SYNTHESIS AND CHARACTERIZATION OF Cu- DOPED TIO_2 NANOPARTICLES BY SOL - GEL METHOD

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Abstract

The study was designed to study the effect of copper doping of TiO_2 with three different copper concentrations and calcined at 500 to 800 °C for 2 hours on the anatase-rutile phase transition and composition. The prepared powder samples were characterized by X-ray Diffraction (XRD), Energy Dispersive X- ray Fluorescence (EDXRF), Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX). The XRD results suggested that the pure TiO_2 powder calcined at 500 °C was in 100 % anatase phase, whereas these materials transformed the mixing of a few anatase phases and mainly rutile phases at 600 °C. Therefore, the phase transition temperature of TiO_2 in this preparation method was 600 °C. The average crystallite sizes of prepared TiO_2 materials by XRD analysis were in the range of 25.50 to 96.39 nm. The average crystallite sizes increased with increasing calcined temperature. The associated work of this research is the addition of $CuSO_4$ to the crystal structure of TiO_2 synthesized by the sol-gel method using titanium(IV) isopropoxide, isopropanol, and copper(II) sulphate, and calcined at 500 to 800 °C. The XRD results of prepared Cu-doped TiO_2 materials described the anatase phase at 500°C and 600 °C, and the mixing of a few anatase phase and mainly rutile phase for Cu-doped TiO_2 nanoparticles at 700 °C. Therefore, the phase transition temperature of Cu-doped TiO_2 nanoparticles was 700 °C. The synthesized Cu-doped TiO_2 materials were fully transformed to the rutile phase at 800 °C. The average crystallite size of Cu-doped TiO_2 materials was in the range of 25.67 to 45.49 nm. The XRD study revealed that all the prepared samples have tetragonal crystal structures that were not changed through the doping process.

Keywords: TiO_2 nanoparticles, Cu-doped TiO_2 nanoparticles, sol-gel method, phase transition

Introduction

TiO_2 has become one of the most important semiconductor materials in daily life. Titanium dioxide was first commercially used during the 20th century for applications that include pigments in paint, UV blockers, batteries and food coloring (Byrne *et al.*, 2019). Titanium dioxide in comparison with other semiconductor catalysts, has many advantages, such as suitable optical and electron properties, chemical stability, corrosion resistance and non-toxicity. Titanium dioxide has been widely used as a catalyst under UV irradiation and was considered the best choice among several other metal oxides (Ahmed, 2015). These include ease of preparation, strong oxidizing ability, long term stability, nontoxicity, high refractive index, high dielectric constant and low cost (Fisher *et al.*, 2013). TiO_2 is naturally present in three main phases: anatase (tetragonal, a= b= 3.785 Å, c= 9.54 Å), brookite (orthorhombic, a= 5.143 Å, b= 5.456 Å, c= 9.182 Å) and rutile (tetragonal, a=b= 4.593 Å, c= 2.959 Å). The thermodynamically metastable phases, anatase and brookite, transition irrevocably into the stable rutile phase at high temperatures (Hanaor and Sorrell, 2011).

Recently, copper has been increasingly investigated as a dopant for titania (Ahmed, 2015). Copper has been previously investigated as a potential dopant in TiO_2 but to date, a detailed systematic analysis of the effect of Cu doping on the phase stability of TiO_2 is lacking (Yoong *et al.*, 2009). It is one of the best candidate metal dopants for TiO_2 surfaces, because of its relative abundance, high electronic conductivity and low cost as compared to noble metals such as Ag and

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Cu is also a metallic element essential to human health and is considered a low toxicity metal to humans.

In this research, the sol-gel method was chosen for the preparation of pure TiO_2 and Cu-doped TiO_2 nanoparticles, because this is the easiest method that can be performed at various calcination temperatures. In the present work, Cu-doped TiO_2 nanoparticles were prepared with titanium(IV) isopropoxide as a precursor, three different copper concentrations, and calcined at 500 to 800ºC.

Materials and Methods

Sample collection

Titanium(IV) isopropoxide and isopropanol were purchased from Academy Chemical Group at 27th street, Pabedan Township, Yangon. The apparatus consists of conventional labware, glassware and modern equipment. Some of the instruments used in the experiments are E-Mettler balance (210 ± 0.1 mg) (LA – 310 S), magnetic stirrer (Bibby), muffle furnace (Range 100-1100 ºC Gallenkamp, England) and thermal control status oven (H 053, 240 V, England).

Preparation of TiO_2 and Cu-Doped TiO_2 Nanoparticles

TiO_2 nanoparticles were synthesized by using the sol-gel method, which involves the hydrolysis and condensation of titanium (IV) isopropoxide. Briefly, 46.16 mL of titanium isopropoxide was added to 200 mL of isopropanol. This solution was stirred for 15 min. To this solution, 200 mL of deionized water was added. This mixture was stirred for another 30 min. The resulting gel was dried in the oven set at 100 ℃ for 12 h. The resulting powder was annealed at 500 °C, 600 °C, 700 °C and 800 °C at a ramp rate of 10 °C/min and held at the target temperature for 2 h. For a 2% copper sample, 45.24 mL of titanium (IV) isopropoxide was added to 200 mL of isopropanol and stirred for 15 min (Solution A). After that, 0.8705 g of copper (II) sulphate ($CuSO_4$) was added to 200 mL of deionized water, which was stirred for 15 min (Solution B). Solution B was added to Solution A and this was stirred for 30 min. The resulting gel was dried in the oven at 100 °C for 12 h. The resulting powder was annealed at 500 °C, 600 °C, 700 °C and 800 °C at a ramp rate of 10 °C/min and held for 2 h. This method was repeated for the 4% and 8% copper samples by altering the amounts of titanium(IV) isopropoxide and $CuSO_4$ (4%–44.32 mL and 1.7375 g; 8%–42.47 mL and 3.5075 g).

Characterization of TiO_2 and Cu-doped TiO_2 materials

The prepared TiO_2 and Cu-doped TiO_2 materials were characterized by X-ray Diffraction (XRD) using a Rigaku X-ray Diffractometer (RINI 2000/PC software, Cat.NO.9240 J101, Japan) at Universities' Research Center, Yangon, Myanmar was used. The morphology and qualitative elemental composition of prepared samples were carried out by using Scanning electron microscope with energy dispersive X- ray (SEM-EDX), EVO-18 Germany at University Research Center, Magway, Myanmar. Qualitative elemental composition of prepared samples was detected by Energy Dispersive X- ray Fluorescence (EDXRF) technique using EDX 7000, Japan at Department of Chemistry, Monywa University, Monywa, Myanmar.

Results and Discussion

Characterization of Prepared TiO_2 and Cu-doped TiO_2 materials

The pure TiO_2 and Cu-doped TiO_2 materials were synthesized from titanium(IV) isopropoxide, $Ti(OC_3H_7)_4$ in iso-propanol ($CH_3CHOHCH_3$), used as solvent. Anhydrous $CuSO_4$ was used as the precursor for Cu doping in TiO_2 materials.

Synthesized TiO_2 and Cu doped TiO_2 materials by XRD Analysis

The effect of copper doping through TiO_2 crystal structure on the anatase to rutile phase transition temperature was analysed by X-ray Diffraction technique. The recorded XRD diffraction patterns for synthesized TiO_2 are shown in Figure 1. XRD patterns of prepared TiO_2 materials calcined at 500 °C (Figure 1(a)) clearly show the identical Miller indices of (101), (103), (004), (112), (200), (105), (211), and (204) with the standard card database, and 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 for (200) were major peaks for the anatase phase of TiO_2.

The calcined temperatures of TiO_2 materials at 600 °C and 700 °C showed the diffraction peak with Miller indices of (110), (101), (200), (111), (210), (211), (220), (002), (310), (221), and (310). The strong intensity peak at a 2θ value of 27.4 with the Miller index (110) proved the transformation of the rutile phase introduced at this temperature. The recorded data were identical with the standard card and it indicated the rutile phase of prepared TiO_2 materials. Moreover, the small additional diffraction peak of the anatase phase at a 2θ value approximately 25 ° existed at calcined temperature of 600 °C (Figure 1(b)). It can be suggested that the phase transformation of anatase phase to the rutile phase co-existed at this calcined temperature. The calcined temperatures of 700 °C (Figure 1(c)) and 800 °C (Figure 1(d)) clearly showed the pure rutile phase of prepared TiO_2 materials. Therefore, the calcined temperature at 600 °C is the phase transition temperature. The main diffraction peaks with Miller indices of the anatase and rutile were (101) and (110), respectively.

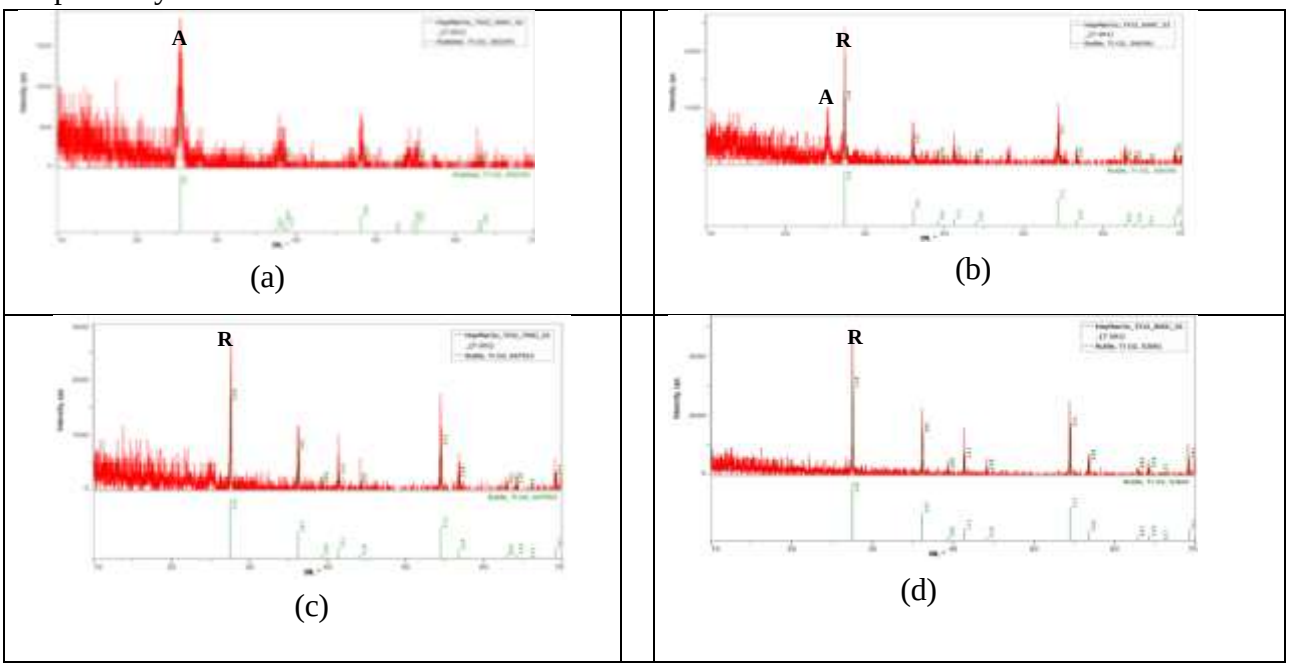

Figure 1. XRD patterns of prepared TiO_2 materials calcined at (a) 500 ºC, (b) 600 ºC and (c) 700 ºC and (d) 800ºC (A: anatase and R: rutile)

The crystallite sizes of prepared TiO_2 and 2%, 4%, and 8% Cu-doped TiO_2 materials calcined at four different temperatures (500 °C, 600 °C, 700 °C, and 800 °C) were identified by X-ray diffraction. The simplest and most widely used method for estimating the average crystallite size is from the full width at half maximum (FWHM) of a diffraction peak using the Scherrer equation, $d = K\lambda / \beta \cos \theta$, where d is the crystallite size, λ is the diffraction wavelength, β is the corrected FWHM, θ is the diffraction angle, and K is a constant close to unity. The crystallite sizes, lattice parameters, and crystal phases of prepared TiO_2 materials were calculated by this method as shown in Table 1. The average crystallite sizes of the anatase phase of TiO_2 materials were in the range of 25.50 to 94.50 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 from 1 to 100 nm. Thus, the prepared TiO_2 materials can be confirmed as TiO_2 nanoparticles.

Table 1. XRD Characterization Data of Prepared pureTiO_2 Materials at Different Calcined Temperatures

Calcined temperature	Average crystallite size (nm)		Lattice parameters (Axial length)			Crystal phase
(°C)	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
800	94.80	94.50	4.5782	4.5782	2.9536	Rutile

The XRD patterns of 2%, 4%, and 8% copper-doped TiO_2 materials were also described in Figures 2 to 4 and Tables 2 to 4. The standard card data from the XRD library confirmed the XRD diffraction peaks of copper-doped TiO_2 materials (2%, 4%, and 8%) calcined at 500 °C and 600 °C; the 2θ values of 25.4° represented Miller indices (101), 37.8° for (004), and 48.06° for (200) were major peaks for the anatase phase of TiO_2. The additional diffraction peaks of a copper crystal doped through TiO_2 materials showed 2θ value of 51°, which indicated the (220) plane for 2% Cu-doped TiO_2 and 2θ value of 43.5°, which indicated the (111) plane for 8% Cu-doped TiO_2. As a result, the intensity ratio of the copper dopant peak is lower in comparison with the host TiO_2 materials.

The XRD pattern of Cu-TiO_2 materials calcined at 700 °C showed that the diffraction peaks at the 2θ values of 25.4° represented diffraction peaks with Miller indices (101); diffraction peaks of 27.50° for (110), 36.70° for (103), 37.8° for (004), 48.06° for (200), 54.16° for (105) and 55° for (211) are major diffraction peaks for the anatase phase of TiO_2 materials for prepared 2%, and 4%. The XRD patterns showed the mixing of a few anatase phases and mainly rutile phases for 8% Cu-doped TiO_2 materials calcined at 700 °C. The XRD diffraction peaks of the copper crystal phase at 43.5° indicated the (111) plane of Cu for 8% Cu-doped TiO_2 materials calcined at 700 °C. At 700 °C, XRD results showed the mixing of the anatase phase and the rutile phase for Cu-TiO_2. Therefore, the phase transition temperature for Cu-doped TiO_2 was 700°C.

The XRD data of synthesized Cu-TiO_2 materials calcined at 800 °C clearly showed that the diffraction peaks at the 2θ values of approximately 27.50° represented Miller indices (110), 36.7° for (103), 37.8° for (004), 48.06° for (200), 54.16° for (105) and 55° for (211), which are major diffraction peaks for the rutile phase of TiO_2 materials. The XRD diffraction peaks of copper

crystal phase at 42.25° and 48.50° indicated the (200) and (202) planes of a metallic CuO plane, and 43.5° indicated the (111) plane of copper doping. Therefore, the pure rutile phases of Cu-TiO_2 materials with tetragonal crystal structures were obtained at calcined temperatures of 800 °C. According to the reported literature, the XRD patterns of anatase phases have a main diffraction peaks at 2θ value of 25.2° corresponding to the (101) plane while the main diffractions of rutile phases are at a 2θ values of 27.4° (110 plane) and 30.8° (121 plane), respectively (Sarteep *et al.*, 2016). The current research data on the synthesized Cu-TiO_2 materials were in good agreement with the reported literatures.

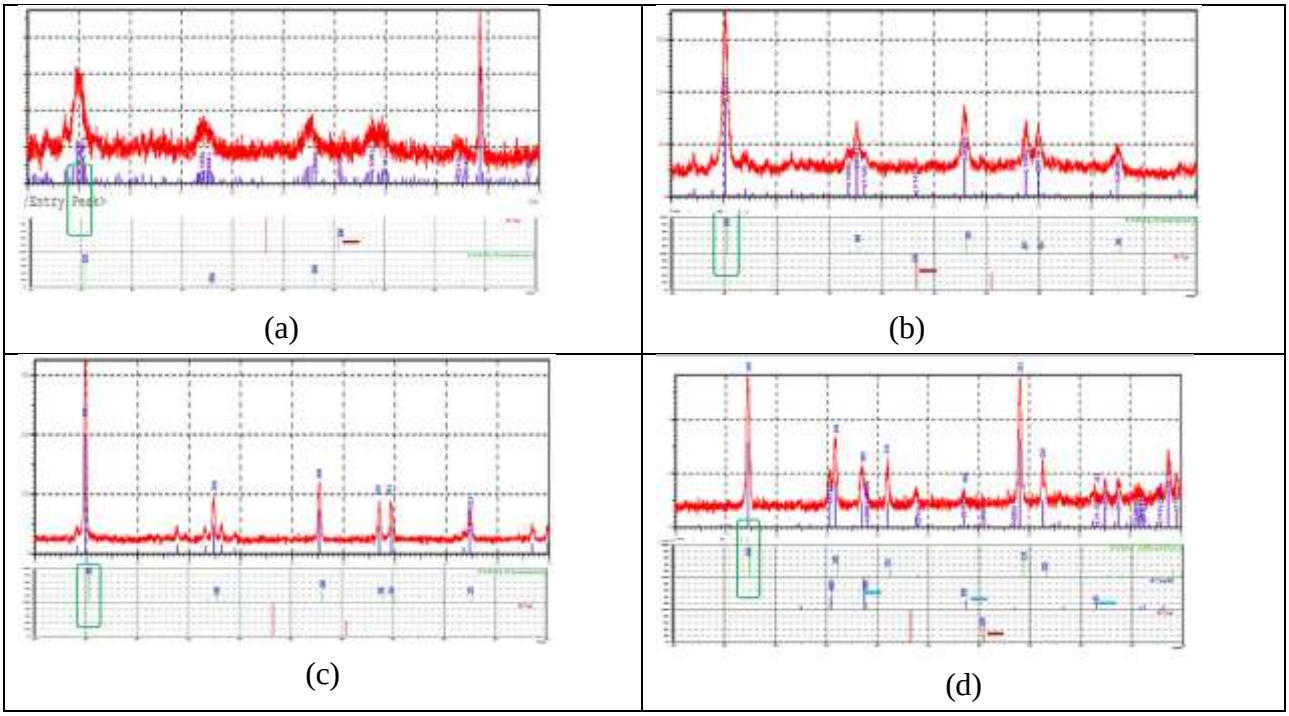

Figure 2. XRD patterns of prepared 2%Cu-TiO_2 materials calcined at (a) 500ºC, (b)600 ºC and (c) 700 ºC and (d) 800ºC

Table 2. XRD Characterization Data of Prepared 2% Cu-TiO_2 Materials at Different Calcined Temperatures

Calcined temperature (°C)	Average crystallite size (nm)		Lattice parameters (Axial length)			Crystal phase
	XRD	Calculated	a / Å	b / Å	c/ Å	
500	22.50	23.56	3.7850	3.7850	9.547	Anatase
600	25.60	25.78	3.7723	3.7723	9.5260	Anatase
700	33.75	34.17	3.7807	3.7807	9.5039	Anatase
800	40.80	40.37	4.579	4.579	2.9566	Rutile

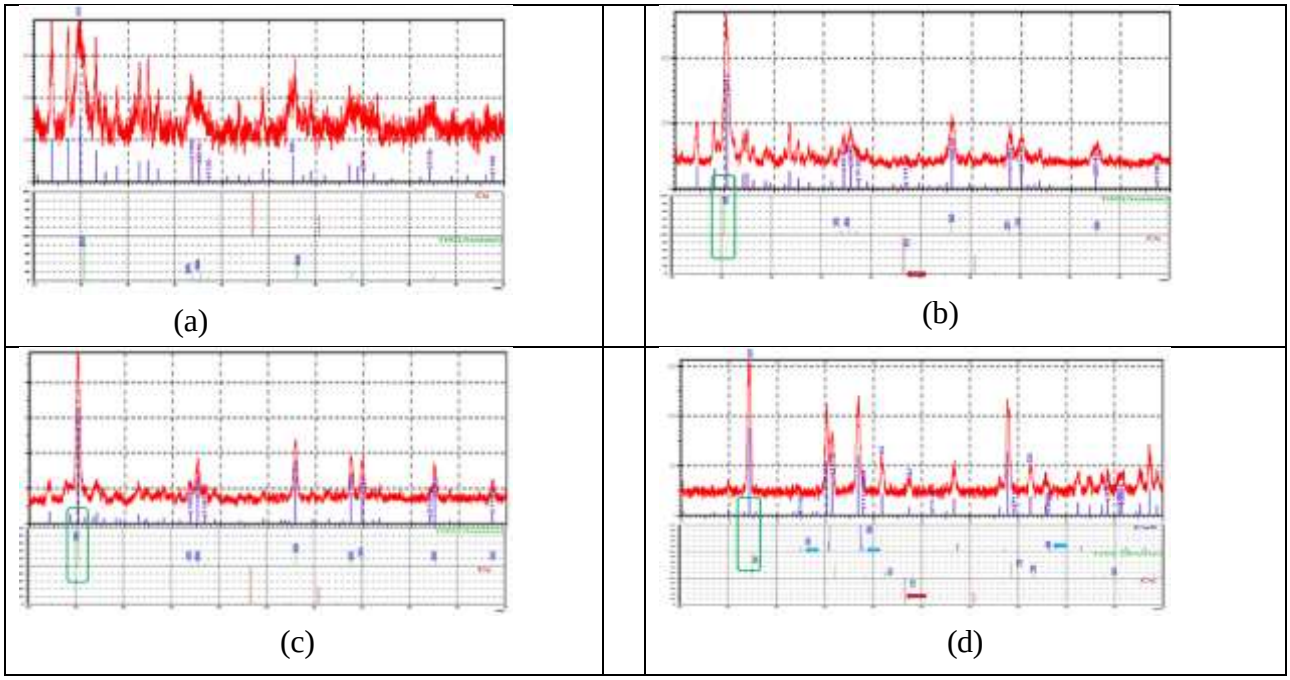

Figure 3. XRD patterns of prepared 4%Cu-TiO_2 materials calcined at (a) 500ºC, (b)600 ºC and (c) 700 ºC and (d) 800ºC

Table 3. XRD Characterization Data of Prepared 4% Cu-TiO_2 Materials at Different Calcined Temperatures

Calcined temperature (°C)	Average crystallite size (nm)		Lattice parameters (Axial length)			Crystal phase
	XRD	Calculated	a / Å	b / Å	c/ Å	
500	28.40	27.71	3.7829	3.7829	9.2569	Anatase
600	32.17	32.19	3.7760	3.7760	9.4860	Anatase
700	41.10	40.81	3.7845	3.7845	9.2559	Anatase
800	46.30	45.49	4.5746	4.5746	2.9478	Rutile

The average crystallite sizes of Cu-TiO_2 materials were in the range of 25.67 to 45.49 nm with a crystal structure of tetragonal in all prepared copper-doped TiO_2 materials, and it can also be proved that the prepared copper-doped TiO_2 materials can be confirmed as Cu-TiO_2 nanoparticles. According to the XRD data, the copper-doping process does not disturb the TiO_2 crystal network due to its transformation from anatase to rutile phase, 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).

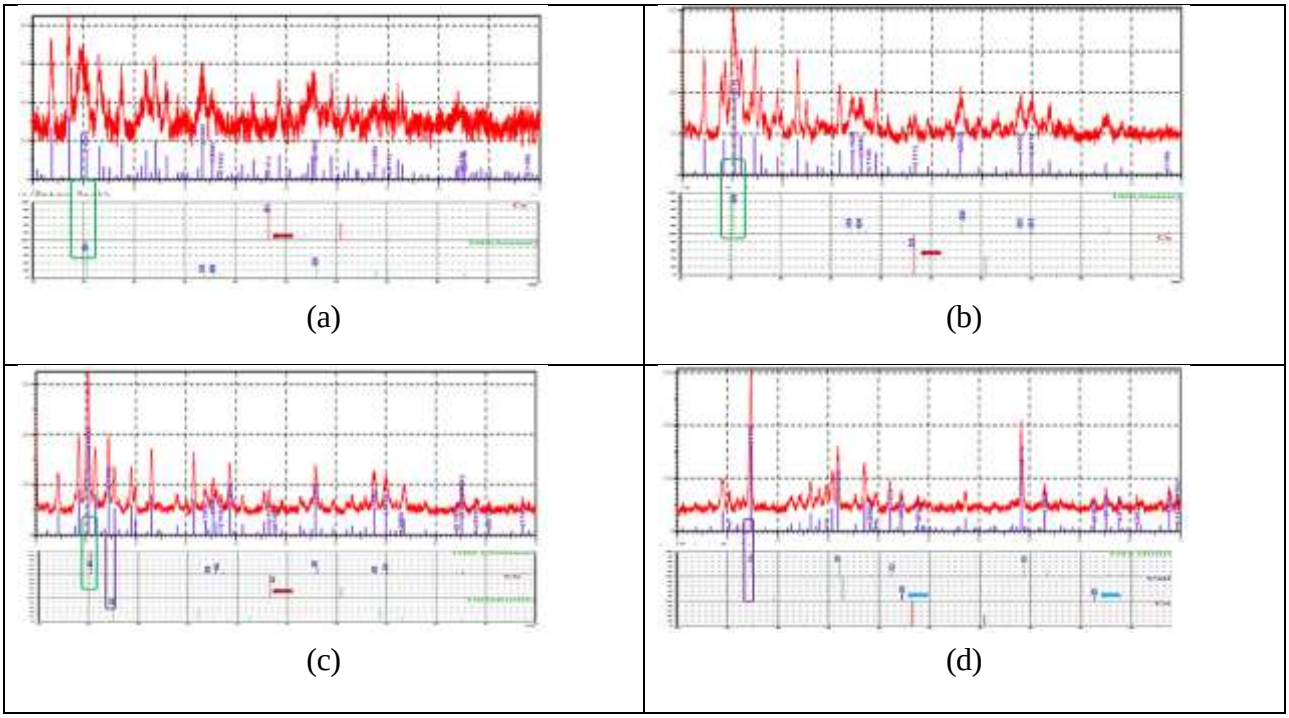

Figure 4. XRD patterns of prepared 8%Cu-TiO_2 materials calcined at (a) 500ºC, (b)600 ºC and (c) 700 ºC and (d) 800ºC

Table 4. XRD Characterization Data of Prepared 8% Cu-TiO_2 Materials at Different Calcined Temperatures

Calcined temperature (°C)	Average crystallite size (nm)		Lattice parameters (Axial length)			Crystal phase
	XRD	Calculated	a / Å	b / Å	c/ Å	
500	24.75	25.41	3.785	3.7850	9.547	Anatase
600	26.87	29.79	3.7380	3.7380	9.4462	Anatase
700	35.90	38.27	3.7845	3.7845	9.2559	Anatase & Rutile
800	42.70	42.15	4.5898	4.5898	2.9598	Rutile

Morphology of Synthesized TiO_2 and Cu-doped TiO_2 by SEM

The surface morphologies of TiO_2 and Cu-doped TiO_2 nanoparticles, calcined at 700 ºC and 800 ºC were investigated by SEM (Figure 5). SEM images of synthesized materials showed that all samples were polycrystalline and highly agglomerated. The agglomerations of doped materials seemed to be excessive compared to pure TiO_2.The copper doped TiO_2 materials consisted of finer particles but were different from TiO_2 materials. The distribution of Cu on the surface of TiO_2 materials is not uniform; there are irregularly shaped particles that are the aggregation of tiny crystals. Most of the particles were agglomerated and of irregular shape; some were tetragonal. The pure TiO_2 materials were large particles, and the copper-doped TiO_2 materials had a small and homogeneous distribution. The crystallite sizes of Cu doped TiO_2 nanoparticles were smaller than those of pure TiO_2 nanoparticles, which is in good agreement with the results of SEM screening of TiO_2 nanoparticles and copper-doped TiO_2 nanoparticles.

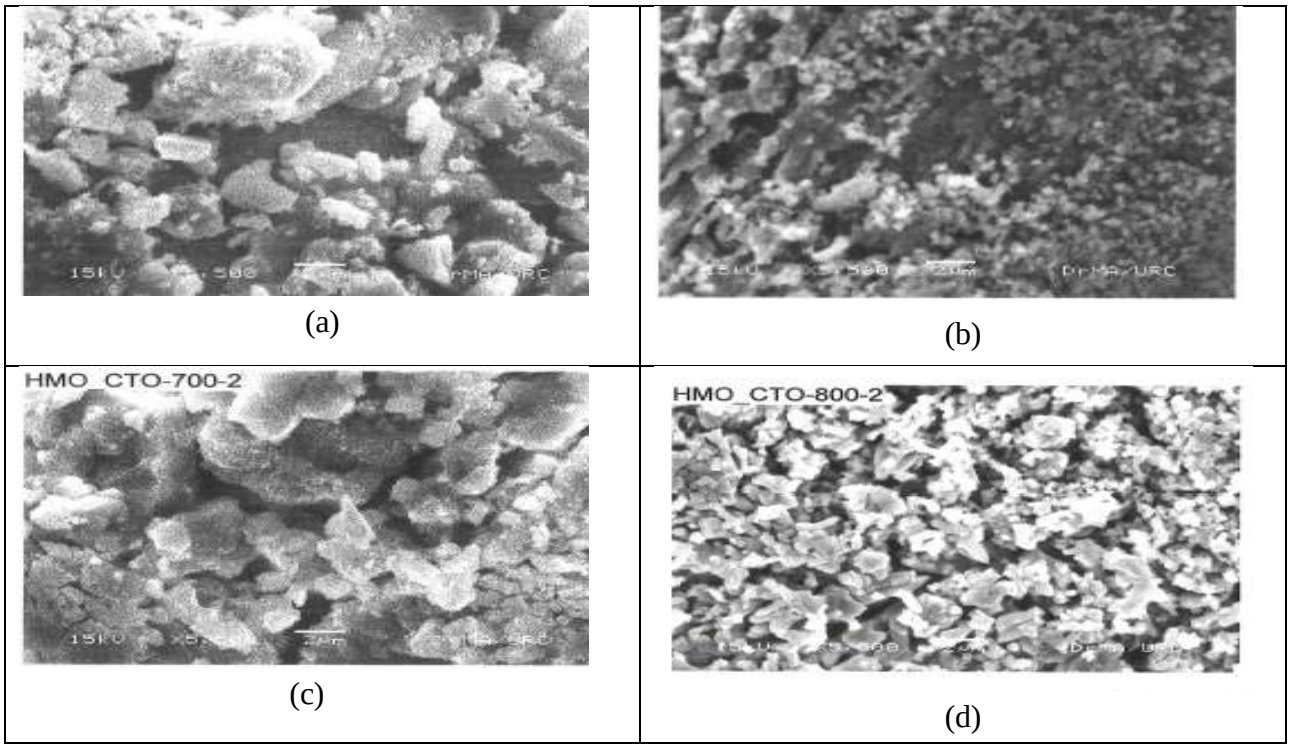

Figure 5. SEM images of (a) pure TiO_2 material calcined at 700 °C; (b) pure TiO_2 material calcined at 800 °C; (c) Cu- TiO_2 material calcined at 700 °C, and (d) Cu- TiO_2 material calcined at 800 °C

Evaluation of Elemental Composition by SEM-EDX and EDXRF

The elemental compositions of synthesized TiO_2 and Cu-doped TiO_2 materials were characterized by SEM-EDX and EDXRF techniques. The elemental compositions of TiO_2 and Cu-doped TiO_2 are shown in Figures 6 (a) and (b) and Table 5. According to the EDX results, the weight percents of Ti in TiO_2 and Cu-TiO_2 were 99.81 % and 63.92 %, respectively, and Cu in Cu-TiO_2 was 36.08 % at a calcination temperature of 800 °C. The relative abundance of elements and EDXRF spectra of Cu-TiO_2 are presented in Table 6 and Figure 7. From EDXRF analysis, the relative abundances of TiO_2 and CuO were 68.92% and 30.06 %, respectively. Therefore, the EDXRF spectrum confirmed the presence of copper dopant in Cu-TiO_2.

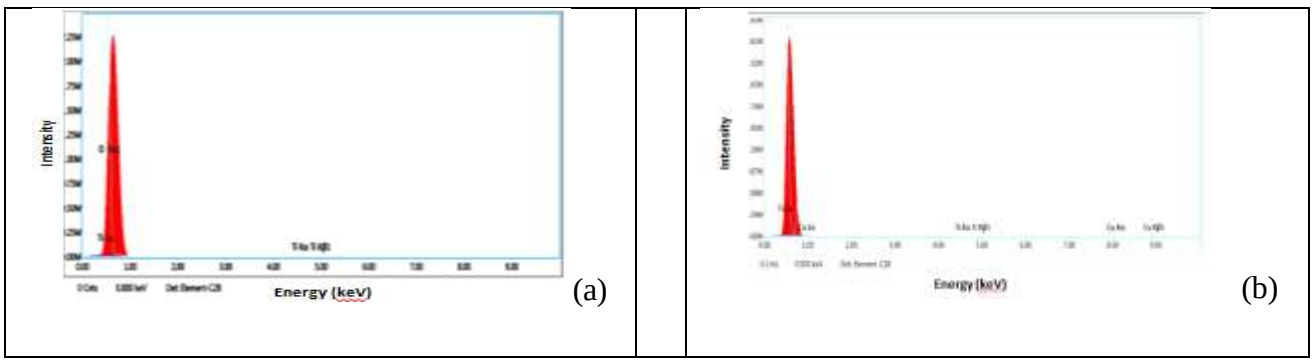

Figure 6. EDX spectrum of prepared (a) pure TiO_2 and (b) Cu-TiO_2 nanoparticles calcined at 800ºC

Table 5. EDX data of Prepared TiO_2 and Cu-Doped TiO_2 Nanoparticles calcined at 800 ºC

Element	Weight (%)	
	TiO_2	Cu-TiO_2
Cu	-	36.08
Ti	99.81	63.92

Table 6. Relative Abundance of the Elements of Cu-Doped TiO_2 Nanoparticles by EDXRF at 800 ºC

Elements in oxide form	Relative Abundance(%)
TiO_2	68.92
CuO	30.06
SiO_2	0.83
CaO	0.09
NiO	0.07
Rb_2O	0.01

Figure 7. EDXRF spectrum of prepared Cu Doped TiO_2 nanoparticles calcined at 800 ºC

Conclusion

The Cu-doped TiO_2 nanoparticles were successfully synthesized by sol-gel method and the effect of copper doping on TiO_2 was examined at different temperatures (500 ºC to 800 ºC). The pure TiO_2 nanoparticles calcined at 700 ºC showed 100 % rutile phase, and the Cu-TiO_2 nanoparticles showed pure rutile phase at 800 ºC. The tetragonal crystal network of TiO_2 did not change due to the copper doping process. Moreover, XRD analysis showed that the phase transformation temperature of pure TiO_2 was 600 ºC and that of Cu-TiO_2 nanoparticles was approximately 700 ºC. According to the XRD data, the average crystallite sizes of Cu-TiO_2 nanoparticles was smaller than that of pure TiO_2 nanoparticles. The surface morphology of Cu-TiO_2 nanoparticles showed that the majority of particles were agglomerated and irregular in shape; some were tetragonal in shape. The EDX spectrum confirmed that Cu ions were successfully doped into the TiO_2 host structure.

Acknowledgements

The authors would like to express profound gratitude to the Department of Higher Education, Ministry of Higher Education, Yangon, Myanmar, for providing the opportunity to do this research and Myanmar Academy of Arts and Science for allowing to present this paper.

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