II. Materials And Methods

A. TiO_2 Synthesis

All the reagents used in the study were of analytical grade. All the TiO_2 nanoparticles derived from the use of $TiCl_4$ in different solvents were synthesized under the same conditions using the Wet Chemical Method. $TiCl_4$ solutions (1M) in toluene, water and methylene chloride were purchased from Sigma Aldrich (Germany). Ammonium hydroxide (32%) was used to precipitate the nanoparticles in the solutions.

$TiCl_4$ (2 mL) was added drop-wise in a 100 mL beaker containing ammonium hydroxide solution, under vigorous stirring for 10 min until an amorphous white precipitate was obtained. The synthesis was done at 60°C in a water bath. The samples were dried in an oven at 80°C to transform the amorphous phase to a solid phase. The dry particles were transferred in tubes and washed several time with warm distilled water to remove the excess $TiCl_4$. All the samples were collected by centrifugation subsequent to acetone supplementation to dry the sample before they were transferred in crucibles for annealing at 350°C for 6 h. The annealed powders were thereafter characterised using XRD, SEM-EDS, FTIR and UV-Vis spectrometry techniques.

B. TiO_2 Characterisations

XRD and SEM were used to investigate the TiO_2 physical properties, i.e. the TiO_2 nanoparticles crystallisation and its surface topographic, respectively. The average size (D) of the annealed TiO_2 nanoparticles was estimated by using the Debye-Schereer's equation:

$$D = 0.9\lambda / (ß \times \cos \Theta) \quad (1)$$

Where:

λ: is the wavelength of the copper anode radiation that used during the XRD analysis, with a value 1.5406 Å,

ß: is the full width half maximum (FWHM) of the peak, in radians, and

Θ: is the Bragg's angle; in degrees.

Chemical properties, such as elemental composition and chemical bonding of the annealed TiO_2 nanoparticles were identified by EDS and FTIR, respectively.

Furthermore, optical properties were studied by running an UV-Vis within a spectra range of 200 to 800 nm.

III. Results And Discussion

The solvents used for $TiCl_4$ solubilisation, have all been shown to be effective as suitable solvents for the synthesis of TiO_2 nanoparticles. The UV-VIS analyses have shown the presence of TiO_2 nanoparticles as shown in Figure 1. The TiO_2 nanoparticles' UV-VIS absorption spectra was determined to fit within the invisible UV range of sunlight, i.e. between 100-400 nm [31]. The TiO_2 nanoparticles could absorb the UV of sunlight for various applications including for dermal applications [32].

TiO_2 nanoparticles had an adsorbance peak at 280nm for UV–VIS spectroscopy studies. The same adsorption wavelength observed herein was reported by various researchers [33, 34]. However, the adsorption peak was higher for TiO_2 synthesised by solubilised $TiCl_4$ in water than when using methylene chloride and toluene.

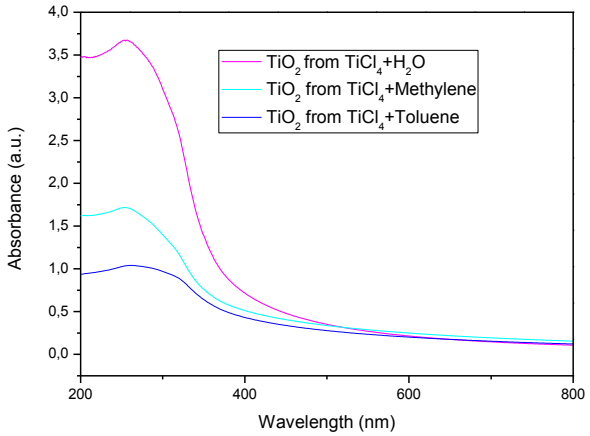

Fig. 1: UV-Vis absorbance of TiO_2 nanoparticles from various $TiCl_4$ solubilisations

Figure 2 shows the XRD patterns of each TiO_2 nanoparticle produced from various $TiCl_4$ solubilisations. The Muller's indices (hkl) was detected at 2Θ (degree) = 25.281; 37.801; 48.050; 53.891; 55.062; 62.690 and 75.032 for hkl = 101; 004; 200; 105; 211, 204 and 215, respectively. Similar peaks were obtained for all synthesised TiO_2. Based on the hkl indices, the atom position of each TiO_2 was determined to be have a body-centred tetragonal. The average size (D) of the nanoparticles was 12 nm; 7 nm and 10 nm for $TiCl_4$ solubilised in water, methylene chloride and toluene, respectively.

SEM images presented in Figure 3 shows that the TiO_2 nanoparticles were quite polydispersed in methylene chloride and toluene than in water, and their maximum size was 124 nm, 100 nm and 120 nm size, respectively. The chemical elemental composition of TiO_2 nanoparticles obtained by EDS is shown in Figure 4, which elucidated that the particles had C, O and Ti : C and O chemical elements, which are indicative of oxidation reactions with which the TiO_2 nanoparticles were derived [35].

FTIR spectroscopy analyses are shown in Figure 5, illustrating peak bands at 3327.65 cm^{-1}, 1635.33 cm^{-1} and 605.53 cm^{-1} for $TiCl_4$ solubilised in methylene chloride and toluene and 3207.61 cm^{-1}, 2350.40 cm^{-1}, 2030.61 cm^{-1}, 1622.16 cm^{-1} and 659.63 cm^{-1} for $TiCl_4$ solubilised in water. Characteristic bands indicated at 1635.33 cm^{-1} and 1622.16 cm^{-1} represent saturated hydrocarbons, i.e. the C=C link. Bands 3327.65 cm^{-1} and 3207.61 cm^{-1} indicated the O-H, with the peaks at 2350.40 cm^{-1}, 2030.61 cm^{-1} corresponding to the C-O stretching alcohols from methylene chloride and toluene. All bands were generated by the chemical and elemental interaction forms of water, methylene chloride and toluene. The presence of TiO_2 nanoparticles was indicated by the peak 605.53 cm^{-1} and 659.63 cm^{-1} for $TiCl_4$ in water and for $TiCl_4$ in methylene chloride and toluene, respectively.