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A study on the free radical generation and photocatalytic yield in extended surfaces of visible light active TiO_2 compounds

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ABSTRACT

Following dip coating procedure, we have fabricated extended photocatalytic surface (40 mm × 25 mm) of TiO_2, nitrogen doped TiO_2 (N–TiO_2), porous TiO_2 (porous-TiO_2), nitrogen doped porous TiO_2 (porous-N–TiO_2) materials over glass slides. A red shift was observed giving a bandgap of 2.56 eV for nitrogen doped TiO_2. Raman Scattering shows predominant anatase phase in all the samples along with rutile phase. Using di-chloro fluorescein (DCFH) as a fluorescence reporter molecule, we have characterized OH radical generation. Results show a 5.69×10^{-8} ppm/cm^2/s of OH radicals are generated in porous-N–TiO_2 coated surface compared to 3.69×10^{-8} ppm/cm^2/s in TiO_2 which confer a 1.54 increase in the utilization of visible light ability to the catalyst. Photocatalytic ability quantified with Methylene Blue degradation gave ~1.48 fold increase under visible light exposure for porous-N–TiO_2 relative to TiO_2 and the same was 1.1 fold for UV–visible light exposure. Further, the best catalytic degradation turn-over of the surface determined to be 4.55×10^{-7} ppm/cm^2/s and 1.61×10^{-7} ppm/cm^2/s respectively for UV–vis and visible light exposure. Thus a robust and simpler dip coating methodology giving enhanced visible light photocatalytic activity in polymer mediated nitrogen doped TiO_2 system has been demonstrated on a large surface area. We conclude that modification of bandgap of TiO_2 by nitrogen doping together with polymer mediated porosity has resulted in a strong visible light activity for this material. Since dip coating approach adopted here is cost-effective and amenable to large scale coating processes, it holds potential in the fabrication of large-scale self-cleansing and antimicrobial surfaces for application in medical and diagnostic industries.

1. Introduction

Photocatalysis is defined as change in rate of chemical reaction or its initiation by catalyst under illumination. Unlike other chemical reactions, photocatalysis undergoes both oxidation and reduction reactions on same surface under illumination [1]. Current research trend in photocatalysis is on fuel generation, chemical conversion, green synthesis, biomass degradation, industrial effluent treatment, smart surface coating, antimicrobial surfaces, and self-cleansing materials [2,3]. It is pertinent to note that such a broadly investigated field of research has emerged with only very few commercial products applicable for industrial and domestic utility for example Global NANO products INC., Percenta nanotechnology, NanoClear. This is primarily because of inability to be fully utilized in visible region of solar radiation, paucity of data in scale-up systems and field conditions.

TiO_2, a wide bandgap material existing in different polymorphs, is one of the important catalysts analyzed extensively for its photocatalytic activity in different applications. Still research is being pursued to improve upon TiO_2 based end products in many demanding applications [2]. Since bandgap of 3.2 eV lies in UV region of electromagnetic spectrum, utility of TiO_2 for commercial applications is limited. In an effort to utilize photons of the visible spectrum by TiO_2, its bandgap need to be modified. Generally it is accomplished with metals and non-metals doping [4,5], and by the formation of heterojunctions [4,6]. One of the compelling methods to achieve visible light activity in TiO_2 is by non-metal doping, especially placing nitrogen in TiO_2 interstitial or substitutional sites [7–9]. In addition to these approaches, minimizing faster recombination through metal based heterojunctions is also pursued that increases generation of free radicals.

Recently, following RF magnetron sputtering, fabrication of 15 mm × 15 mm surfaces of TiO_2 coated on metal sheets have been attempted and validated its photocatalytic effect on microbial system [10]. To make this photocatalyst system commercially viable in any of the emerging applications, it should meet the criterion of low cost and reusability. Commercial level reusability

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of TiO_2 can be achieved by say, incorporating it in a reusable matrices/substrates. Recent development in magnetic core-shell based system supports magnetic separation for recycling of catalysts [11]. In chemical and biotechnological industries, immobilized catalysts are most commonly used. The ability of a photocatalyst to perform in real time applications can be quantified following series of methodologies or instrumentation based analysis [11–16]. In this work, to partially address the above mentioned concerns, we have fabricated 40 mm × 25 mm surfaces of TiO_2 and its compounds with lower bandgap, through simple dip coating method. Further to modify bandgap, nitrogen has been incorporated with urea in precursor coating solution.

To improve the ability to absorb photons and generate large concentration free radicals, photoactive surface per unit coated surface is maximized by the formation of porous structures on the glass slide. Finally, to quantify the amount of OH^* generated, DCFH – a fluorescing probe which emits fluorescence upon activation by OH^* radicals, has been analyzed for its applicability for quantifying the photocatalytic ability of a photocatalyst [16,17].

2. Materials and methods

2.1. Chemicals and reagents

Tetra ethyl ortho silicate (TEOS), 2-proponal, titanium tetra isopropoxide (TTIP), nitric acid (HNO_3) were purchased from Fischer, urea purchased from Finar, PEG-20000 purchased from SRL, methylene blue from Spectrum, and (Di-Chloro Fluorescein) DCFH purchased from Cayman Chemicals Company. All chemicals were used as received without further purification.

2.2. Preparation of precursors for surface coatings

2.2.1. Preparation of precursor solution for silica coating

Solution A consists of 5.5 ml of TEOS dissolved in 19.62 ml of 2-proponal, stirred for 5 minutes at room temperature. Solution B consists of 1 ml of HNO_3 mixed with 1.25 ml of H_2O and 19.25 ml of 2-proponal stirred for 5 min at room temperature. Solution A added to Solution B and stirred for 30 min at room temperature. Resultant solution was used as such for preparation of silica coating over the glass substrate.

2.2.2. Preparation of TiO_2 precursor solution

To 100 ml of H_2O with 1% of HNO_3. 9 ml of TTIP added slowly to the solvent under vigorous stirring at room temperature. Stirring continued for 24 h at room temperature, resulting transparent solution. Hydrolyzed solution was condensed at 50 °C for 6 h.

2.2.3. Preparation of N–TiO_2 precursor solution

While preparing nitrogen doped TiO_2, urea as precursor for nitrogen has been utilized. Titanium precursor solution with urea has been taken in 4 different nitrogen to titanium molar ratios, namely 1%, 10%, 20% and 60% in the final solution, referred respectively as N1, N10, N20 and N60. It is prepared by taking 100 ml of H_2O containing 1% of HNO_3. 9 ml of TTIP added slowly to the solvent under vigorous stirring at room temperature for 24 hours. Thus, hydrolyzed solution was condensed at 50 °C for 6 h.

2.2.4. Preparation of porous-TiO_2 precursor Solution

Polyethylene glycol (PEG-20,000) has been added in the following three different concentrations: 50 mg, 150 mg, and 500 mg, named as P1, P2, and P3 respectively, prior to preparations of titanium precursor solutions to give p-TiO_2 precursor solution.

2.2.5. Preparation of porous-N–TiO_2 precursor Solution

PEG 150 mg and N 20 concentration of urea has been taken to prepare porous nitrogen doped TiO_2 precursor solution as discussed above.

Resultant precursor solutions thus prepared were used as such for coating of TiO_2 compounds over the Si coated glass slides.

2.3. Dip coating of material over glass slides

Indigenous dip coating system with 1.25 μm precision at minimum movement of 6 μm with a load of 2 kg has been assembled with Holmarc (India) linear translator stages and motion controller. 22 ml of prepared coating solutions was taken in 25 ml glass beaker. With a withdrawal speed of 96 mm/min, dip coating of silica solution and Ti-hydroxide solution has been performed at 25 °C. Silica coating has been performed for one cycle and dried at 100 °C for 15 min.

On this dried silica coated slides, 24 cycles of Ti compound precursors have been coated with 15 s immersion period [18] and 5 s hold period outside the solution. This results in 40 mm × 25 mm area on the glass slide getting coated. Total transit time per cycle calculated to be 72.5 s. For 24 cycles of coating on a single glass slide, it took about 29 min. Coated slides were air dried for 5 min, followed by heating at the rate of 5 °C/min and held at 150 °C for an hour. It was followed by calcination at 400 °C for three hours. Typical dip coated slides are shown to scale in Fig. S1, (Supplementary Materials).

2.4. Characterization

2.4.1. Spectroscopic characterization

Raman scattering of thin films were measured using Renishaw inVia Raman Microscope equipped with 514 nm laser source at 10 μW incident power. UV DRS was carried out in Perkin Elmer spectrometer, Model: Lambda 650, equipped with an integrating sphere attachment. Data were analyzed with $BaSO_4$ as reference. Photoluminescence of thin films were measured by JY Fluorolog-FL3-11 with 450 W Xenon lamp having PMT detection system. Chemical state of catalyst samples analyzed through X-ray Photo electron Spectroscopy model Kratos AXIS ULTRA with Al-kα X-ray ($h\upsilon = 1486.6$ eV). Photocatalytic ability of the samples slides has been quantified by tracing the degradation of dyes using custom configured Ocean Optics spectrophotometer having UV–vis light source and USB 2000 detector. Spectrometric data acquisition and analysis were done using *SpectraSuite* data acquisition system.

2.4.2. Microscopic characterization

Scanning Electron Microscope images of the surface coated slides were acquired using Hitachi S-3400N, 15.0 KV secondary electron detection. Atomic Force Microscope images of coated surfaces were scanned in tapping mode using Bruker Multimode 8 enabled with Scanasyst. High resolution Optical Microscope images of coated photoactive surfaces and sections of thin films were acquired using Olympus-BX51 polarizing microscope with UC30-40X objective.

2.4.3. Quantification of photocatalytic activity

Dyes exhibit strong adsorption, quantification of their degradation has been very difficult due to camouflaging of adsorption with degradation in the absorption spectra (Fig. S2 Supplementary Material). To circumvent this effect, and to quantify the degradation yield of photocatalyst coated surfaces, semi-continuous flow degradation of a dye molecule (Methylene Blue) has been carried out. 80 W Fluorescent light and 36 W UV light were used to induce photocatalytic activity. In order to include the contribution of photocatalytic activity independent of UV exposure and differentiate the same, a combination of UV light and pure visible light sources are used. Total number of moles of dye molecules degraded over a period of time has been measured from the number of moles of dyes added to the