Synthesis and Characterization of TiO_2 and Ag Doped TiO_2 Nanoparticles by Sol-Gel Method

Hay Mar Oo[1], Hlaing Hlaing Oo[2], Cho Cho[3]

Abstract

The research is focused on the preparation and characterization of TiO_2 powders by the sol-gel method. They were calcined at 500 to 700 °C and then characterized by X-ray Diffraction (XRD), Energy Dispersive X-ray Fluorescence (EDXRF), Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX). The XRD results suggested that the pure TiO_2 powder formed at 500 °C was in the anatase phase, whereas the materials formed at 600 were mixing of a few anatase phases and rutile phases, and a pure rutile phase at 700 °C. Therefore, the phase transition temperature of TiO_2 was 600 °C in this synthesis. The average crystallite sizes of prepared TiO_2 range from 25.50 to 96.39 nm. The average crystallite size was increased with increasing calcined temperature. The other path followed is the study of the addition of $AgNO_3$ to the TiO_2 (doping) through ions materials by XRD analysis were synthesised by the sol-gel method using titanium tetra isopropoxide, isopropanol, and silver nitrate and calcined at 500 to 700 °C. The presence of silver in the TiO_2 network has been established by XRD and SEM-EDX techniques. The XRD results of prepared Ag-TiO_2 materials suggested that the anatase phase in the tetragonal crystal structure at 500 °C and pure rutile phases appeared to be the predominant phase of rutile in the tetragonal crystal structure at 600 °C and 700 °C. The average crystallite sizes of prepared Ag-TiO_2 materials by XRD analysis were in the range of 15.79 to 54.53 nm. Thus, the prepared Ag-TiO_2 nanoparticles of pure anatase phase and pure rutile phase were calcined at 500 °C and 700 °C. The XRD study revealed that the prepared TiO_2 and Ag-TiO_2 materials were nanomaterials and anatase and rutile phases of a tetragonal crystal system.

Keywords **:** TiO_2 nanoparticles, Ag-TiO_2 nanoparticles, sol-gel method, phase transition

Introduction

Metal oxide photocatalytic degradation of organic pollutants has attracted significant attention by researchers because of its usefulness in tackling environmental contaminants. Titanium dioxide is one of the most widely studied semi-conducting photo catalysts for the degradation of organic contaminants from water and air, because of its physical and chemical stability, high catalytic activity, high oxidative power, low cost and ease of production (Seery *et al.,* 2007). The TiO_2 exists mostly as rutile and anatase phases which both of them have the tetragonal structures. Among these polymorphs, rutile and anatase have been widely studied (Rajamannan *et al*., 2013).

Many studies have been carried out to improve the photocatalytic activity by reducing the recombination reaction by the insertion of noble metals and it is found that doping with silver has been of considerable interest because of its potential applications. The importance in medical applications of silver and the antibacterial activity of TiO_2 together led researchers to think about the manufacture of silver doped titanic coated sanitary wares, medical devices, food preparation surfaces, air conditioning filters, *etc* (Seery *et al.,* 2007).

The low cost and easy preparation of silver (Ag) make it extremely suitable for industrial applications. Silver can trap the excited electron from TiO_2 and leave holes for the degradation reaction of organic species. It also results in the extension of their wavelength response towards the visible region. TiO_2 exhibits remarkable properties such as hydrophilicity as well as antibacterial and self-cleaning activity. Due to its optical activity, TiO_2 is often used in photocatalytic decomposition and more recently as a photocatalyst for the reduction of CO_2

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to methanol. Due to silver properties, doping TiO_2 with Ag improves the photocatalytic reactions and anti-microbial activity which makes it a current interest. Many researchers have worked on Ag-doped TiO_2 for different photocatalytic applications (Abdel *et al.,* 2015).

In the present research work, the sol-gel method was chosen for the preparation of pure TiO_2 and Ag doped TiO_2 nanoparticles, because this method is convenient and can be performed at various calcination temperatures. Moreover, it could have provided a simple, economic, and effective method to produce nanoparticles. Silver doped TiO_2 nanoparticles were prepared with titanium tetra isopropoxide as a precursor and calcined at 500 ºC, 600 ºC and 700 ºC. The characterization of prepared samples was performed by modern techniques (X-ray Diffraction (XRD), Energy Dispersive X-ray Fluorescence (EDXRF), and Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX).

Materials and Methods

Preparation of TiO_2 and Ag Doped TiO_2 Nanoparticles

TiO_2 nanoparticles were synthesized using the sol-gel method, involving hydrolysis and condensation of Titanium tetra isopropoxide (TTIP). The 5 mL of TTIP was diluted with 20 mL of isopropanol. This solution was added dropwise to the distilled water maintained at an appropriate pH 2-3 using concentrated HNO_3. The solution was stirred for 2 h and then kept in a water bath maintained at a temperature of 60 °C-70 °C for 20 h. The obtained TiO_2 particles were dried at 100 °C. The Ag doped TiO_2 nanoparticles were prepared using the sol-gel method. In an ultrasonic bath (135 W), 50 cm^3 of water was added dropwise to 7.50 mL of TTIP previously solubilized in 20 mL of isopropanol. After 30 minutes, 1.60 g of silver nitrate was added to the mixture solution to obtain Ag-doped TiO_2 materials. The mixture solution was kept under stirring for 2 hours, and it was centrifuged for 15 min. After being centrifuged, the paste was dried in an oven at 70 ºC until a dry powder was formed. The dry powders were grounded with a motar and pestle. The dry sample powders were sintered at different calcination temperatures for 5 hours, Ag doped TiO_2 nanoparticles were obtained. The prepared TiO_2 and Ag doped TiO_2 materials were calcined at 500 to 700 °C.

Characterization of Prepared TiO_2 and Ag doped TiO_2 materials

The prepared TiO_2 and Ag doped TiO_2 materials were characterized by X-ray Diffraction (XRD), Regaku X-ray Diffractometer, RINI 2000/PC software, Cat.NO.9240 J101, Japan at Universities' Research Center, Yangon Myanmar was used. The products were sprinkled on a pre-greased glass slide and diffractograms were recorded between the angles of 20° and 80°. The morphology and qualitative elemental composition of prepared samples were carried out by using a Scanning electron microscope - Energy Dispersive X- ray (SEM-EDX), EVO-18 Germany at the Universities' Research Center, Magway, Myanmar was used. The qualitative elemental composition of prepared samples was detected by the Energy Dispersive X-ray Fluorescence (EDXRF) technique using EDX 7000, Japan at Department of Chemistry, Monywa University, Monywa, Myanmar was used.

Results and Discussion

Characterization of Prepared TiO_2 and Ag doped TiO_2 materials

The pure TiO_2 and Ag doped TiO_2 materials were synthesized from titanium isopropoxide, $Ti(OC_3H_7)_4$ in isopropanol ($CH_3CHOHCH_3$), used as solvent. $AgNO_3$ was used as the precursor for Ag doped in TiO_2 materials

SEM Observation

The surface morphologies of TiO_2 and Ag doped TiO_2 materials calcined at 500 ºC, 600 ºC and 700 ºC were screened by SEM, and the SEM images of prepared materials were presented in figure 1. Similar morphology can be observed for the TiO_2 and Ag-TiO_2 materials.

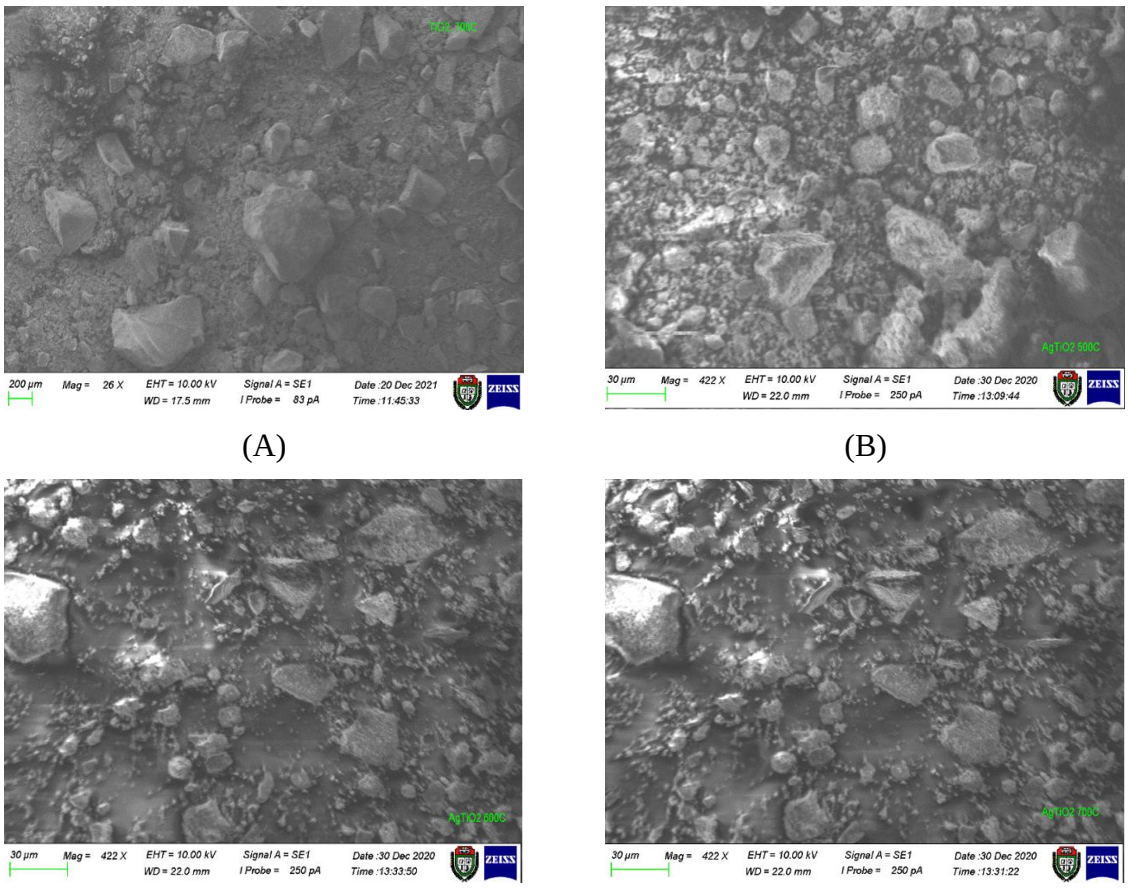
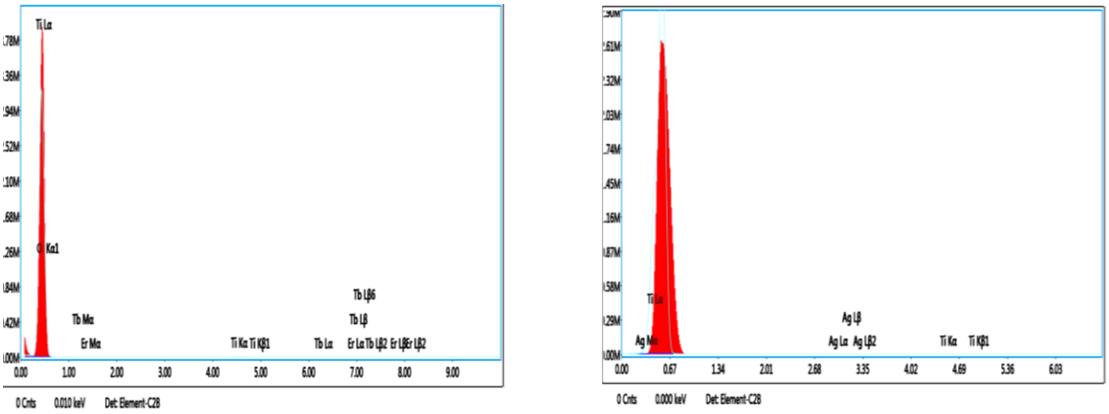


Figure 1. SEM images of (A): pure TiO_2 material calcined at 700 °C; (B): Ag- TiO_2 material calcined at 500 °C; (C): Ag-TiO_2 material calcined at 600 °C, and (D): Ag-TiO_2 material calcined at 700 °C

SEM images showed the presence of irregular size particles in prepared TiO_2 and Ag doped TiO_2 materials and agglomerates comprising high roughness and complexity. The silver doped TiO_2 materials consisted of more fine particles but were different from TiO_2 materials. The distribution of Ag on the surface of TiO_2 materials is not uniform, irregularly shaped particles are the aggregation of tiny crystals. The particles were spheroid or oblate spheroid and loosed. These small particles are aggregated into micro-sized particles. The pure TiO_2 materials were large particles, and the silver doped TiO_2 materials were small and homogeneous in distribution.

EDX Analysis

The elemental determination of synthesized TiO_2 and Ag doped TiO_2 materials was characterized by the EDX technique, the EDX spectrum is shown in figure 2 (a) and (b). The weight ratio and atomic ratio of Ag and TiO_2 are listed in Table 1. The weight percentage of Ag in the silver doped TiO_2 is predicted as 28.71% for Ag doped TiO_2 at 700 °C. The confirmation of dopant existence is indicated by the EDX spectrum of Ag doped TiO_2 that the presence of Ag metal and TiO_2 and Ag ions are successfully doped into the TiO_2 host structure.



(a) (b)

Figure 2. EDX spectrum of prepared (a) pure TiO_2 and (b) Ag dopedTiO_2 nanoparticles calcined at 700 ºC

Table 1. EDX data of Prepared TiO_2 and Ag Doped TiO_2 Nanoparticles calcined at 700 ºC

Element	Weight (%)		Atomic weight (%)	
	TiO_2	Ag-TiO_2	TiO_2	Ag-TiO_2
Ag	-	28.71	-	15.17
Ti	99.81	71.29	99.94	84.83

Relative Abundance of Elements in Prepared TiO_2 and Ag doped TiO_2 by EDXRF Analysis

The relative abundance of elements in Ag doped TiO_2 sample calcined at 700 ºC was carried out by EDXRF analysis. The EDXRF spectra of Ag doped TiO_2 was shown in figure 3 and the relative abundance of Ag doped TiO_2 sample calcined at 700 ºC are described in table 2. From EDXRF analysis, TiO_2 and Ag_2O are the main constituents and their relative abundance are 85.841% TiO_2 and 9.372% Ag_2O, respectively.

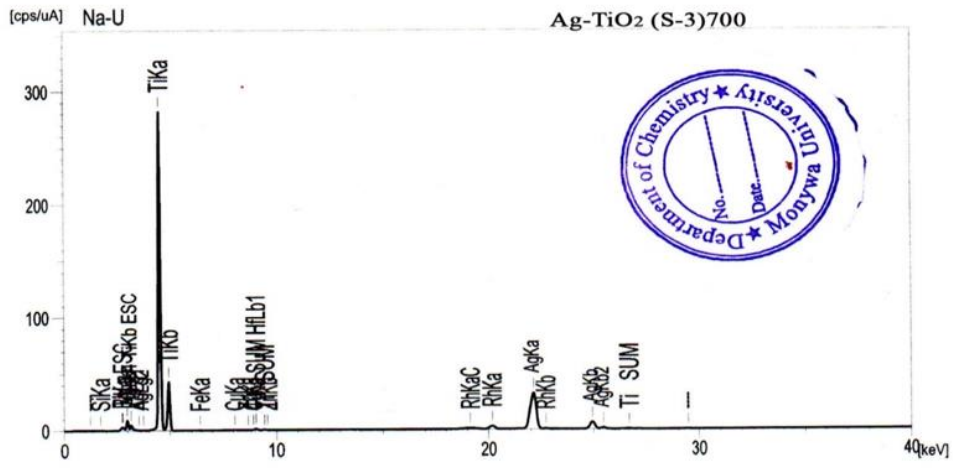


Figure 3. EDXRF spectrum of prepared Ag Doped TiO_2 nanoparticles calcined at 700 ºC

Table 2. Relative Abundance of the Elements of 5% Ag Doped TiO_2 Nanoparticles by EDXRF at 700 ºC

Element	Relative Abundance(%)
TiO_2	85.841
Ag_2O	9.372
SiO_2	4.723
Fe_2O_3	0.030
CuO	0.022
ZnO	0.012

Crystal Phase Detection of Prepared TiO_2 and Ag doped TiO_2 materials by XRD Analysis

The XRD examination was done to examine the crystal structure, crystallite sizes, and phase compositions of the prepared TiO_2 and Ag doped TiO_2 materials. The recorded XRD diffraction patterns are shown in figures 4 to 9. The average crystallite size (D) of the pure TiO_2 and Ag doped TiO_2 samples calcined at different temperatures was estimated using Scherer's formula, $D = 0.9\lambda / \beta \cos\Theta$. The crystallite sizes, lattice parameters, and crystal phases of prepared TiO_2 materials were summarized in Table 3. The diffraction peaks of the prepared TiO_2 materials calcined at 500 °C (figure 4) clearly showed that they originated at Bragg's angle 2θ values of 25, 38, 48, 53, 62 and 68° were assigned to the planes (101), (103), (200), (105), (211), and (204), respectively. It coincides with the standard card data of the pure anatase phase (Card number 202243). The standard card data also confirmed the diffraction peaks at the 2θ values of 25.48° represented miller indices (101) and 48.18 (200) were major peaks for the anatase phase of TiO_2.

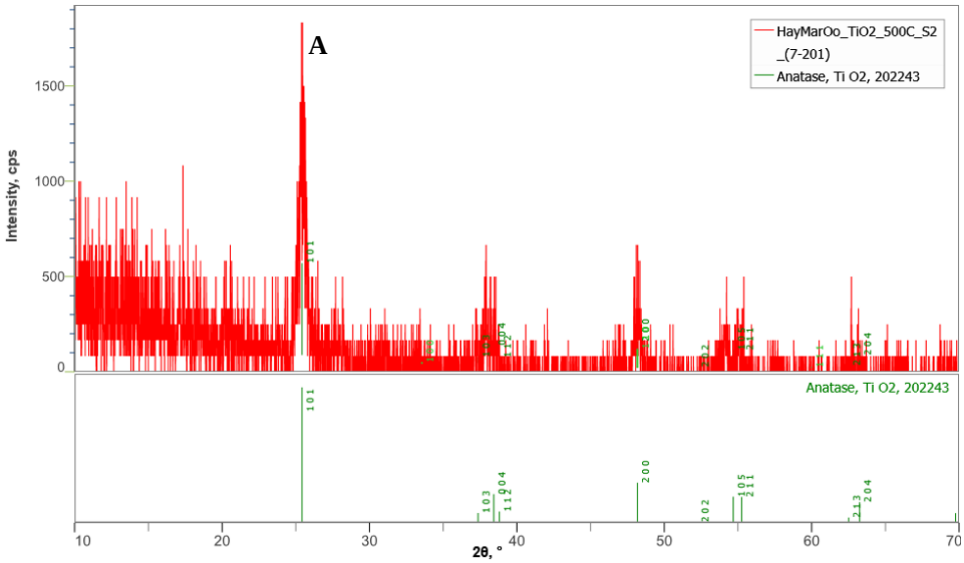


Figure 4. XRD patterns of prepared TiO_2 materials calcined at 500ºC (A: anatase)

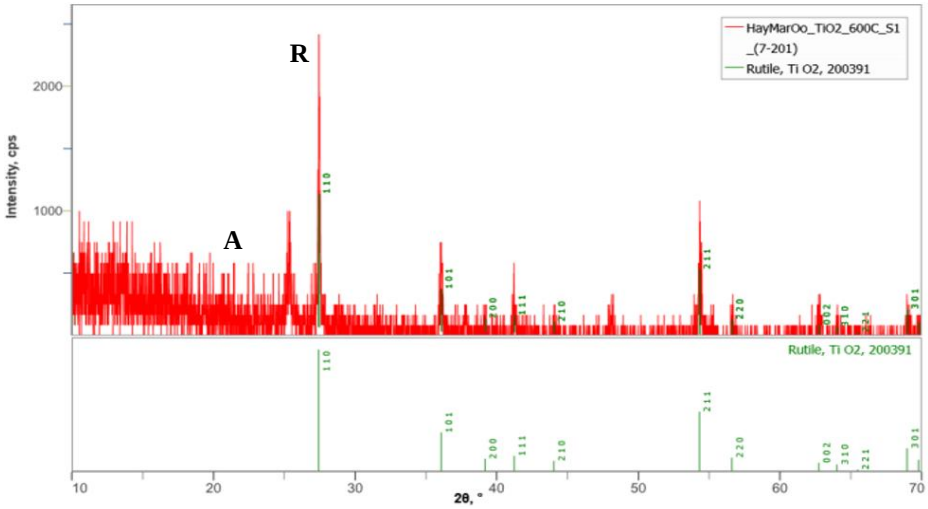


Figure 5. XRD patterns of prepared TiO_2 materials calcined at 600 ºC
(A: anatase and R: rutile)

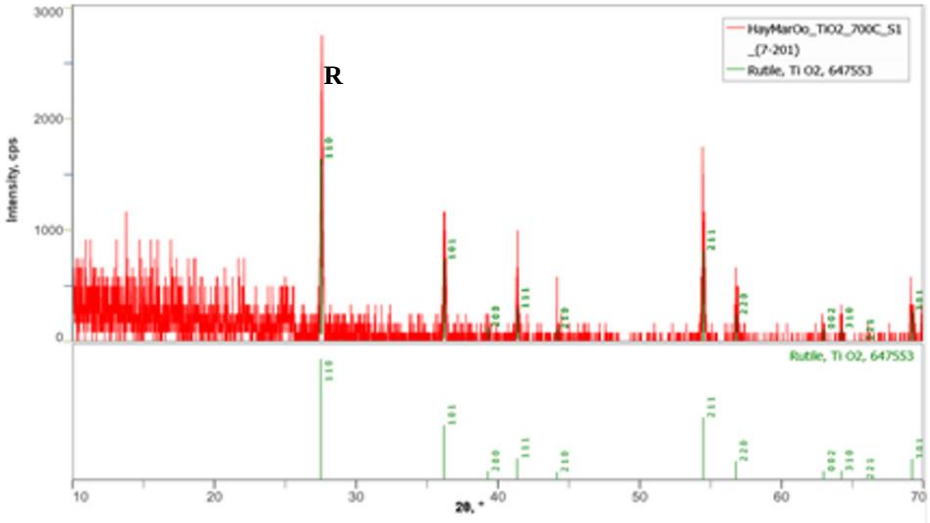


Figure 6. XRD patterns of prepared TiO_2 materials calcined at 700ºC

Table 3. XRD Characterization Data of Prepared pureTiO_2 Materials at Different Calcined Temperatures

Calcined Temperature (°C)	Average Crystallite Size (nm)		Lattice Parameters			Crystal Phase
	XRD	Calculated	a / Å	b / Å	c/ Å	
500	25.50	25.67	3.7873	3.7873	9.5079	Anatase
600	35.60	35.42	3.7873	3.7873	9.5079	Anatase & Rutile
700	93.75	96.39	4.5805	4.5805	2.9721	Rutile

The calcined temperatures of TiO_2 materials at 600 °C and 700 °C showed the miller indices of 110, 101, 200, 111, 210, 211, 220, 002, 310 221, and 310. The recorded data were identical with standard card and it indicated rutile phase of prepared TiO_2 materials. However, the small additional diffraction peak of anatase phase at 2θ values approximately 25 ° was

observed at the calcined temperature of 600 °C (figure 5), it can be suggested that phase transformation of anatase phase to rutile phase and these two phases were co-existed at this calcined temperature, while the calcined temperature of 700 °C (figure 6) clearly showed pure rutile phase of prepared TiO_2 materials. Therefore, the calcined temperature at 600 °C is the phase transition temperature. The average crystallite size of the anatase phase of TiO_2 materials was in the range of 25.50 to 96.39 nm with the crystal structure being tetragonal in all prepared TiO_2 materials. The average crystallite sizes of prepared TiO_2 materials were within the range of nanoparticles of 1 to 100 nm. Thus, the prepared TiO_2 materials can be confirmed as TiO_2 nanoparticles.

The XRD characterization of silver-doped TiO_2 materials was also described in figures 7 to 9 and table 4. The XRD patterns of prepared Ag doped TiO_2 materials calcined at 500 °C (figure 7) showed the identical miller indices of 101, 004, 112, 200, 105, 211 and 204 compared with standard card database, and pure anatase phase. The standard card data also confirmed the diffraction peaks at the 2θ values of 25° represented miller indices (101), 38° for (004), and 48° for (200) were major peaks for anatase phase of TiO_2. The diffraction peak of a silver crystal phase at 2θ value of 64° indicates the (220) plane.

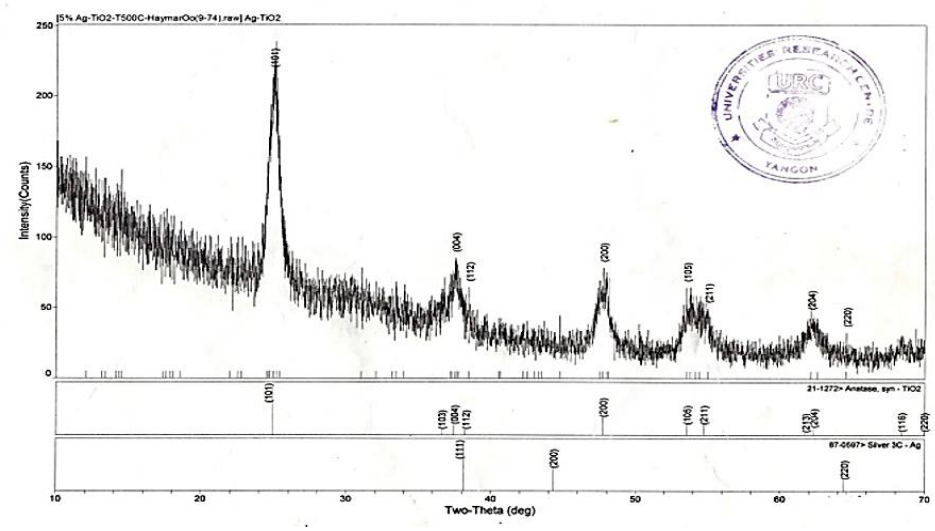


Figure 7. XRD patterns of prepared silver doped TiO_2 materials calcined at 500ºC

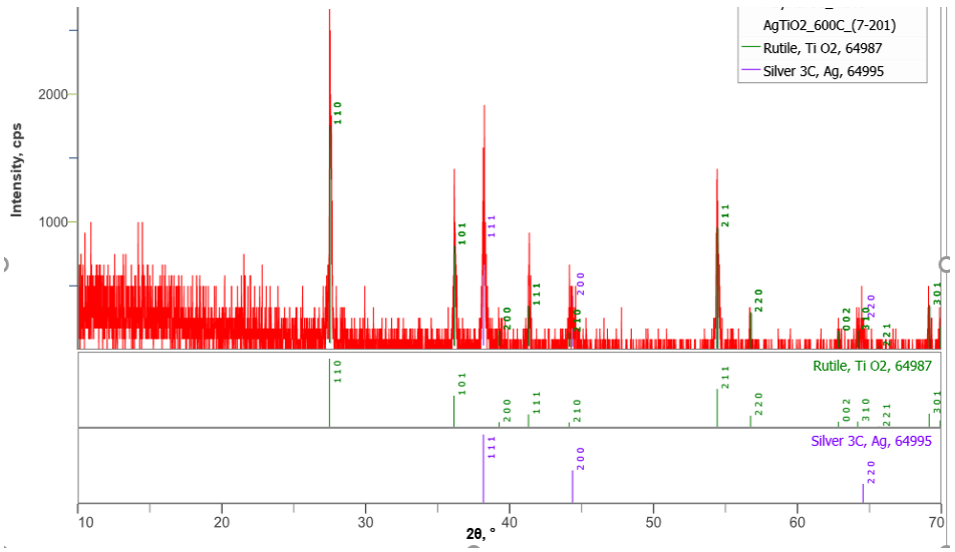


Figure 8. XRD patterns of prepared silver doped TiO_2 materials calcined at 600ºC

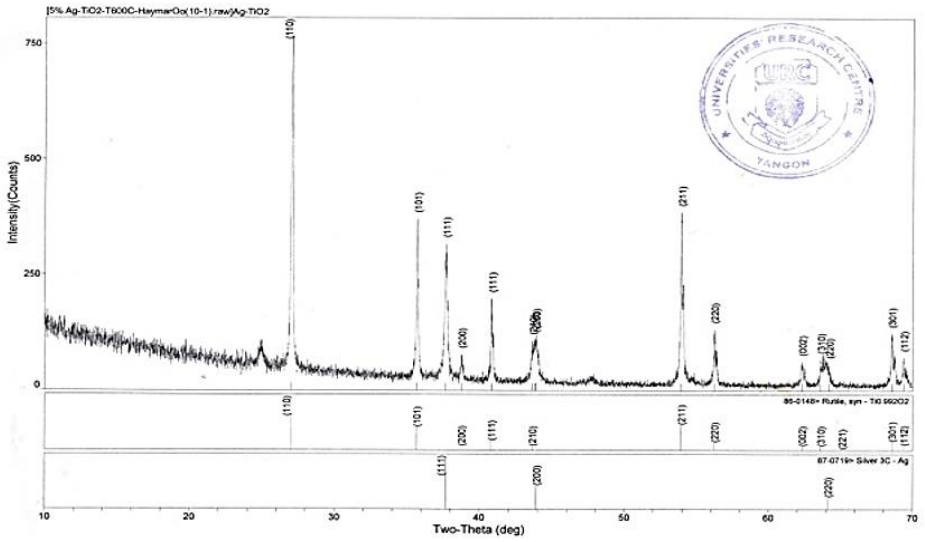


Figure 9. XRD patterns of prepared silver doped TiO_2 materials calcined at 700ºC

Table 4. XRD Characterization Data of Prepared Ag doped TiO_2 Materials at Different Calcined Temperature

Calcined Temperature (°C)	Average Crystallite Size (nm)		Lattice Parameters			Crystal Phase
	XRD	Calculated	a / Å	b / Å	c/ Å	
500	15.79	16.15	3.9571	3.9571	9.4303	Anatase
600	54.53	47.38	4.1618	4.1618	2.9749	Rutile
700	54.53	47.38	4.1618	4.1618	2.9892	Rutile

XRD profiles of prepared Ag doped TiO_2 materials calcined at 600 °C and 700 °C (figures 8 and 9) clearly showed that the diffraction peaks at the 2θ values of approximately 27° represented miller indices (110), 36° for (101), 41° for (111), 54° for (211) and 69° for (301) are major diffraction peaks for the rutile phase of TiO_2 materials. The XRD diffraction peaks of the silver crystal phase at 37° and 44° indicate the (111) plane of Ag_2O and the (200) plane of a metallic AgO plane, respectively. Therefore, the calcined temperatures at 600 °C and 700 °C were more doping of Ag in TiO_2 nanoparticles.

The average crystallite size of Ag doped TiO_2 materials was in the range of 15.79 to 54.53 nm with the crystal structure as tetragonal in all prepared silver doped TiO_2 materials, and it can also be proved that the prepared silver doped TiO_2 materials can be confirmed as Ag-TiO_2 nanoparticles. Doping with silver does not disturb the crystal structure of anatase and rutile TiO_2 indicating that the metal dopant is merely placed on the surface of the crystals without being covalently anchored into the crystal lattice (Nainani *et al*., 2012). The average crystallite sizes increased with increasing calcined temperatures. The crystallite sizes of Ag doped TiO_2 nanoparticles were smaller than pure TiO_2 nanoparticles.This is in good agreement with the results of SEM screening of TiO_2 nanoparticles and Ag doped TiO_2 nanoparticles. The XRD patterns of **anatase** phases have a main diffraction peak at 2θ value of 25.2° corresponding to the 101 plane while the main diffractions of **rutile** phases are at 2θ values of 27.4° (110 planes) and 30.8° (121 planes), respectively (Sarteep *et al*., 2016).

Conclusion

The pure TiO_2 and Ag doped TiO_2 nanoparticles were successfully synthesized by the sol-gel method at room temperature and calcined at 500 ºC for the anatase phase and 700 ºC for the pure rutile phase of TiO_2 in the tetragonal crystal structure. According to the XRD data, the average crystallite size of Ag doped TiO_2 nanoparticles was smaller than pure TiO_2 nanoparticles, and it also confirmed the particle sizes increased with increasing calcined temperature. Moreover, XRD analysis evaluated the phase transformation temperature of TiO_2 and Ag doped TiO_2 nanoparticles, approximately 600 ºC. From SEM micrographs, Ag doped TiO_2 was observed to have a few microns size agglomerates comprising spherical or oblate spherical shape of primary particles, and an EDX spectrum confirmed that Ag ions are successfully doped into the TiO_2 host structure. The XRD, SEM-EDX, and EDXRF data proved the incorporation of silver in the TiO_2 network.

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