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SYNTHESIS AND IMMOBILIZATION OF TiO_2 ON BOROSILICATE GLASS TUBE: ITS CHARACTERIZATION AND LEACHING PROCESS

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Abstract: Titanium dioxide has good optical properties and is mostly utilized in environmental clean-up as photocatalyst but its agglomeration in water and difficulties in separation at nano scale limits its industrial applications. Pure TiO_2 nano particles with BET specific surface area of 108.98m^2/g and XRD crystallite size of 9.66nm were synthesized using sol-gel method. The synthesized TiO_2 was immobilized on the borosilicate glass tube by dip-coating method using coating enhancer. The synthesized samples were calcined at 450°C at 2 h. The samples were characterized using some of the nano particle characterization techniques: X-Ray Diffraction (XRD), UV-Vis Diffused Reflectance Spectroscopy (UV-Vis DRS), Brunauer- Emmitt-Teller (BET), Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX), ThermoGrametric Analysis (TGA). The total average thickness of the coating after calcination at 450°C is 913.67 nm and the thickness after ultrasonicating for 1 h in an ultra sonicator (Cardiff Cf 21YY-021914) were determined as the average step height of 172.33nm using a Bruker Dektak XT Stylus Profilometer (Alpha-Step IQ). The thin coating of 18.8% of the photocatalyst were obtained after ultrasonication showing the effectiveness of coating enhancer to immobilized TiO_2 on borosilicate glass tube and can have its application in photocatalytic degradation mostly in wastewater treatment plant. Immobilizing titania photocatalyst (TiO_2) with addition of tetraethyl orthosilicate (TEOS) as coating enhancer increases the attachment strength of the TiO_2 to the wall of borosilicate glass and therefore prevents TiO_2 from agglomerating when in contact with water.

Keywords: Synthesized TiO_2 Nanoparticles, Characterization.

Introduction

Titanium dioxide (TiO_2) is a flexible material with most suitable application in photo catalysis. The use of TiO_2 in heterogeneous photo catalysis has been widely studied as an alternative physio-chemical treatment for various environmental applications. Traditionally, TiO_2 has three crystallographic phase which include anatase, rutile and brookite. Only the rutile is thermodynamically stable. Anatase and brookite are metastable which can transform to rutile when thermally treated. Titanium dioxide(TiO_2) was recognized by researchers as ideal semiconductor with good photo catalytic properties like high refractive index and ultraviolet absorption with good photoelectric conversion efficiency, photo-and chemical stability , very low solubility as well as non-toxicity (Hung et al.,2016).Although TiO_2 has large potential application in environmental clean-up and protection, the difficult to separate TiO_2 at nano level still be a great challenge that hinders its application in industrial scale (Xiuzhen et al.,2013).. Therefore, the key important aspect for the application of TiO_2 photocatalyst is to enhance the separation efficiency. Recently, researchers have focused interest on suspension photo catalytic reactor system due to major advantage of high catalytic efficiency (Colins et al.,2013). But high energy demand to keep the TiO_2 particles in suspension by providing turbulent regime within the system makes its operation uninteresting. Also, it is very difficult and expensive to separate the TiO_2 catalyst from the liquid after treatment operation. Considering the above reasons, heterogeneous photo catalysts active layer immobilized on a support material is of growing interest. It was reported that immobilizing TiO_2 photocatalyst on a thin layer can improve removal efficiency of organic pollutant in water (Yadini et al.,2014). The deposition of TiO_2 as photocatalyst on a solid support has been well documented (Deivission et al.,2018). The challenge of immobilizing a photocatalytic active layer on a support material is still on the weak attachment strength which can bring about high load of photo catalyst being leached especially when operating in a flow reactor system. Therefore, in this work, TiO_2 nanoparticles were synthesized through sol-gel method with the use of titanium tetraisopropoxide (Sigma Aldrich) as titanium precursor. The TiO_2 nanoparticles produced were characterized and immobilized on the borosilicate glass tube through dip-coating method. The immobilization process was assisted using tetraethyl orthosilicate (TEOS) as coating enhancer which increases the attachment strength of the TiO_2 to the borosilicate glass. The total average thickness of the coating and thickness after ultrasonication for 1h in and ultra sonicator (Cardiff Cf 21YY-021914) were determined with the average step height of 913nm using a Bruker Dektak XT Stylus Profilometer (Alpha-Step IQ) on the coating deposited on a borosilicate flat glass coated in the same way the borosilicate glass tube was coated with the same condition. To justify for the attachment strength with coating enhancer in this work, the leaching test was conducted through ultrasonication of coated glass sample. The aim of this research work is to prepare TiO_2 nanoparticles using sol-gel method, characterize for the optical property of the prepared TiO_2 nano particles, immobilize the TiO_2 on a borosilicate glass tube through dip-coating method with TEOS) as coating enhancer and investigation on the leaching of immobilized TiO_2 to assess the adherence strength of TiO_2 coating on the borosilicate glass tube with tetraethyl orthosilicate as coating enhancer.

Experimental Methods

Preparation titania (TiO_2) nanoparticles

A modified method according to Soni et al.,2018 was adopted for the preparation of TiO_2 nanoparticles. To 100 ml de-ionized water, add 8ml of glacial acetic acid and mixed 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 dried in an oven at 90ºC for 2 h to get solid TiO_2. Finally, the solid material obtained was grounded and annealed at 450º C for 2 h. The solid photo catalyst was characterized using XRD, BET, SEM-EDX, DRUV-Vis, FT-IR, TEM, XPS

Preparation Of Tetra Ethylorthosilicate (TEOS) Solution as Coating Enhancer to The Borosilicate Glass

This solution was used to pre-coat borosilicate glass tube as coating enhancer and barrier inter- layer between the glass tube and the titania nanoparticles. The TEOS coating serves as a barrier since the formation of the anatase titania can be hindered by cations moving from the glass into main bulk of titania during calcination treatment of the coated borosilicate glass. Here, the method of preparation of TEOS solution was done following the method according to Colin et al.,2013. Mixture of 77ml of 2-propanol, 5ml of water (H_2O) and 4ml of trioxonitrate (V) acid (HNO_3) was added in drop to 22ml TEOS at room temperature. The resultant solution was properly stirred for 2 h using a magnetic stirrer.

Coating Procedure of TEOS On Borosilicate Glass Tube

Coating operation was carried out after the pre-treatment of the borosilicate tube in ultrasonic bath (US- 021914) with solution of ethanol and distilled water (1+1) by volume and dried at 100ºC for 12 h. This method of coating was done following the modified method according to Samer et al., 2019. The TEOS solution was stirred for 1 h before coating began. The borosilicate tube was dip-coated in the fresh solution of TEOS at pulling rate of 100 mm min^{-1} to act as coating enhancer between the photocatalyst and the borosilicate glass tube. Then the borosilicate tube with coating enhancer was first dried at 150ºC in an oven before raising the oven temperature to 300ºC for 3 h. The coating with doped- TiO_2 /SiO_2 gel was followed by dip-coating method at the same rate previously described at the same pulling rate of 100 mm min^{-1}. After coating, the tube was placed in an oven (DHG-9030A) to dry at heating rate of 5ºC/min until 110ºC for 2h. Then, the tube was calcined at 450ºC for 2 h in a Carbolite muffle furnace (England, Sefield). After calcination, the tube was allowed to cool and ready for photo catalytic application. The total average thickness of the coating after calcination at 450ºC is 913.67 nm and the thickness after ultrasonicating for 1h in an ultra sonicator (Cardiff Cf 21YY-021914) were determined as the average step height of 172.33nm using a Bruker Dektak XT Stylus Profilometer (Alpha-Step IQ) on the coating deposited on a borosilicate glass coated in the same way the borosilicate glass tube was coated with the same condition. The thin coating of 18.8% of the photocatalyst observed after ultrasonication.

Results and Discussion

Uv-Vis Drs Analysis of Doped Titanium Photocatalyst

The UV-Vis diffused reflectance spectra in a wave range of 200-800nm was carried out using V-650 Spectrophotometer.

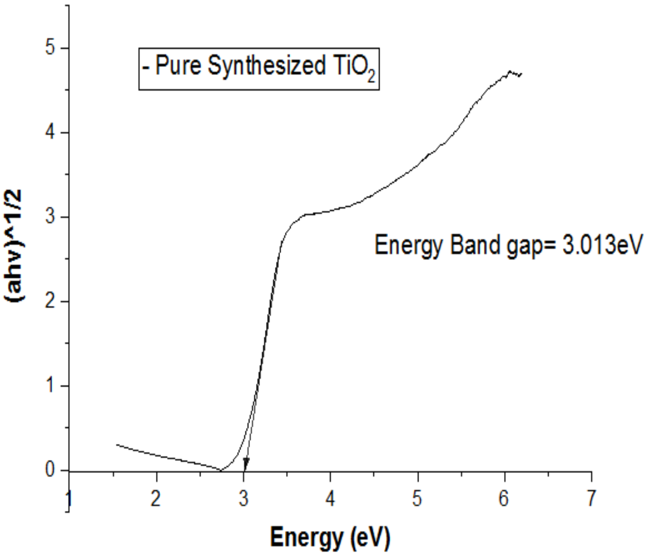

Fig 1: Bandgap Energy of Synthesized TiO_2 Calcined at 450ºC for 2h

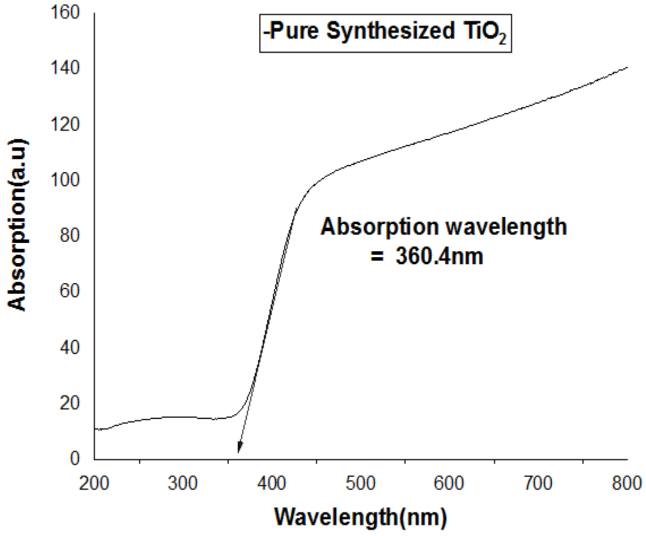

Fig 2: UV-VIS Spectra of Synthesized TiO_2 calcined at 450ºC for 2h

Figure 1 and 2 show UV-Visible diffused reflectance spectra of TiO_2 was determined in a range of wavelength from 200 to 800nm.The optical band gap of pure synthesized TiO_2 was obtained from a plot (ahv)^1/2 vs (hv) based on the Tauc equation and Kebelka-Monk function as represented in equation (2) and (1) respectively(Soni et al.,2018) .

$$F(R)=\frac{(1-R)^2}{2R} \quad \text{……………………………………} (1)$$

$$(F(R)hv)^{1/2}=A(hv-E_g) \quad \text{……………………………………} (2)$$

Where, hv is the energy of photon, A is constant, E_g is the energy band gap of the sample (Fe-TiO2), R is the reflectance of the UV radiation from the measuring instrument and (F(R)) is proportional to absorption constant (a). By plotting (ahv)^1/2 versus Energy(hv), the energy band gap of Fe-doped TiO_2 can be determined by extrapolating the linear part of the plot to a point where (ahv)^1/2 is zero. Fig 1and 2 show the energy band gap and absorption spectra of pure TiO_2 nano particle calcined at 450°C for 2 h. In Fig 2, TiO_2 has absorption wavelength in ultra-violet (UV) region with absorption edge of 360.4nm with no noticeable absorption in the visible light region (400 to 700nm). Figure 1 shows the Tauc plot for direct band gap energy of pure TiO_2 to be 3.013 eV with absorption wavelength of 360.4nm. The value of the band gap energy obtained here can be compared with the standard value of 3.0eV and 3.2 eV for rutile and anatase from of TiO_2 respectively (Soni et al.,2018). The absorption wavelength of 360.4nm can be compared with the standard value of 385nm confirming that the absorption wavelength of the synthesized TiO_2 is on the ultra violet range (below 400nm).

Thermo Grametric Analysis (TGA)

This 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 thermogravimetric 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°C/min from room temperature to 900 °C under circulation of nitrogen and dry air.

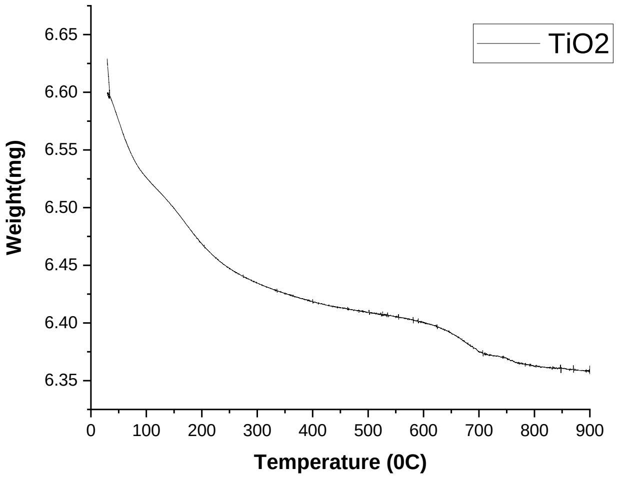

Figure 2: Thermogram of TiO_2 Photocatalyst Calcined at 450^{0}C for 2 h.

The sample catalyst whose thermogram are displayed in figure 3 was dried at 90 ^{0}C and calcined at 450^{0}C for 2 hours in a muffle furnace. The obtained thermogram for TiO_2 in figure 3 shows 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°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°C and 781.5 °C beyond which no weight loss was observed. The reason for the weight loss with respect to the temperature is due to removal of physically adsorbed water and to indicate the importance of calcinations on the thermal strength of the sample catalyst.

XRD Analysis

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°. The count time of 2sec with 0.3 angle of rotation.

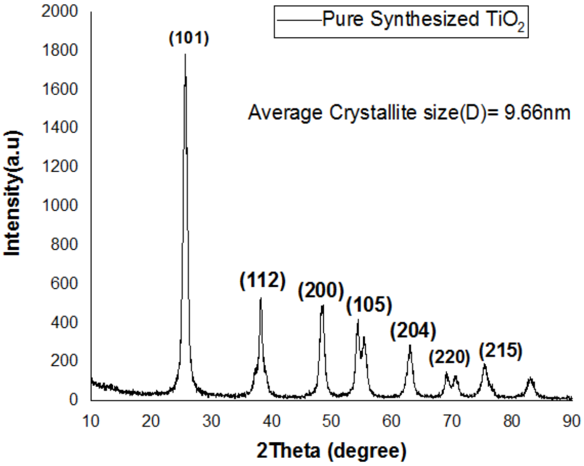

Figure 4: XRD Spectra of Pure (Undoped) TiO_2

Fig 4 shows the XRD pattern of the TiO_2 nano particles. The characteristics diffraction peaks of anatase at 25.5°, 38.2°, 48.3°, 54.5°,63.1°, 69.1°,75.5° correspond to the reflection from the planes (101), (112), (200), (105), (204), (220) and (215) (Moradi et al.,2016) The results obtained show that all the TiO_2 synthesized are in anatase phase. Fig 4 shows that as the diffraction angle increases, the intensity of diffraction peaks (crystallinity) decreases. In this case, high crystallinity was obtained at diffraction angle of 25.5° from (101) lattice place.

BET Analysis

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.

Table 1: BET surface area analysis,

Sample	Calcination Temp (^{0}C)	Surface Area $_{BET}$(m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)	Particle size (nm)	Crystal* Size(nm)	Bandgap** (eV)
PureTiO_2	450	108.987	0.070	11.645	55.05	9.66	3.013

* Obtained from XRD data, ** Obtained from UV-Vis DRS data.

The data on specific surface area, particle size, pore volume and pore size of the synthesized TiO_2 nanoparticles were shown in table 1. The particle size of the sample was calculated using the BET surface area data. The surface area of TiO_2 was calculated to be 108.987m^2/g for titania (TiO_2) nano particles with accompanied crystal size of 9.66nm. and particle size of 55.1nm. Xiuzhen et al, 2013 synthesized anatase TiO_2 and compared the BET specific surface area of synthesized anatase titania with commercial anatase TiO_2 nanoparticle with values 186.25m^2/g and 50m^2/g respectively. Therefore, large specific surface area obtained,108.987m^2/g for titania (TiO_2) nano particles in this research will provide more surface-active sites to be used as adsorbent in photocatalytic applications, thus increase efficiency of photo catalytic process at industrial scale.

SEM and EDX Analysis of Pure Synthesized TiO_2

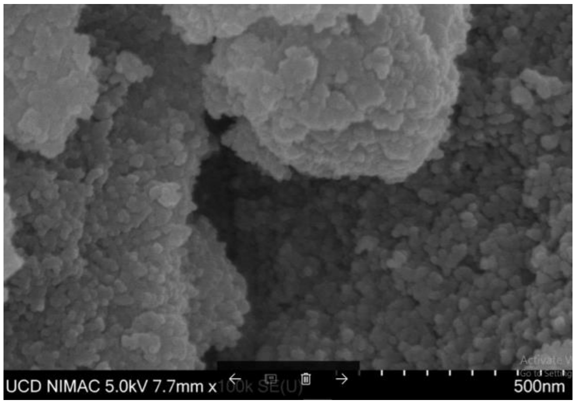

Fig 5a: SEM Image of Pure TiO_2

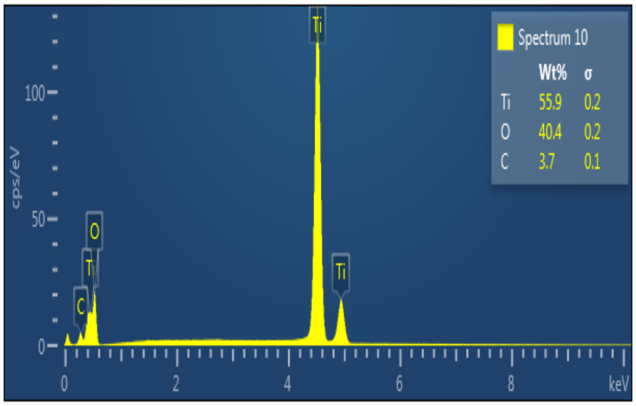

Fig 5b: EDX Spectra of Pure TiO_2

Figure 5 (a) and 5(b) show the SEM image and EDX spectra of Pure synthesized TiO_2 nanoparticle calcined at 450°C for 2 h. It can be seen that TiO_2 nanoparticles are properly produced in agglomeration. In figure 5b, the EDX spectra and elemental analysis indicate that synthesized TiO_2 has no trace of impurity and crystalline with characteristic high peak. The chemical compositional analysis shows that the percentage of titanium in TiO_2 mixture is 55.9% which proves that the TiO_2 nano particles produced in this work by sol-gel method is pure indeed with high concentration of titanium.

Conclusions

Pure TiO_2 nano particles have been prepared using sol-gel method. The prepared sample was calcined at 450°C at 2 h. The prepared sample was characterized using some of the nano particle characterization techniques (XRD, UV-VisDRS, BET, SEM, EDX AND TGA). The EDX results of the characterization show that the prepared TiO_2 is pure with no trace of impurity

The total average thickness of the coating after calcination at 450°C is 913.67 nm and the thickness after ultrasonicating for 1h in an ultra sonicator (Cardiff Cf 21YY-021914) were determined as the average step height of 172.33nm using a Bruker Dektak XT Stylus Profilometer (Alpha-Step IQ) on the coating deposited on a borosilicate glass coated in the same way the borosilicate glass tube was coated with the same condition. The leaching operation was conducted on the immobilized TiO_2 using ultrasonication and the result shows that the thin coating of 18.8% of the TiO_2 photocatalyst were obtained after ultrasonication with 172.33nm thickness. The XRD analysis show that the average crystallite size of the produced TiO_2 is 9. 66nm.The BET analysis shows that the produced TiO_2 has large specific surface area of 108.98m^2/g. The XRD analysis indicates that the produced TiO2 is in anatase phase and can be utilized for optical application in environmental clean-up.

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Conflict Of Interest: The author declares that there is no conflict of interest linked with this research work.

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