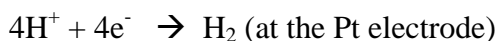
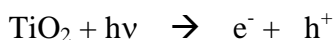


Synthesis of Titania Nanostructures for Photocatalytic Applications

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Titania powders have been used in paints from ancient times as they are inexpensive, harmless and chemically stable. It is a well known photocatalyst with application to water and air purification for health protection, hydrogen production by photoelectrolysis, photovoltaic cells, antimicrobial coatings, antifogging and self cleaning mirrors, glasses, windows etc. The main advantages of TiO₂ are its ability to withstand photocorrosion, low cost, low toxicity and good quantum yield. Though photocatalytic activity of TiO₂ was first reported in 1938, (in photobleaching of dyes)¹ study of photocatalytic activity of TiO₂ had not developed widely. In the late 1960s, in Japan Akira Fujishima demonstrated solar photoelectrolysis of water using TiO₂ (which is exposed to near UV light) and Pt black as electrodes. The work was reported in Nature² in 1972 and it attracted the attention of many scientists and numerous related reports were published. The photochemical reactions taking place at the electrodes are:



Since TiO₂ absorbs only UV light which constitutes only 3% of solar spectrum, from the view point of hydrogen production technology, it is not very attractive. So research shifted to use of TiO₂ in photocatalytic destruction of pollutants. For the purpose of oxidation of pollutants the reduction reaction happening at the Pt electrode ($2\text{H}^+ + 2e^- \rightarrow \text{H}_2$) is no more important and hence a Pt electrode (either as a separate electrode or as porous coating on titania particles) is not necessary. As both oxidation and reduction sites are located on the TiO₂ surface and reduction of adsorbed oxygen proceeds on the surface TiO₂ particles can be used at ambient conditions.

The limitations of TiO₂ as a photocatalyst are its high band gap (3.2 eV for anatase phase), high rate of photogenerated hole – electron recombination and low photocatalytic activity under high pollutant concentrations. In order to overcome the limitations intense research activities are being pursued to 1) bring down the band gap to visible region, by suitable doping with cations and anions 2) create and stabilize oxygen deficiency which enhances visible light photoactivity and 3) make suitable material architecture like 3-dimensional ordered nanostructures that allow high accessibility for pollutants to all surface area, efficient light harvesting, separation of electron - hole pairs and stabilization of oxygen deficiency³.

The thrust areas in which TiO₂ photocatalyst find application are water and air purification, self cleaning and antifogging mirrors, glasses, windows etc., and antimicrobial activity. Since environmental pollution including water and air is a serious concern intense research activity is being pursued in pollution control and there are many studies which report application of TiO₂ photocatalysis for pollution cleanup since 1970s. For gas streams and water purification use of TiO₂ nano-powders are generally avoided because of difficulty in handling, separation from the suspended media, and inefficient illumination. Therefore to construct a practical water or air purification system immobilization of nanoparticles on a suitable support is very essential. The support or substrates should have extremely large surface area, should be UV-visible transparent, generate low pressure drop, facilitate contact with the pollutant and have good adherence for the nanoparticle.

In the present work we will report our studies on synthesis of nanostructured pure and N-doped TiO₂ coatings, TiO₂ nanotube powders and suspensions for dip coating, self organized nanotubular TiO₂ films and their characterization as well as development of large surface area coating techniques for photocatalytic applications.

Nanostructured Thin Films of Pure and N-doped TiO₂.

Pure and N-doped TiO₂ thin films were synthesized on various substrates using an indigenously developed spray pyrolysis facility. The spray pyrolysis set up consists of an aerosol generator, precursor solution, gas delivery systems and a substrate heater, all housed inside the deposition chamber coupled to an exhaust system.

The precursor solution for the synthesis of pure TiO₂ and N-doped TiO₂ (titanium-oxy-acetylacetonate in ethanol and titanium-oxy-acetylacetonate solution in ethanol containing nitrogen generating amines like ethylene diamine, hexamine etc.) were atomized into micron sized droplets using a static ultrasonic nebulizer. The generated aerosols were then transported onto the heated substrate. At the hot zone near the substrate surface the solution undergoes vaporization and the solute vapors undergo decomposition at the substrate surface to give the desired coating. The coatings synthesized in the temperature range 350 to 550 C, up on XRD analysis, were found to be of anatase phase. The grain size estimated from HRSEM studies lays in the range 10 to 20 nm. The Raman spectra of the films show characteristic feature of the anatase phase. The band gap of the films were evaluated from the results of ellipsometric and UV-visible spectroscopic studies. The band gap determined using the techniques showed a direct nature and the values obtained were in the range 3.65 to 3.93 eV. We did not observe any remarkable reduction in band gap for the N-doped TiO₂ films with respect to pure TiO₂ films.

The antimicrobial activity of the pure and N-doped TiO₂ thin films were evaluated by exposing the test surfaces to the pathogen *Pseudomonas aeruginosa* cultured in a 10 % nutrient broth and then exposing the surface to UV and visible light for different periods. Nitrogen doped thin films were found to have anti-bacterial properties under U.V. and visible light. Whereas pure TiO₂ films showed bactericidal properties only under UV light.

Self Organized Nano-tubular Arrays of TiO₂.

Titanium dioxide nanotube arrays are technologically promising because they have efficient light harvesting, separation of electron - hole pairs, stabilization of oxygen deficiency and allow high accessibility for pollutants to all surface area. In this backdrop self organised TiO₂ nanotube arrays of high aspect ratio were grown by electrochemical anodization technique using fluoride ion containing organic as well as aqueous electrolytes. The as prepared self organised TiO₂ nanotubes were annealed at different temperatures and subjected to various characterizations for investigating their properties. The morphological characterizations were done using FESEM. The crystal structure of the nanotubes was studied by using X-ray diffraction and Raman spectroscopy. XRD and Raman results revealed that the as grown samples were amorphous and annealing at temperatures above 350 up to 500 C in air makes it crystalline anatase phase and above 500 C only rutile phase was observed. By varying the experimental parameters such as voltage, bath temperature and time of anodization it was observed that the aspect ratio of the nanotubes can be tuned for the desired applications. Length of the nanotubes was found to be varying from 500nm to 12 μm, diameters from 80 to 200 nm and the wall thickness from 10 to 20 nm with voltage and anodization time. It has been found from the image analysis that the self-organised nanotube arrays possess a short range order up to seven lattices (tubes) for longer nanotubes. The band gap studies of the as prepared and annealed samples were done by UV-visible absorption spectroscopy and photo luminescence. The measured band gap was found to be 3.1 eV.

TiO₂ Nanotube Powders and Suspensions

Titanium dioxide nanotube powders and powder suspensions are useful for dip, spray and spin coatings. Dip and spray coating techniques are advantages that large and irregular surfaces can be coated. TiO₂ nanotube powders were made as suspensions by electrochemical technique. In this technique Ti metal foils are anodized in an appropriate aqueous chloride bath at room temperature at constant voltage (20 to 50 V). TiO₂ nanotube powders were formed during anodization which settled at the bottom after prolonged time, it was then centrifuged. Titania nanotube powder suspensions were made by adjusting electrolyte bath chemistry. The suspended powders did not settle even after a week. To prolong the colloidal stability suitable surfactants were added. The nanotube powders were characterized using FESEM, TEM and XRD. The as prepared powders were amorphous. On drying at 60C in an oven it transformed to anatase phase. The anatase phase was found to be stable till 550 C and above 600 C rutile phase was found to be the stable one.

Technique for Coating Large Surface Area and Irregular Shape.

For practical application coatings on large surface area as well as irregular shapes are essential. The most common method for coating irregular shape and large surface area is dip coating. In our study titania nanotube powder suspension synthesized electrochemically and stabilized by adding suitable surfactants is identified as the solution for dip coating. Commercially available borosilicate glass wool mats are chosen as the support material because it is inexpensive, transparent in the titania absorption region, facilitates good adherence of TiO₂ particles and has large surface area. Dip coating experiments are underway.

Combustion Chemical Vapor Deposition (C-CVD)

A novel open air, flame mediated coating process that employs aerosol delivery to transport coating precursors to the deposition region of interest was developed indigenously to get uniformly coated large surface area of any shape. In the flame mediated process the flame forms the CVD reactor and the non-equilibrium rapid heating characteristics of the flame are used to derive nano-structured coatings. In this technique the ultrasonic or compressed air generated aerosols of 1 to 5 micron size are premixed with the fuel and coaxially injected into the annular burner and combusted. Inside the flame, the precursor undergo desolvation, rapid thermal vaporization and at the substrate surface decomposition reaction. Desired surface coverage is achieved by executing computer controlled movement of the substrate mounted on board the raster stage. Desired thickness is achieved by carrying out deposition in multiple passes.

Laser Pyrolysis

Laser pyrolysis is a variant of the flame pyrolysis in which the flame is replaced with a laser. In this technique precursor aerosols are fed into a quartz tube through which a CW-Nd:YAG laser (1064) is coaxially coupled. Photo-thermal decomposition of the precursor by the laser beam at the substrate results in the formation of nano-crystalline coatings. Large surface area coatings are obtained by using a computerized raster stage. The primary requirement for laser pyrolysis is that the emission line of the laser overlaps with an absorption line of one or more precursors. If this requirement is not met one has to use additional photocatalysts which will absorb laser energy and transmit to the precursor by shocks. The strength of the technique is that the process can be controlled through systematic parameters such as beam cross section, absorber concentration and laser power. Development of nanostructured pure and doped TiO₂ coatings (on large surface area and irregular shapes) are in progress.

Summary

The presentation outlines the research activities being pursued to improve the efficiency of TiO₂ as photocatalyst, which includes doping of TiO₂ to bring down the band gap in to the visible region, synthesis of novel material architectures like self organized nanotube arrays which improves electron - hole pair separation, enhances stabilization of oxygen deficiency for making it more visible light active and increases accessibility for pollutants to all surface area. In addition development of synthesis techniques to support TiO₂ nanoparticles, with good adherence, over large surface area of any shape for effective utilization of light, easy handling and facilitation of contact with pollutants are discussed.

References

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