DEVELOPMENT OF TiO_2-SiO_2 NANO PARTICULATE COMPOSITE USING BAMBOO LEAF ASH AS SILICA SOURCE AND ITS CHARACTERIZATION FOR ENVIRONMENTAL APPLICATIONS

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Abstract: This research work employed natural renewable silica source; *Bambusa Vulgaris* leaf ash (bamboo leaf ash) using sol-gel method to produce TiO_2-SiO_2 nano particulate composite. Also, tetraisopropoxide (TTIP) was used as titanium source. The produced TiO_2-SiO_2 nano particulate composite were characterized using X-ray diffraction (XRD), Ultraviolet Visible Diffused Reflectance Spectrophotometer (UV-Vis DRS), Gas Sorption Analyzer based on BET, Scanning Electron Microscope (SEM), Thermogravimetric Analysis (TGA), and Fourier Transformation Infrared (FT-IR) The XRD results indicate that when TiO_2 was disperse over the SiO_2 the crystallite peaks obtained are all in anatase phase. The TGA analysis shows that TiO_2-SiO_2 nano composite can be applied in high temperature operation. FT-IR spectra shows the presence of Ti-O-Si bond interaction with O-H as a result of physically adsorbed water in the composite. BET analysis reveals that supporting TiO_2 on SiO_2 surface increases the surface area of TiO_2 by 2.7% and pore volume by 2.8% with the particle sizes within the nano range. SEM and EDX analysis show that the produced TiO_2-SiO_2 and doped TiO_2-SiO_2 nanoparticles were relatively spherical and the produced TiO_2-SiO_2 contains no impurity.

Keywords: TiO_2-SiO_2 nano- particulate composite, Characterization of TiO_2-SiO_2.

Introduction

The need for environmental clean-up through the use of renewable energy has resulted in frequent use of nanoparticles in photocatalytic process. Photo-catalysis employs the catalytic activity of semiconducting metal oxide to generate strong oxidizing radicals from semiconductor surface in the presence of light energy equal or higher than the band gap energy of semiconductor. Among different semiconductors oxides, titanium oxide (TiO_2) is considered to be the best choice due to its high photo catalytic activity, chemical stability, resistance to corrosion, commercial availability, low cost, non-toxicity, and favorably wide band gap (3.2) (Raquel et al.,2018). For the fact that titania photocatalyst is not perfect, its wide energy band gap (3.0–3.2 eV) limits its photocatalytic performance since it can only be excited by the ultraviolet light with wavelength less 400nm ($\lambda < 400$ nm), such that less than 5% of the irradiated solar energy can be effectively used (Tong et al.,2012). Also, its photo catalytic activity can be tremendously limited by nano particulate agglomeration and its quick recombination of electron–hole pairs (Pelaez et al.,2012.).

In nano-size regime, titania particles interact with photons to emit oxidative specie and at the same time adsorbs the target pollutants onto the surface through proper oxidation and reduction mechanism. Since what matters most in the photoactivity of titania nanoparticles are the surface area and its band-gap energy. Therefore, it is necessary to develop a titania (TiO_2) nano composite through different arrangements and bearing in mind to increase the surface area and to extend the photo-responsiveness of TiO_2 from ultraviolet light to visible light .One of the prominent arrangements hinges on increasing the surface performance of titania by attaching titania on the frame work of silica in other to have stable composite (TiO_2-SiO_2 composite) with high surface area and stability due to the presence of silica (Jun et al.,2008).Since silica source can be obtained from agricultural material (bamboo leaf ash), the synthesis of TiO_2-SiO_2 nano sized composite is very cheap and a novel technology in photo catalytic process. Therefore, this research work focused on the development of TiO_2-SiO_2 nano particulate composite using bamboo leaf ash as silica source and its characterization for environmental applications.

Methods

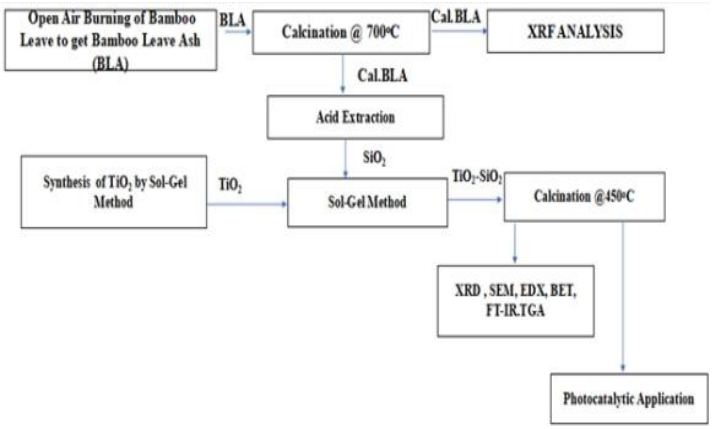

Figure 1: Schematic diagram of Synthesis of SiO_2-TiO_2 composite using BLA as silica source.

From figure 1, the dried bamboo leaves were collected, washed and dried before burning in an open air to get bamboo leave ash (BLA). The BLA was calcined in a muffle furnace at 700°C for 2 h to get calcined BLA which was utilized for silica extraction. The calcined BLA was characterized using XRD, UV-Vis DRS, TEM,SEM,EDX,BET,FT-IR,TGA. The calcined BLA was

utilized for silica extraction in form gel according to Kalapathy et al.,2000**.**

Preparation of TiO_2- SiO_2 Composite Nano particles Using Silica Derived from Bamboo Leaf Ash (BLA).

A modified methods according to Soni et al.,2018 and Fatima et al.,2015 were adopted for the preparation of TiO_2 nanoparticles. 8ml of glacial acetic acid was added into 100 ml de-ionized water separately and stirred to get solution A. Then, 17.5 ml (16.40 g) titanium tetraisopropoxide was dissolved in 50 ml of anhydrous ethanol with continuous stirring to get solution B. Solution B was added into solution A drop wise with stirring continuously for 2 h and finally aged for 24 h at room temperature. The TiO_2 gel formed was dispersed in a silica gel previously prepared from bamboo leaf ash according to Kalapathy et al.,2000 and the mixture gel was dried in an oven at 90^{o}C for 2 h. Finally, the solid material obtained was ground and annealed at 450^o C for 2 h. The solid photo catalyst was characterized using X-Ray Diffraction (XRD), Brunauer- Emmitt-Teller (BET), Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX), Fourier Transformation Infrared Spectra (FT-IR), Thermo Gravimetric Analysis (TGA).

Results & Discussion

Thermogravimetric Analysis (TGA) of TiO_2-SiO_2 Photocatalysts is an analytical technique that measures the change in weight of a sample with respect to heating temperature. GA is employed to study the major constituent of sample material, its decomposition and stability at high temperature. Thermal gravity analysis (TGA) of the samples was performed using Q-500 thermo gravimetric analyzer with quadruple mass spectrometer (TA-MS coupled system). the temperature of the furnace was inbuilt and was programmed to increase at the rate of 10^{o}C/min from room temperature to 900 ^{o}C under circulation of nitrogen and dry air.

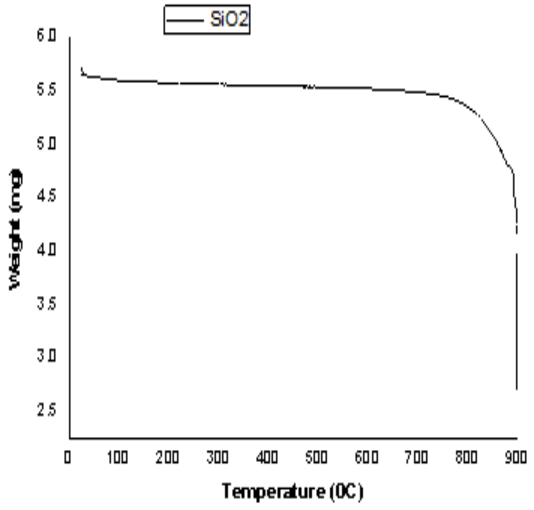

Figure 2: Thermogram of SiO_2 Calcined at 450^{0}C for 2 h**.**

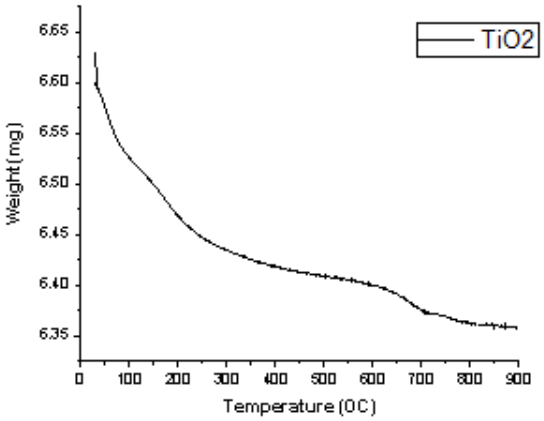

Figure 3: Thermogram of TiO_2 Photocatalyst Calcined at 450^{0}C for 2 h.

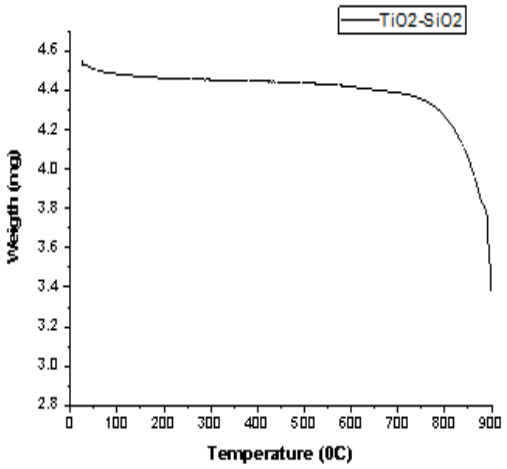

Figure 4: Thermo gram of TiO_2-SiO_2 Photo catalytic Composite Calcined at 450^{0}C for 2 h.

The sample catalyst whose thermogram are displayed in figure 2 – figure 4, were dried at 90 ^{0}C and calcined at 450^{0}C for 2 hours in a muffle furnace. The obtained thermogram for pure TiO_2 in figure 3 showed an endothermic peak as a result of evaporation of bonded water molecules in the sample with weight loss of 1.3% between 29 ^{0}C and 77^{0}C.The second weight loss of 2.7% occurred at about 763.3^{o}C which can be attributed to elimination of adsorbed hydroxyl group and recessive water molecules on the surface of the TiO_2 sample. A weight loss of 0.02 % was observe from figure 3 between763.3^{o}C and 781.5 ^{o}C beyond which no weight loss was observed Figure 2 and figure 4 are the thermogram of silica and titania-silica composite (TiO_2-SiO_2 composite) dried at 90 ^{o}C and calcined at 450 ^{o}C which shows a weight loss of 4.3% between 25.7^{o}C and 741^{o}C due to desorption of physically adsorbed water molecule. The second weight loss of 19.3% was also observed at 896.8 ^{o}C due to the breaking of Si-O-Ti linkage and elimination of hydroxyl group from the sample catalyst thereby reducing the acid site density at the TiO_2 catalyst surface. The reason for the weight loss with respect to the temperature is to

indicate the importance of calcinations on the thermal strength of the sample catalyst. Loading of TiO_2 on the surface of silica grants the former the thermal stability with its structural water being removed up to 896.8 ^oC. In this case silica addition to titania to have silica-titania composite can promote titania to its application in high temperature operation.

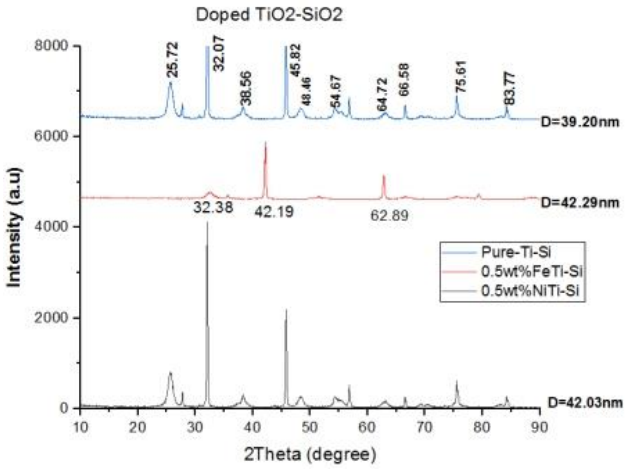

Figure 5: XRD Spectra of Doped TiO_2- SiO_2 and Undoped TiO_2- SiO_2 samples

X-ray diffraction (XRD) analysis was performed using D/max diffractometer with serial number 079298-A3138-A1 and the diffractometer was recorded with CuK_α radiation over a 2θ range of 10 to 90^o.The count time of 2 sec with 0.3-degree angle of rotation.

Figure 5 shows the XRD pattern of structure of crystals of TiO_2, SiO_2-TiO_2 and doped SiO_2-TiO_2 composite sample. It is observed that undoped SiO_2-TiO_2 composite show different peaks within the 2θ diffraction angle. This behavior shows that titanium is highly dispersed in the silica matrix at the surface and exist as crystal size of 39.20nm sufficient to be detected by XRD since the ionic radius of Si^{+4} and Ti^{+4} are reported to be 0.41Å and 0.68 Å respectively (Jun et al.,2008).The diffraction peaks follows the standard peak at 2θ of anatase titanium and therefore indicating that the titania fixed on the silica surface are all in anatase phase.

Table 1: BET surface area analysis of synthesized pure TiO2 and 0.5wt%Ni doped- TiO_2 at different calcination temperatures.

Sample	Calcination Temp (^0C)	**Surface Area $_{BET}$(m^2/g)**	Pore Volume (cm^3/g)	Pore Size (Å)Pore size	Particle Particle size (nm)	Crystal* Crystallite Size(nm)	Bandgap** (eV)
BLA	450	7.556	0.005	11.193	794.08	NE	NE
Pure SiO_2	450	157.718	0.102	10.859	38.04	NE	NE
PureTiO_2	450	108.987	0.070	11.645	55.05	9.66	2.96
TiO_2-SiO_2	450	111.984	0.072	11.322	53.58	39.20	3.14

BLA- Bamboo leaf ash, undoped TiO_2-SiO_2, NE- Not evaluated. * Obtained from XRD data, ** Obtained from UV-Vis DRS data.

The Brunauer-Emett-Teller surface area (S_{BET}) and desorption pore volume (Vp) were evaluated by Barrett-Joyner Halenda (BJH) method and determined by N_2 physisorption using micromeritics instrument, Gemini (VII) version 3.04 with serial number 0128 at 5 sec equilibration time. Table1 shows the parameter evaluated by BET at 450^{o}C calcination temperatures for TiO_2, SiO_2 and **TiO_2-SiO_2** nanoparticulate composite. The data on specific surface area, particle size, pore volume and pore size of the sample catalyst were shown in table 1. The BET surface area and pore volume and pore size result obtained at 450^{o}C indicates that bamboo leaf ash (BLA) has the largest particle size of 794.08 nm with low surface area of 7.556(m^2/g).. The particle size of the samples was calculated using the BET surface area data. It was observed that silica(SiO_2) has high surface area of 157.718m^2/g than titania(TiO_2) with surface area of 108.987m^2/g **.**Therefore, supporting TiO_2 on SiO_2 to have undoped TiO_2-SiO_2 increases the surface area of the TiO_2 by 2.7% with the average particle size of TiO_2-SiO_2 to be 53.58nm and surface area 111.984 m^2/g providing the advantage of producing TiO_2-SiO_2 composite at 450^{o}C calcinations temperature for photo catalytic degradation. Hence, the undoped TiO_2-SiO_2 nano particles with particle size of **53.58nm** showed the retention of nano sized particles with the temperature (Raj et al,2010). Bamboo leaf ash prepared before silica extraction by burning of the bamboo leaf in open air and the resultant ash was calcined in a muffle furnace for 2 h at 700^{o}C was found to display pore surface area of 7.556m^2/g with large particle size of 794.08nm**.** The results obtained for crystallite size calculation using Sherrer equation when compared with results obtained for particle size showed increase in particle size, which could be attributed to the agglomeration and crystal growth of the sample particles and also supporting the pure TiO_2 on SiO_2 to increase the surface area of TiO_2.

Table 2 : XRF analysis of the Bamboo leaf ash

S/N	Chemical Formula	Values (%)
1	SiO_2	**68.31**
2	Al_2O_3	3.28
3	Fe_2O^3	1.02
4	CaO	9.02
5	MgO	3.94
6	Na_2O	0.51
7	K_2O	6.42
8	SiO_3	1.76
9	Cl	0.45
10	P_2O_5	0.9
11	TiO_2	**0.17**

The ash obtained after calcination of bamboo (bambosa vulgaris) leaves was subjected to XRF analysis to identify the constituent elements in oxide form in the ash and the result of the analysis was presented in table 2. Tables 2 shows that calcined bamboo leave ash contains significant amount of silica in oxide form (SiO_2) by 68.31% wt.

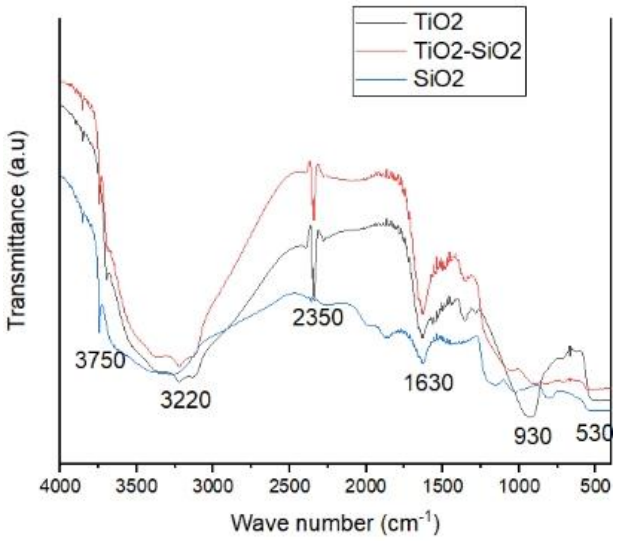

Figure 6: FT-IR pattern of Pure SiO_2, Pure TiO_2 , Ni-Doped TiO_2 andTiO_2- SiO_2 Composite.

The FT-IR spectroscopy studies were carried out using Vertex-70 Spectroscope with serial number 2007832, PAT.US 7.034.944 in a high temperature flow infrared cell reactor which must be cooled using liquid nitrogen for good results.

Figure 6 shows the FT-IR of SiO_2-TiO_2 with absorption peaks corresponding to stretching vibration of the O-H and bending vibration of adsorbed water molecules around 3000 cm^{-1}- 3500 cm^{-1} and 1500 cm^{-1}- 2000 cm^{-1} respectively. Also, the intense broad band observed at 930 cm^{-1} and 530 cm^{-1}- was due to Ti-O-Ti vibration.

The TiO_2 has broad band at 930 cm^{1}. The absorption band of TiO_2 at 930cm^{-1} disappeared on addition of SiO_2 and shifted to a higher band of 3220 cm^{-1}. This confirms the formation of Si-O-Ti bond.

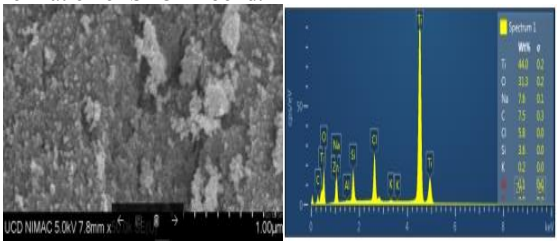

Figure 7(a): SEM Image of undoped TiO_2-SiO_2
Figure 7 (b): EDX Spectra of TiO_2-SiO_2

Figure 7(a) and 7 (b) show the SEM image and EDX spectral of TiO_2-SiO_2 nano-particle composite calcined at 450^{o}C at 2 h. It can be seen that TiO_2 nanoparticles are dispersed over the SiO_2 surface. The EDX spectra of TiO_2-SiO_2 and elemental analysis indicate that 44% of Ti^{4+} ion was dispersed over the 3.6 % Si^{4+} surface in agglomerated form with some traces of impurities as shown in figure 7 (b). This translates to formation of aggregated TiO_2 from the agglomeration of the TiO_2 crystallite. On the other hand, the SEM micrographic Image of pure synthesized TiO_2-SiO_2 nano-particle composite calcined at 450^{o}C at 2 h shows that the particles are relatively spherical in shape.

Conclusions

The TiO_2-SiO_2 nano particulate composite were prepared using sol-gel method with bamboo (*Bambusa Vulgaris*) leaf ash as silica source and tetraisopropoxide (TTIP) as titanium source. Pure TiO_2 nano particles have been prepared using sol-gel method. The prepared sample was calcined at 450^{o}C at 2 h and characterized using some of the nano particle characterization techniques (XRD, UV-Vis DRS, BET, SEM, EDX, FT-IR , TGA and XRF).

XRD results indicate that when TiO_2 was disperse over the SiO_2 the crystallite peaks obtained are all in anatase phase. The TGA analysis shows that TiO_2-SiO_2 nano composite shows an endothermic peak with desorption of surface adsorbed water at temperature less than 100^{O}C and can be applied in high temperature operation. FT-IR spectra shows the presence of O-H bond in stretching vibration mode and the surface adsorped water in bending vibration and the

formation of SiO_2- TiO_2 bond. BET analysis reveals that supporting TiO_2 on SiO_2 surface increases the surface area of TiO_2 by 2.7% and pore volume by 2.8% with the particle sizes within the nano range. SEM and EDX analysis show that the produced TiO_2-SiO_2 nanoparticle composite was relatively spherical and the produced TiO_2 contains no impurity.

List of Abbreviations

XRD -X-ray diffraction.
UV-Vis DRS -Ultraviolet Visible Diffused Reflectance Spectrophotometer.
BET - Brunnauer Emmett and Teller gas sorption analyzer.
SEM - Scanning Electron Microscope,
TGA-Thermo Gravimetric Analysis (TGA).
FT-IR- Fourier Transformation Infrared.
EDX- Energy Dispersive X-ray
XRF- X-Ray Flourescence.
TiO_2 - Titanium (iv) oxide or titania.
SiO_2- Silicon (iv) oxide or silica,
SiO2 - TiO_2 Silica - Titania Composite.
BLA- Bamboo Leaf Ash

Declarations:

Availability of Data and Materials: The data generated in this research work was original laboratory data from spectrum of nano technological equipment available in environmental and sustainable catalysis laboratory, University College Dublin, Belfield, Dublin 4, Ireland

Competing Interests: The author declares that there is no competing interest linked with this research work.

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Authors' contribution

The development of SiO_2-TiO_2 nano composite carries substantial operational advantage in photocatalysis and chemical industry in general, supporting titania with silica (SiO_2) helps to increase the surface area of exposure of titania (TiO_2) significantly. Also this can make adsorption of pollutant on TiO_2 simple in a heterogeneous mixture especially in wastewater treatment simple due to nano size of the TiO_2. This is not only to improve adsorption efficiency but has the potential to save cost due to separation.

-O. C. S is the original author who carried all the laboratory experimental work and characterization of the produced sample in environmental and sustainable catalysis laboratory, University College Dublin, Belfield, Dublin 4, Ireland

-O.P.C is an author who is the chairman supervisory committee of the research work and also being the author who contributed for the design of the experimental reactor used in the work.

AOB is a second author who is a member of the supervisory committee, and he contributed in the interpretation of nano technological equipment results.

BDH is a third author who is a member of the supervisory committee and contributed in the proper experimental method needed to give good result.

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Authors Information: Not applicable

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