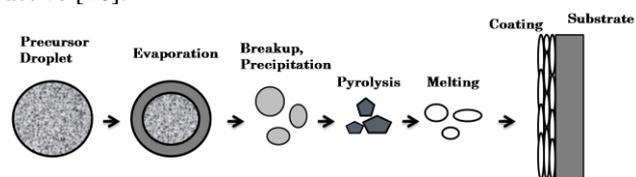


Figure 1.2: Schematic view of reactions during SPPS process
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Atmospheric plasma spraying has its importance for developing successful extrinsic coatings [26] with powder feed stocks. In this process nanostructured coatings can be achieved in the range of 10-100 nm [27].

The advantages of SPPS process are nanostructured coatings are obtained through the process [28]. Over conventional method the biggest advantage of SPPS are can eliminate the agglomeration taking place in powder feedstock. In SPPS the physical and chemical reactions occur in one step [29]. The SPPS process also overcomes the preparation step of powder that is costly and also control the deposit chemistry [29].

Titanium dioxide coating technology ranks first among manufacturers in customer service and product quality. TiO_2 as a white pigment is used in architectural paints where manufacturers offer wide variety of colors [30]. Titania coatings are also used on vehicles, high value plastics, self-cleaning glasses, antifogging glasses and treatment of pollutants in waste water. TiO_2 is a photo catalyst and so industries apply coating of TiO_2 on the reactors to minimize powder recovery after reaction [30].

The Titania (TiO_2) has two catalytic phases namely rutile and anatase. The two phases have many differences

based on their structures and functions. In anatase phase the affinity for adsorption for organic compounds will be high compared to that of rutile phase. The anatase phase also exhibits the lower recombination rates compared to that of rutile phase, this criteria is due to the greater hole trapping rates with 10-fold. The commercially available anatase has the particle size less than 50 nm. These anatase particles corresponding to UV range of 385 nm have 3.2 eV band gap [31].

There are some exceptions with rutile phase which is thermodynamically stable having the particle size larger than 200 nm. The Rutile particles having excitation wavelengths extending into visible range at 410 nm has 3.0 eV a smaller band gap. The phase of Titania that is more photochemically active is anatase; this is due to the combined effect of higher capacity for surface adsorption and lower recombination rates [31].

The applications of Titania coatings are they have, 80 % of worlds Titania consumption are in production of paints, varnishes, paper and plastics. Other 8 % are used applications such as printing inks, fibers, rubber, foodstuffs and cosmetics. Titania (TiO₂) is an important and commonly used photocatalyst and has wide applications. They are used in solar cells [32], photocatalysis [33, 34], gas sensors [34] and microelectronics in the recent years [35]. Titania coatings are also used in the medical implants due to their in vivo corrosion behavior property necessary for the implants coatings that also acts as a chemical barrier against the release of metal ions from implants.

TiO₂ crystallizes in three types Anatase, Rutile, and Brookite (Landoft and Bornstein 1984), Rutile being the most stable of the three types (Henrich 1985). Brookite has not appeared so far in thin film form and rutile has been extensively studied both theoretically and experimentally. Anatase phase importance is studied in solar cell technology (Graetzel 1991) and the way in which its electronic properties differ from those of rutile (Furro et. al. 1994). This distinctness is in agreement with the study of the electronic and optical properties of thin anatase thin film (Tang et. al. 1994). TiO₂ is an excellent material which shows most promising prospect in environmental purification, photoelectrochemical solar energy conversion and optical coating application (Fujishima et. al. 2000).

These applications are due to several properties such as remarkable activity, chemical stability, non-toxic (Raseshwar and Ibanez 1995), highly oxidative photogenerated holes, high energy conversion, highly transparent and high refractive index (Tryl et. al. 2000). Due to its high dielectric constant thin films of TiO₂ have also been studied for application as a gate insulator for Metal Oxide Semiconductor (MOS) device applications, with reduced leakage current (Paily et. al. 2002). This is an inherently n-

type semiconducting material due to stoichiometric oxygen deficiency in the film structure, with a wide band gap typically 3.1 eV and a high index of refraction of about n=2.6, the TiO₂ anatase is an n-type semiconductor (Gugliemi et. al. 1992), Forro et. al. 1994).

The photocatalytic activity of plasma sprayed Titania coatings were studied spectrophotometrically by monitoring rate of decomposition of methylene blue under UV-light. The changes in the concentration of methylene blue solution were monitored by the change in the absorbance peak intensity at the maximum absorbance of methylene blue solution at 664 nm with time as observed in literature [39].

The experiment was carried out in dark using methylene blue solution as stock solution. The UV light was irradiated using UV lamp. The UV lamp was circulated with water throughout the experiment for cooling. The coatings were immersed in the solution, after irradiation of UV light at different interval of time the samples were collected. The methylene blue color decolorized due to the photodecomposition/ oxidation reactions resulting carbon-dioxide, water and mineral acids. The samples are measured for absorbance using UV Visible spectrophotometer at 664 nm [39]. The Schematic representation of the experimental setup is shown in Fig 1.3. The reaction is as below,

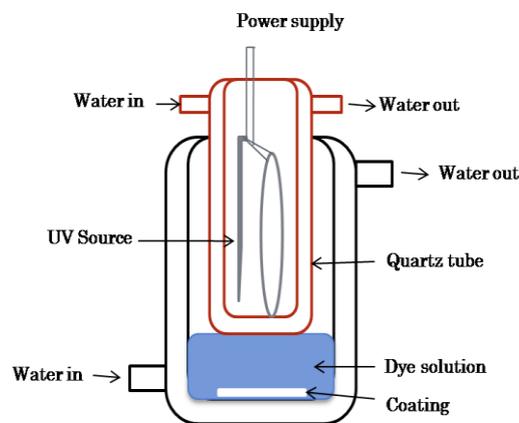
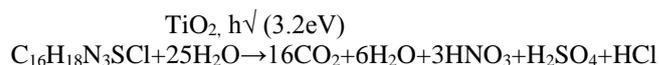


Figure 1.3: Experimental setup for photocatalytic process

Many dyes possess negatively charged groups present in the structures. The adsorption of the dye in acidic solution is stronger on the surface of the photocatalyst having improved decomposition of the pollutants; this is due to the amphoteric properties of TiO₂ particles [36]. In many studies the cationic dye was preferred i.e., methylene blue, because this favors the adsorption on surface of TiO₂ and the decompositions favoring at high pH values, this was put forward by Guillard et. al. [37].

II Factors affecting the photocatalytic behavior of Titania plasma sprayed coatings

Factors such as plasma power, flow rate of carrier gas, the phase composition (i.e., amount of anatase and rutile phases), crystallite size of the phases due to the variation of plasma power and factors such as recombination influence the behavior of photocatalytic activity. The combination of Micro-Raman technique and X-ray diffraction (XRD) together with surface roughness testing provides surface-relevant information relate the surface microstructure of the Titania coatings to their photocatalytic performance.

A. Effect of phase composition on Photocatalytic activity

From (Brulacov et.al.) studies [39] the induction plasma-sprayed coatings were deposited from agglomerated anatase powder. The coatings crystalline contents were mainly composed of anatase and rutile with traces of oxygen-deficient phases. From the study it was observed that the concentration could be controlled by injection of surplus oxygen into the plasma jet as well as adjusting the powder carrier gas flow rate.

The Raman microprobe technique was proven to be a useful technique for spatial characterization of the coating surface owing to its high sensitivity to the TiO₂ phase composition and the crystalline quality of the coatings. The photocatalytic degradation of 4-chlorophenol in aqueous solution showed encouraging performance of some coating compositions. In spite of the rather low anatase content of the coatings, the presence of Titania multi-phase heterostructures acting as coupled semiconductor systems appears to enhance the photocatalytic effect [39].

Studies by D. C. Hurum et. al. [38] showed higher photo degradation of organic contaminants due to better activity of anatase phase of TiO₂ compared to the rutile phase. Synthesis of pure anatase phase by plasma spraying was difficult because of the high plasma flame temperature that favored rutile phase and also rutile phase was thermodynamically stable compared to anatase phase. Superior photocatalytic performance could be obtained by preserving high amount of anatase phase in the coatings [38].

The traditional models illustrated the increased photocatalytic activity of Titania in mixed phase due to the prevention of anatase recombination and rutile sink. This allowed anatase generating holes that moved to the surfaces. This model data did not support the data of some researchers. The current model illustrate that the rutile centers are more integral to the activity of catalyst.

According to data collected from Hurum et.al. Titania catalyst with mixed phase exhibits greater photo effectiveness due to the following reasons,

- (1) The range of photo activity that was extended into the visible region due to the smaller band gap of rutile.
- (2) The slower rate of recombination due to the transfer of electrons from rutile to anatase that stabilized charge separation.
- (3) The catalytic hot spots that were generated at the anatase/rutile interface due to the transfer that occurred because of the small size of the rutile crystallites. The above process was based on the interface between the particle size and TiO₂ phases [38].

Mari Carmen Bordes et. al. [39] studied on the atmospheric plasma spray of the nano/ submicron sized TiO₂ particles. The coatings had bimodal microstructure with agglomerates with partially melted particles retaining the nano/ submicron structures of initial stage and the melted matrix surrounded the structures. The partially melted areas had increased porosity. The unmelted region had anatase particles. Due to the increase of the submicron size particles that had a large amount of anatase in the unmelted regions illustrated the higher photocatalytic activity of the coating. The variation of the methylene blue concentration with irradiation time of solutions with different percentages of submicron sized particles showed the decrease in the methylene blue solution with the irradiation time [39].

Many works have been carried out with suspension plasma spray in which Laura Toma et.al. [40] Studied photocatalytic behavior of TiO₂ coatings with two different thermal spray processes one was plasma spraying process and the other was High Velocity Oxygen fuel spraying process. In this study nanosized particle of anatase was agglomerated by spray spraying using the organic binder polyvinyl alcohol to get spherical sized particles. TiO₂ P25 powder was used for reference material. Both the conventional techniques showed the lamellar microstructure. In HVOF coatings there was observation of anatase whereas in SPS coatings the anatase was preserved. Titania surfaces using SPS technique was fabricated for photocatalytic applications. In many studies sodium polyacrylate was used as dispersant for suspension preparation [40].

Dianying Chen et.al.[41] studied the SPPS process for the development of porous TiO₂ coatings using titanium isopropoxide solution as the precursor solution. Precursor solution was prepared by titanium isopropoxide in water by hydrolysis and condensation processes with hydrochloric acid. In the phase study it was observed that there is increase in the rutile phase due to the increase of plasma power. The spraying of coatings with the plasma power 45.5 KW, showed the complete transformation of anatase to rutile phase. In the as-sprayed coatings the crystallite formation of the anatase and rutile phase resulted due to the heat treatment of plasma jet.

This study also showed that there was the effect on the phase composition due to varying plasma power. From the study it was evident that the anatase content decreased with the increase in the rutile content due to the increase in the plasma power [41].

In another study Dianying Chen et.al.[42] used the precursor solution as titanium isopropoxide dissolved in ethanol maintained at 1.5 M concentration. The SPPS was done to develop a dense TiO₂ coating. By the phase analysis with XRD and Raman the coatings were confirmed with the composition exclusively with rutile phase of Titania [42].

So, the higher photocatalytic activity of the SPPS coating with Titanium isopropoxide solution will be due to the slower rate of recombination and the enhanced catalytic activity due to the small size of the rutile particles in the formulation and the intimate contact with the anatase particles with comparable sizes. All these facilitate the in-situ formation of Titania phases in SPPS coating.

A. *Effect of plasma spray parameters such as plasma power, powder feed rate and flow of argon carrier gas on photocatalytic behaviour*

Cheng Zhang et.al. [45] Studied the comparison of photocatalytic performance of TiO₂ coatings on steel and FTO glass substrates. Here the coatings were generated at three different plasma powers 16kW, 20kW and 24kW. The results showed that the coatings synthesized at the plasma power (16 kW) and powder feed rate (10.9 g/min) of TiO₂ coating on FTO glass shows 25 % decomposition, which is nearly 2.5 times better than TiO₂ coating on the steel substrate for the same exposure duration. The improved photocatalytic activity of TiO₂ coating FTO substrate was attributed to the bimodal porosity in the coating microstructure.

In the same study the performance of photocatalytic activity was measured for plasma-sprayed TiO₂ coatings synthesized by varying plasma powers and powder feed rates. The photocatalytic activity overall increased with the exposure time, which is due to larger MB decomposition with an increased reaction time. The results showed a mere 6 % of MB decomposition, indicating poor photocatalytic performance at the lowest powder feed rate (3.9 g/min) and a photocatalytic performance that increased to 12 % at the highest powder feed rate (10.9 g/min) at lower plasma powers. So, this study concluded that the lower plasma power and higher powder feed rate were the favorable processing parameters for higher porosity content in coating that creates a higher surface area resulting in increased reaction (i.e., decomposition) rate for MB solution [45].

Dianying Chen [41] studies showed the XRD patterns of the as-sprayed Titania coatings at different plasma

powers. The as-sprayed coatings using plasma powder below 36 KW were composed of anatase and rutile phase mixtures and with the increase of plasma power, the peak intensity of rutile increases. At 45.5 KW plasma power, anatase disappears and only rutile phase. The Raman spectra of the as-sprayed titania coatings shows the peaks around 395, 517, 639 cm⁻¹ that are assigned to the fundamental vibration modes of anatase phase with the symmetries of B_{1g}, A_{1g}, B_{1g}, respectively and the peaks around 448, 612 cm⁻¹ are assigned to E_g and A_{1g} modes of the rutile phase.

Dianying Chen et.al.[42] studies showed the XRD and Raman analyses showed that the coatings were composed of crystalline anatase and rutile in the as-sprayed coatings. The coating was built up by the accumulation of deposits from the multiple single-scans, the crystalline anatase and rutile in the as-sprayed coatings must be the result of crystallization of these unpyrolyzed gel-like precursors after arriving at the substrate.

R. A. Spurr et.al.[43] studies showed the increase in the plasma power, the intensity of anatase peak decreased and the intensity of rutile peak increased, which clearly showed the decrease in the anatase content with the increase in plasma power.

Higher the plasma powers higher the temperature it produces. With the increase of plasma power, the plasma jet temperature and length increases. It was observed, the plasma jet length was approximately 50 mm at plasma power 45.5 KW, from the place of the substrates location in the study. Since all the coatings were deposited at the same standoff distance, the heat treatment of plasma jet on the coatings surface was stronger with the increase of plasma power. When the unpyrolyzed precursors arrive at the substrates, they experienced in situ pyrolysis and crystallization on the coating surface due to the plasma jet heat treatment effect. The effect of plasma jet heat treatment on the anatase to rutile phase transformation increased with the increase in plasma power. Thus, the rutile content increases with the increase of plasma power. The coating front-face temperature measured by pyrometer was approximately 770 °C using the plasma power of 45.5 KW, which was higher than the anatase to rutile transformation temperature. Therefore, the anatase completely transforms to rutile in the coating sprayed using the plasma power of 45.5 KW [43].

The coating sprayed using the 21 KW plasma power had the average grain sizes of anatase and rutile particles 26 nm and 50 nm, respectively. With increasing the plasma power from 21 KW to 36 KW, the anatase grain size gradually increased from 26 nm to 39 nm, while the rutile grain size has a little increase from 50 nm to 56 nm. With further increase of the plasma power to 45.5KW, the anatase completely transformed to rutile and the rutile had an average grain size of 75 nm.

Moreover, the grain size of rutile will be always larger than that of anatase in the as-sprayed coatings [43].

In the study the SPPS method was used to deposit porous TiO₂ coatings. The single scan experiments indicated the droplets do not undergo the pyrolysis process in the plasma jet and will form the gel-like deposits on the substrates. The formation of crystalline anatase and rutile in the as-sprayed coatings was the result of plasma jet heat treatment on the gel-like deposits. Plasma power will have a significant effect on the coating phase composition. With the increase of plasma power, the coating anatase content decreases with the increase in the rutile content [41].

From the studies of Brulacov et.al.[44] it was observed that a high flow rate of the argon carrier gas has a profoundly positive effect on the amount of anatase maintained in the coating and its crystallinity both of which appear to control its photocatalytic performance.

B. Crystallite sizes of anatase and rutile phases

There was rapid electron transfer from the small rutile crystallites to the lower energy anatase lattice trapping sites, there was more stable separation of charges under the visible illumination, where this process will be in the presence of small rutile crystallites. The photogenerated electrons are transferred to the trapping sites of anatase allowing the holes lost to recombination reach the surfaces. Now, there was electron transfer to the surface trapping sites from the anatase trapping sites. By competing recombination, the stabilization of charge separation activates the catalyst and rutile originating hole participate in oxidative chemistry. Due to slower rates of recombination there was increase in photodecomposition efficiency [61].

C. Effect of porosity on photocatalytic activity

From the study of Cheng Zhang et.al [45], the effect of porosity on photocatalytic activity of plasma-sprayed TiO₂ coating on steel substrate were studied varying the processing parameters viz. plasma power and powder feed rate and the relationship between the porosity content and the rate of decomposition of methylene blue (MB) dye was correlated to the coatings microstructure with the photocatalytic activity. The results were the coatings with the highest porosity content exhibited the best photocatalytic efficiency. Anatase is well accepted as a photocatalytic favored phase while rutile, due to its high electron-hole recombination rate, is less desired for photocatalytic applications [46-48]. So, the study showed the rutile as the major phase. The coating with the highest porosity content exhibited improved photocatalytic performance [45].

TiO₂ coatings are usually deposited as a thin and porous coating for the photocatalytic applications. The key requirement is high degree of porosity in the coating as they provide more surface area and establish TiO₂ layer to accept more electrons from the dye in unit time. [49-51].

Plasma spray process is a rapid manufacturing process that reduces the deposition time from hours to few minutes for the large scale deposition of TiO₂ coating. Moreover, plasma spraying enables tailoring of the porosity in the coating [52]. Several researchers have investigated plasma-sprayed TiO₂ coatings for evaluating the property of photocatalytic activity [53-60]. The studies are focused for studying the effect of, (i) type of substrate and, (ii) anatase or rutile phase content on the photocatalytic properties of TiO₂ coating.

Lee et. al. studied on the deposition of nanostructured TiO₂ coating on stainless steel by plasma spraying and found that lower plasma power resulting in higher anatase phase fraction and smaller grain size [53]. Such coating exhibited improved photodecomposition characteristics.

Kanazawa and Ohmori [54] studied on the deposition of TiO₂ coating on PET polymer substrate which resulted the melting of PET substrate due to intense heat of plasma. The plasma-sprayed TiO₂ coating on stainless steel substrate with an external bias voltage displayed improved photocatalytic property, as it reduced recombination of photogenerated electron-hole pairs [55]. The coatings with TiO₂/Pt composite synthesized using plasma spray showed no benefit of Pt addition on the photocatalytic property under visible light [56]. TiO₂ coating has also been deposited using suspension plasma spray (SPS) technique [57, 58].

TiO₂ coating synthesized by suspension plasma-sprayed using internal and external feedstock injection exhibited high photocatalytic activity, in spite of having the rutile as major phase [57]. The reason for photocatalytic activity exhibited by the rutile phase is not clearly understood [57].

Bannier et. al. [58] studied on suspension plasma spray to deposit TiO₂ coatings on steel and glass substrates. The coatings had a bimodal microstructure with anatase phase content between 32 and 72% and showed improved photocatalytic activity compared to that of sol-gel process for TiO₂ coating. No correlation was found between the photocatalytic activity and the anatase content. The correlation between plasma spraying parameters and coatings photocatalytic performance were also investigated [59]. The coating at the lowest plasma power had highest porosity displayed excellent photocatalytic efficiency due to higher surface area.

The formations of high porosity TiO₂ coatings were due to the lowest plasma power and higher powder feeding rate. There was improved photocatalytic performance of the coating due to the high porosity content. The TiO₂ coating deposited on the FTO glass using same processing parameters, showed 2.5 times better photocatalytic performance as compare to the coating on steel substrates. This improvement was due to the formation of bimodal porosity (micron and submicron size pores) and the improved transmittance in TiO₂ coating on FTO glass, which enhanced the diffusion and reactions kinetics of MB decomposition. In the phase composition the anatase phase in starting powder transformed into rutile phase in the plasma-sprayed coating. So the porosity content has a dominating effect than phase type for TiO₂ coatings photocatalytic performance [45].

Dianying Chen et.al. [41] studied that the coating surface microstructures were different from the single scan deposits morphologies on room temperature substrates. The gel-like smooth film and semi pyrolyzed hollow-shell structures disappear in all of the as-sprayed coatings, which was because of the high temperature plasma jet repeatedly scanned over the substrate during the plasma-spray process, it had a strong heat treatment effect on the coating surface; resulted the gel like deposits, semi-pyrolyzed hollow-shell structures will in situ pyrolyzed on the coating surface under the plasma jet heat treatment and form the aggregates and porous coatings. All of the as-sprayed coatings were very porous.

D. Other factors effecting photocatalytic activity

The increased photodecomposition efficiency of the SPPS coating may be due to the slower rates of recombinations. The utility of photocatalyst like Titania depends on the ability of conversion of the photons to chemical energy. The promotion of an electron from valence band to the conduction band is due to the absorption of energy from the ultra-band gap leaving positively charged hole in the valence band. Low photo efficiency was due to the recombination of the charged pairs. The electrons and holes in small quantity move to the surface. With an adsorbed compound the reaction is occurs by direct electron transfer to the surface reaction or to the recombination sites. Typically due to smaller size of rutile particles enhances the photocatalytic activity which we have observed in the SPS and SPPS coatings [61].

E. Effect on phases of TiO₂ due to thermal treatment

Dianying Chen et.al. studied the XRD patterns of the gel powders calcined at different temperatures for 1 h. The

gel powders calcined at 250 °C were amorphous. When the temperature was increased to 350 °C, the anatase TiO₂ crystalline phases were formed. However, the broad and weak peaks implied poor crystallinity and fine grains. When the calcination temperature was increased from 350 °C to 500 °C, the peaks became sharper and stronger, indicating the increase in crystallinity of the anatase TiO₂ powders. At 500 °C, rutile TiO₂ crystalline peak started to appear. With increasing the temperature from 500 °C to 700 °C, the peak intensity of rutile increased and at the same time, the peak intensity of anatase decreased. At 700 °C, the anatase almost completely transforms to rutile [41].

F. Use of Methylene blue dye in the photocatalytic activity

Sivalingam et.al.[61], studied photocatalytic activity with five dyes chosen based on the various functional groups. pH was varying during the progress of reaction for all dyes examined. Since the pH variation was minimal for Methylene blue, it was chosen for the study for the effect of catalyst loading, pH, initial dye concentration and various transition metal ion doping on TiO₂. Effect of initial concentration on the degradation of Methylene blue with catalyst loading of 1 kg/m³ at natural pH conditions were studied along with the time variation of various dye concentration under (i) acidic and (ii) basic pH with catalyst loading of 1 kg/m³ and initial concentration of 150 ppm.

The effect of transition metal ion doping on the photocatalytic degradation of Methylene blue with initial the concentration of 200 ppm with catalyst loading of 1 kg/m³ was studied. The nano-sized, high surface area pure anatase phase Titania prepared by solution combustion method was employed for the photocatalytic degradation of various dyes. The effects of catalyst loading, initial concentrations of the dyes, pH, and metal doping with Cu, Pt, Mn on TiO₂ was investigated. The photo activity of the combustion synthesized Titania powder was better than commercial Degussa P-25[49].

The widespread application of methylene blue (MB) originates from the fact that it is mainly nontoxic and convenient for the use as a dye. MB exhibits strong absorption in the visible light but not in the UVA region. This fact presents the perceived effectiveness of the MB test, which was considered by the International Organization of Standardization (ISO) as a standard test for photocatalytic surfaces [62, 63].

TiO₂ nano fluid has good dispersion, so even without a dispersant, it can still remain in stable suspension for a fairly long time. The presence of TiO₂ plays an important role in the degradation of methylene blue. The rate constant for methylene blue calculated using the Langmuir-Hinshelwood equation is 0.0365 (min⁻¹), and the surface adsorption of

methylene blue on TiO₂ is 0.0437 (min⁻¹). The changes in concentration of methylene blue are mainly controlled by the adsorption of methylene blue on TiO₂ nanoparticles. Experimental results have shown that the prepared TiO₂ has good photocatalytic activity for decomposition using methylene blue.

The effect of initial concentration of Methylene blue on the photocatalytic degradation rate was investigated over the concentration range of 50–200 ppm, since the pollutant concentration is an important parameter in water treatment the concentration has a significant effect on the degradation rates and rate of decrease in the dye concentration is faster when the initial concentration is less. The degradation rate is lower for higher initial concentration as the order decreases and, therefore, the Langmuir–Hinshelwood rate form was proposed to model the experimental data. The external diffusion is negligible in the concentration range of our investigation. Adsorption and surface reaction was assumed to be the rate controlling steps and these parameters were determined using L–H rate form [61].

II. METHOD OF TiO₂ PHOTOCATALYST PREPERATION

The TiO₂ photocatalyst can be prepared using many methods have been reported for nano powders such as chemical solution decomposition (CSD), chemical vapor decomposition [65-68] two-step wet chemical method [69], sol–gel [70, 71], ultrasonic irradiation [72, 73], ethanol thermal and hydrothermal [74-77]. The most widely used TiO₂ in photocatalysis is commercial Degussa P25 produced by flame hydrolysis of TiCl₄ at temperatures greater than 1200 °C in the presence of hydrogen and oxygen. In the recent literature [70, 71, 78-80] say that the sol–gel is the most commonly used method for the preparation of photo catalysts, it may be whether only TiO₂ or doped TiO₂. The advantage of these methods (wet chemical methods, which include sol–gel) is that they facilitate the synthesis of nanometer sized crystallized TiO₂ powder of high purity at relatively low temperature [72]. Other Researchers used modified sol–gel method [81, 82], ultrasonic assisted sol–gel method [83], aero gel method [84], method similar to sol–gel [85], sol–gel and photo-reductive decomposition [86], precipitation [87], two-step wet chemical method [88], and extremely low temperature precipitation [89].

III. CONCLUSION

The photocatalytic activity of the plasma sprayed titania coatings are influenced by number of factors that include phase composition, plasma spray parameters such as plasma power, powder feed rate, flow of argon gas, crystallite sizes of the TiO₂ phases, thermal treatment, recombination rates are factors

discussed above. The phase composition of the Titania coatings as anatase and rutile infer most. Some results showed in the plasma sprayed Titania coatings the presence of anatase phase showed higher photocatalytic activity and some showed in the presence of mixed phase of anatase and rutile and these variations occurring may be due to the parameters during the plasma spraying. The plasma power is another factor which influences the catalytic activity of TiO₂, by which the temperature with the duration of the heat applied influence the change of the phases from the anatase to the rutile indeed the crystallite sizes of the anatase and the rutile particles.

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