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Bactericidal effects of reactive thermal plasma synthesized titanium dioxide photocatalysts

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Abstract. Nanocrystalline titanium oxide powder has been synthesized by reactive plasma processing. The precursor powder of TiH_2 was oxidized ‘in-flight’ in a thermal plasma reactor to effect complete conversion of TiH_2 to nano-sized TiO_2 powder. Characterization of the powder by various analytical tools indicated that the powder consisted of nano-sized titanium dioxide particles consisting predominantly of the anatase phase. Bactericidal action of illuminated TiO_2 on pure culture of Escherichia coli was studied. The plasma synthesized TiO_2 nano powder catalyst was found to be highly effective for the killing of Escherichia coli. The efficiency of photocatalytic disinfection, used to inactivate Escherischia coli as function of time is discussed.

1. Introduction

The provision of clean drinking water has become a serious problem in the 21st century and an efficient solution must be needed. Water supply resources consist of a variety of physical, chemical and biological constituents. Particularly, reclamation of wastewater is more and more widely practiced since the availability of fresh water supply becomes increasingly scarce. Therefore, disinfection of wastewater for use is increasingly practised in many countries.

The conventional water disinfection technologies involve chlorination and ozonation. Chlorine has been widely used for the treatment of water disinfection throughout the world. The well-known interaction of chlorine with organic materials that produces harmful disinfection by-products called ‘chloro-organic compounds’ with trihalomethanes, which are presumed to be carcinogenic chemicals, led to the employment of new alternative methods that have gained great interest in recent years for the scientific community [1].

One of the most promising advanced oxidation technologies is photocatalysis for water and air purification [2–4]. The most widely used photocatalyst is TiO_2, because of its very efficient photoactivity, its lack of toxicity, and its high stability. In particular, nano-crystalline titania is extensively studied for many environmental applications such as decomposition of toxic organic compounds, destruction of pollutants from contaminated water and air and killing of harmful bacteria and cancer cells. The photocatalytic process breaks down the organic compounds into simple molecules such as carbon dioxide and water [5-8].

The findings of Matsunaga et al. created a new avenue for sterilization and resulted in attempts to use this novel photocatalytic technology for disinfecting drinking water and removing bio-aerosols from indoor air environments [9-11]. Killing of cancer cells with the TiO_2 photocatalyst for medical applications has also been reported [12].

When irradiated, TiO_2 particles that is in direct contact with or close to micro-organisms produces the highly reactive oxygen species such as hydroxyl radicals, which attack the microbial surface. The fundamental mechanism of the photocatalytic killing process is important in a practical system to efficiently kill a wide array of micro organism. Matsunaga et al. believed that direct photochemical oxidation of intracellular coenzyme A to its dimeric form was the root cause of decreases in respiratory activities, which leads to cell death [9]. Sunada et al. found that the endotoxin, an integral component of the outer membrane of E.Coli, was destroyed under TiO_2 photocatalytic reactions. Maness et al. [14] also reported bactericidal activity of TiO_2/UV reaction and its killing mechanism. According to these authors lipid peroxidation reaction followed by lost of respiratory activity, which leads to the death of E. coli. From the above results, unsaturated fatty acid (polyunsaturated phospholipids) in the cell membrane is the primary site for reactive photo generated oxygen species attack during photocatalytic reactions. Oxidative attack of the cell membrane leads to lipid peroxidation. The combination of the cell membrane damage and further oxidative attack of internal cellular components, ultimately results in cell death [13, 14].

Nano-crystalline titanium oxide powder for photocatalytic applications is prepared by a variety of techniques including the sol–gel method, solvo-thermal process, reverse miscellar, hydro thermal method and electrochemical methods [5,6,15,16,17]. Thermal dissociation of alkoxide, flame aerosol processing and plasma processing using liquid precursors have also been used [18-20]. The main disadvantage of the solution precursor plasma route is that it consumes large energy for vaporization of the solvent.

A novel method involving ‘in-flight’ oxidation of TiH_2 in thermal plasma jet has been developed in our laboratory for bulk synthesis of nano-crystalline titania [21]. Reactive plasma processing (RPP) is a novel technique, which takes advantage of the high temperature and high enthalpy of the thermal plasma jet to effect ‘in-flight’ chemical reactions in the presence of a reactive gas to synthesize nano-sized powders of advanced ceramics, novel coatings and convert minerals and industrial wastes to value-added materials. The major advantages of the (RPP) technique include versatility, short processing time, large throughput, adaptability to process thin films and coatings. Also, the process can be customized to synthesize any desired product. The technique is ideally suited for large-scale production.

The present paper reports the experimental method adopted to synthesize nano crystalline TiO_2 powder by reactive plasma processing (RPP). X-ray powder diffraction (XRD), Scanning electron microscopy (SEM), Raman spectroscopy, Diffused reflectance spectroscopy and Fourier transform-infrared spectroscopy (FTIR) were used to characterize the synthesized powder. Photocatalytic activity of the bactericidal action of illuminated TiO_2 on pure culture of E.coli was studied under UV irradiation.

2. Experimental method

2.1 Reactive plasma synthesis of nano-sized TiO_2 powder

The reactor assembly consists of the plasma torch mounted on the reactor, which is a double-walled stainless steel cylindrical vessel 300 mm in diameter and 600 mm in length. The torch electrodes and the reactor are cooled by water. The powder is injected into the plasma jet through a side port provided at the anode of the plasma torch. There is provision to inject oxygen or any desired reactive gas downstream the plasma jet. A mixture of argon and nitrogen was used as the plasma gas. The powder feed rate and carrier gas flow rate were monitored and controlled. The experimental run consisted in establishing a stable arc between the electrodes.

TiH_2 powder (38-53 micron size) was injected into the plasma jet by using argon as the carrier gas. Oxygen gas was introduced 10 mm downstream of the exit of the plasma torch. TiH_2 dissociates to form Ti particles and hydrogen gas in the plasma jet that are subsequently converted to TiO_2 and water vapour, which escapes along with the exhaust gas stream. Titanium oxide formed collects as nano-sized dust on the walls of the reactor. Typical operating parameters are given in table 1.

Table 1. Typical operating parameters

Arc voltage (volts)	40
Arc current (amperes)	400
Nozzle diameter (mm)	8
Primary plasma gas (Ar) flow rate (lpm)	25
Secondary gas (N_2) flow rate (lpm)	2
Carrier gas (argon) (lpm)	8
Reactive gas (air) (lpm)	30
Ti (TiH_2) powder feed rate (gpm)	5
Torch Input Power (kW)	16
Electro-thermal efficiency (%)	60

Titanium oxide is scraped from the reactor wall and characterized by XRD, SEM, RAMAN, UV-VIS diffuse reflection spectrophotometer and FTIR.

2.2 Preparation of E.Coli Culture

The cultures of E.Coli were grown aerobically overnight from stock suspension in Luria Bertani (LB) medium on a rotary shaker. The 100 ml aqueous samples containing 10^{-6} Colony forming unit (CFU)/ml initial E.Coli concentration were prepared by serial dilution method and subjected to photocatalytic treatment. The photocatalytic experimental set up was kept in laminar air flow hood after proper sterilization. A 125 W low-pressure ultra violet lamp was provided as an illumination source. The lamp emitted radiation over a wavelength range of 360 nm. The intensity of UV light falling on the quartz cell was 580 Lux measured by a Lux meter.

2.3 Photocatalytic Experiments

The bactericidal effects of reactive thermal plasma synthesized titanium dioxide photocatalysts were studied. The bacterial suspension with TiO_2 catalyst were stirred under magnetic stirring and exposed to UV light radiation. At regular intervals of time, the aliquots of irradiated samples were withdrawn and kept in dark. Analyses were in triplicate and control was also carried out under the same conditions. The number of viable cells in the suspension of all light treatments and control run were determined by plating aliquots of withdrawn samples on to agar plates by using spread plate method. These plates were incubated at 30^0 C for 24 hours and the bactericidal activities of the samples were evaluated based on the decrease in the colony forming units of E.coli formed on agar plates. The plasma synthesized TiO_2 nano powder catalyst was found to be highly effective for the killing of E. coli. The efficiency of photocatalytic disinfection used to inactivate E. coli as function of time with respect to reactive plasma synthesized TiO_2 nano powders was discussed.

3. Results and Discussion

3.1 Phase structure

Results of X-ray diffraction of the plasma-synthesized powder (sample A1) shown in the figure 1. consisted only of titanium dioxide. Diffraction peaks due to TiH_2 or Ti metal could not be detected showing complete conversion of the starting powder of TiH_2 to TiO_2, which was present in both the anatase and rutile phases. The amount of anatase phase in the sample was ascertained using the expression

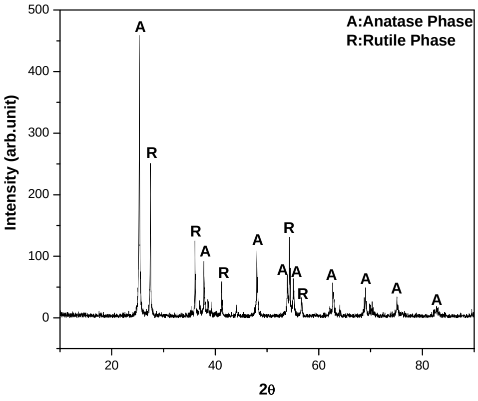

Figure 1. X-ray diffraction pattern of plasma synthesized TiO_2 nano powders

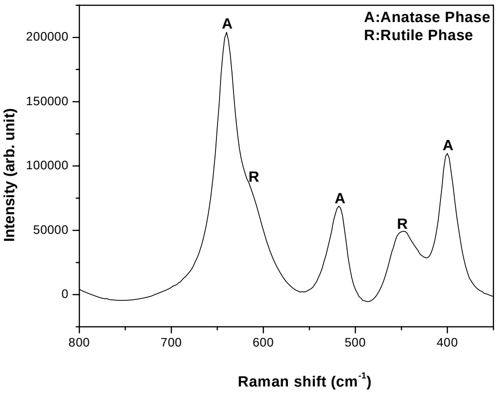

Figure 2. Raman spectrum of plasma synthesized TiO_2 nano powders

$$W_A = I_A / (I_A + I_R) \qquad (1)$$

In the above expression, W_A is the weight fraction of anatase in the mixture, I_A and I_R are the area under the diffraction peaks corresponding to reflections from the 101 peak of anatase and 110 rutile peak.

Phase structure is the most important factor that influences the photo-catalytic properties. Among the various polymorphs of titanium oxide, anatase is photo-catalytically more active than the other phases. The as-synthesized powder (sample A1) consists of a mixture of anatase and rutile phases, with about 70 % anatase phase.

3.2 Raman spectroscopy

The Raman spectra of the as-synthesized TiO_2 nano powder (sample A1) are shown in the figure 2. The spectra showed characteristic bands corresponding to the anatase phase of TiO_2 at 640, 519, 399 cm^{-1}. The most intense lines of rutile at 452 and 612 cm^{-1} can also be seen in the figure, with the line at 613 appearing as a shoulder in the anatase peak of 640 cm^{-1}. The results are in good agreement with A. Gajovic and co-workers [22, 23].The characteristic bands due to the anatase phase are more intense than those of rutile in the as-synthesized TiO_2 nano powder is in agreement with the results of X-ray diffraction.

3.3 FESEM

Scanning electron microscopic images of the synthesized powders are shown in figure 3. It is seen from the figure that the sample A1 consists of nano-sized particles with spherical or near-spherical morphology. The particle size is seen to be distributed in the range of 10 nm - 50 nm ranges. It is also seen that more than 60 % of the particle are distributed in the 20-30 nm ranges. A certain fraction of the powder is also seen to consist of nano-agglomerates.

3.4 TEM Analysis

Transmission electron microscopic images of the synthesized powders are shown in figure 4. It is seen from the figure that the sample A1 consists of nano-sized particles with spherical or near-spherical morphology. The particle size is seen to be distributed in the range of 10 nm - 50 nm ranges. It is also seen that more number of spherical particles are distributed in the 20-30 nm range. A certain fraction of the powder is also seen to consist of dispersed particles.

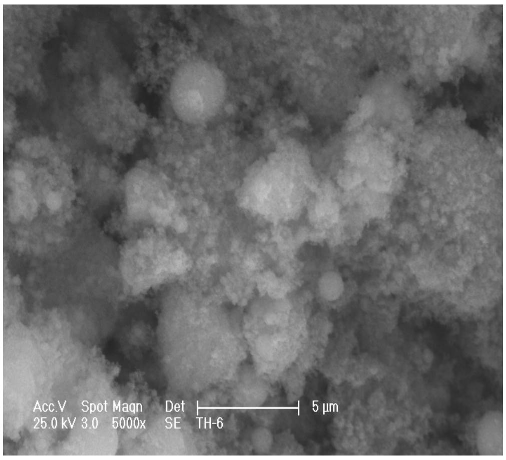

Figure 3. SEM photograph of TiO_2 powder

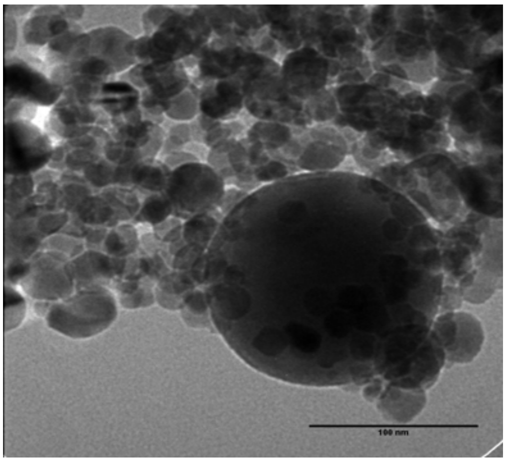

Figure 4. TEM photograph of TiO2 powder

3.5 Diffuse reflection spectroscopy

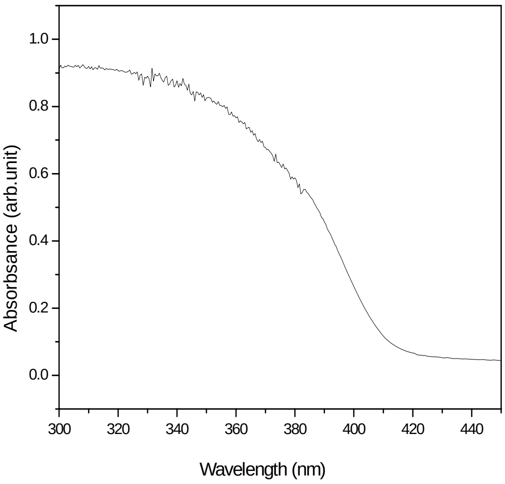

Figure 5. UV–VIS spectra of plasma synthesized TiO_2 nano powders.

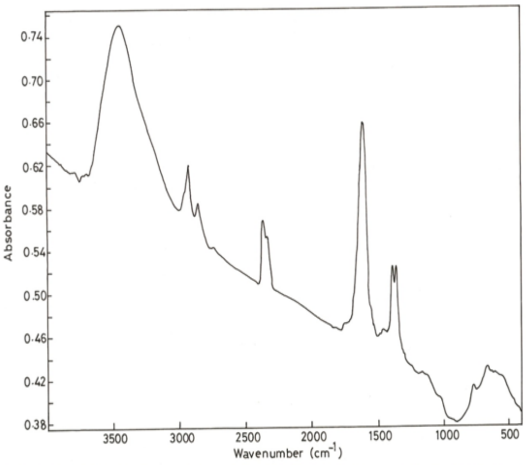

Figure 6. FTIR spectra plasma synthesized TiO_2 nano powders.

It is evident from the figure 5 that UV-absorption edge of plasma synthesized TiO_2 nano powders (sample A1) extended to longer wavelength (towards visible region), which is beneficial for improving the photo absorption and photocatalytic performance of TiO_2 under visible light, whereas the standard powder absorbs only UV region.

3.6 *FTIR Analysis*

The FTIR spectra of the plasma synthesized powders (sample A1) are shown in figure 6. The broad peak appearing betweens 3200-3600 cm^{-1} is assigned to the stretching vibrations of the OH groups. The peaks in the range of 1620-1630 cm^{-1} are attributed to the bending vibrations of surface adsorbed molecular water. The main peaks appearing in the range 400-700 cm^{-1} correspond to Ti-O and Ti-O-Ti stretching vibrations [24, 25].

The role of surface hydroxyl content on the photocatalytic activity of titania powder has been studied by Boonstra and co-workers [26], who showed that the surface photoactivity for a TiO_2 powder is proportional to the concentration of hydroxyl groups on the surface. The surface hydroxyl groups can act as the centres for photocatalytic reactions. The combination of hole (h^+) and the surface hydroxyl group results in the formation of the highly reactive OH radical bound to the surface. The presence of OH group from the FTIR spectra confirms consequence of OH radical's concentration from the TiO_2 powder to participate higher photocatalytic reactions for bacterial inactivation.

3.7 Photocatalytic Bactericidal activity performance study

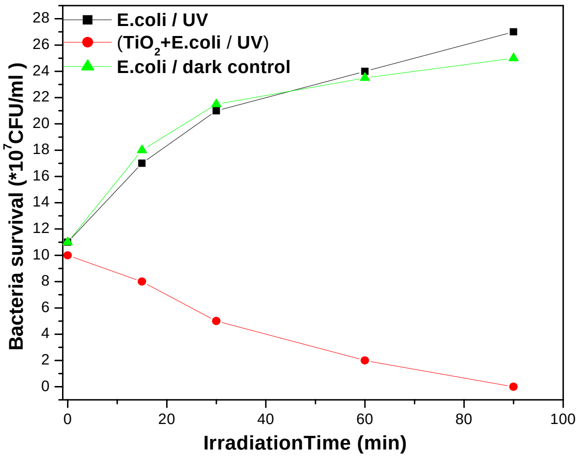

Figure 7. Inactivation of E.coli under UV illumination over plasma synthesized TiO_2 powders

The bactericidal activities of the plasma synthesized titania powders (sample A1) were evaluated by the inactivation of E.coli at various conditions are shown in the figure 7. The results show that the bacterial inactivation by UV light is strongly enhanced by the presence of TiO_2. The number of surviving bacteria increases exponential with respect to time for the E.coli without TiO_2 powder exposed to the UV light exposure. The control run under dark conditions are also grows exponentially with respect to UV light exposure.

The data in figure 7 for the inactivation of E.coli by plasma synthesized titania powder is due to photocatalytic oxidation process. From figure 7 it is observed that under UV irradiation, plasma synthesized titania powder mixed with E.coli culture take 90 min duration for complete inactivation of E.coli, whereas E.coli culture exposure to UV light grows exponentially with respect to UV irradiation time upto 90 min. The above results confirm the efficient inactivation of E.Coli against the reactive oxygen species (OH radicals) produced by the plasma synthesized powder during the photocatalytic reactions.

The control run under dark conditions after 90 min of stirring at 32 ^{0}C are also grows exponentially with respect to irradiation time. This result shows that all the bacteria survive in presence or absence of TiO_2. This indicates that the disinfection with TiO_2 in the dark does not occur and the absorption of E.coli on TiO_2 catalyst is insignificant.

After the photo catalysis experiment, the titania powder mixed with E.coli exposed to UV light were kept at dark for 48 hours and then the aliquots were cultured on to agar plate in order to analysis any recover of microorganism, which results no recovery of micro organism was observed under dark. This result indicates that the oxidative species developed at the TiO_2 surface caused severe damaged to the cell walls

Inactivation of bacteria by TiO_2 photocatalysis using (320-400 nm) has been considered as one of the most effective disinfection technologies, since no carcinogenic, mutagenic or malodorus compounds are formed during the process.

Phtocatalytic activity of titanium dioxide for bacterial inactivation depends on various factors including the phase structure, particle size, surface area, crystallinity of the powder, surface adsorbed water molecules and hydroxyl group etc [26-28]. The overall catalytic activity is due to the synergistic effect of all these factors.

Photo catalytic oxidation process proceeds by absorption of a photon of suitable energy by the photo catalytically active material that generates an electron and a hole, which can migrate to the surface of the catalyst, reacts with adsorbed molecules/gases to produce highly reactive radicals and species that are responsible for oxidation of organic compounds, or bacterial destruction. The positively charged hole react with adsorbed water molecules on the surface of the catalyst and creates the highly reactive and short-lived hydroxyl radical OH•. The photogenerated electrons are primarily used in the conversion of O_2 to the super-oxide radical O_2^- or the singlet oxygen, which can, in turn, stimulate other radical chain reactions involving H_2O_2 or O_3.

The surface photoactivity for a TiO_2 powder is proportional to the concentration of hydroxyl groups on the surface. The production of OH radicals on the surface of the catalyst is related to the adsorbed –OH groups, which can be determined by FTIR with encouraging results. The higher the concentration of surface OH groups, which results higher the photocatalytic activity for bacterial inactivation and can throw light on the relative photo catalytic activities of sample A1 [8, 29].

From the above results, it is evident that the photocatalytic efficiency for bacterial inactivation of plasma synthesized TiO_2 powder is functionally as effective under UV light.

4. Summary and conclusion

Complete conversion of the precursor material to nano-crystalline titania was accomplished in a single step process. Studies show that bulk synthesis of TiO_2 nano powder can be accomplished by reactive plasma processing. The TiO_2 nano powders synthesized under reactive plasma processing produces higher anatase phase content with higher crystallinity which results in outstanding photocatalytic efficiency for bacterial inactivation. Evidence for the formation of hydroxyl groups on the surface of the powder could be obtained by FTIR results, which were further corroborated by improved photo catalytic performance for bacterial inactivation.

Another important finding of the present investigations is the enhanced photo catalytic performance of the plasma-synthesized powder in the visible spectrum due to the shifting of the absorption edge of to the visible region. The extension of the absorption edge towards visible region has wide application for societal environmental concerns, such as purification of water, air, etc. Since a larger fraction of the solar spectrum is available for the photocatalytic process, the plasma-synthesized powder can be effectively used for indoor as well as outdoor applications.

The Photocatalytic bactericidal activity of plasma-synthesized nano powder was effectively used to kill bacteria. Thus plasma-synthesized titania powder is a possible alternative/complementary for drinking water treatment method.

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