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# Visible light driven photocatalyst of vanadium ( $V^{3+}$ ) doped $TiO_2$ synthesized using sonochemical method

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**Abstract.**  $TiO_2$  has been widely investigated due to its superior photocatalytic activity under ultraviolet irradiation among the photocatalyst materials. In this research, vanadium ( $V^{3+}$ ) was doped into  $TiO_2$  to enhance its light response under visible irradiation for wider application. Vanadium was introduced into  $TiO_2$  lattice at various concentration respectively 0.3, 0.5, 0.7 and 0.9% using simple and fast sonochemical method. X-Ray Diffraction data show that vanadium doped  $TiO_2$  crystallized in anatase phase with  $I4_1amd$  space group. X-Ray Diffraction pattern shifted to lower value of  $2\theta$  due to vanadium dopant. It indicated that  $V^{3+}$  was incorporated into anatase lattice. UV-Vis Diffuse Reflectance Spectra was revealed that the doped  $TiO_2$  has lowered reflectance and enhanced absorption coefficient in visible region than undoped  $TiO_2$  and commercial anatase  $TiO_2$ . Band gap energy for undoped and doped  $TiO_2$  were respectively 3.22, 3.05, 2.93, 3.03 and 2.40 eV. Therefore vanadium doped  $TiO_2$  had potential to be applied under visible light.

## 1. Introduction

Modification anatase  $TiO_2$  with various metal dopants have been reported as one of strategy to enhance its optical absorption and photocatalytic activity under visible irradiation. Vanadium dopant has produced a higher optical absorption and lower band gap energy than Ce, Cr, Fe, and Ni dopant [1-3] thus vanadium is an attractive dopant to be studied. Vanadium in anatase lattice shown the urbach tail phenomenon [4] therefore resulted in decreasing the band gap energy and enhancing the absorption of anatase in visible light. Vanadium also affected on the phase transformation of anatase  $TiO_2$  since vanadium has the low solubility in anatase phase (about 5 at %) [5]. Low level of vanadium (0.3%) does not induced the phase transformation and only leads a small shift in absorption edge through solid state synthesis [6]. However, 0.3% of vanadium was reported to induce the phase transformation from anatase into rutile [3] while sol gel method was employed. It can be concluded that the structural transformation and the band gap reduction can be influenced by concentration of vanadium and the synthesis method employed in photocatalyst's production.

Sonochemical method is fast and simple method which nowadays developed in synthesis of semiconductor materials. Ultrasound wave can assisted the chemical reaction and resulted in smaller particle size, homogenous particle distribution, high surface area and high purity of material. Irradiation of ultrasound wave into solution given an acoustic cavitation which is produced through bubble formation, bubble growth and collapsing the bubbles in liquids [7]. Acoustic cavitation provide an extremely high temperature and pressure in short duration to facilitate the chemical reaction on



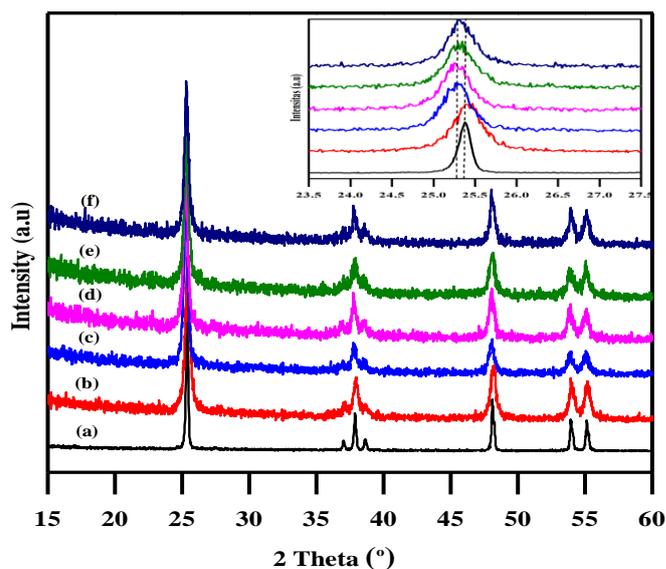
synthesis process. Sonochemical method has been applied in synthesis of TiO<sub>2</sub> nanoparticle [8], Pt, Ru doped TiO<sub>2</sub> [9] and V doped TiO<sub>2</sub> 1-5 at % [10]. No sufficient work reported to produce low content of vanadium doped TiO<sub>2</sub> using sonochemical method, therefore it became important to explore this efficient method on synthesis of vanadium doped TiO<sub>2</sub>. Sonochemical method at low frequency was applied in this research to study the effect of vanadium concentration (0.3-0.9 at %) on structure and optical characteristics of anatase TiO<sub>2</sub>.

## 2. Experimental

Titanium isopropoxide (TTIP, sigma Aldrich) was dissolved into 40 mL ethanol:deionize water (3:1v/v). Stoichiometric amount of vanadium acetylacetonate (V(acac)<sub>3</sub>, sigma aldrich) in 20 mL ethanol: deionize water (3:1v/v) added into titanium solution at 0.3, 0.5, 0.7 and 0.9% atomic ratio of vanadium III (V<sup>3+</sup>). The homogenous mixture transferred into ultrasonic bath reactor and irradiated with low frequency ultrasound wave 40 KHz for 40 minutes. The obtained precipitates aged, filtered and washed with ethanol then dried at 105°C for 2h. The dry powders subsequently pressed into pellet and calcined for 2h at 500°C. Undoped TiO<sub>2</sub> was also synthesized using the same method with the absence of vanadium. The white powder produced for undoped TiO<sub>2</sub> and pale brown to brown for vanadium doped TiO<sub>2</sub> corresponding with increasing the vanadium concentration. The structure of synthesized materials were studied by Powder of X-Ray Diffracton (XRD). The optical properties were characterized by UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS). For further information, the synthesized materials also compared with commercially anatase TiO<sub>2</sub> purchased from Sigma Aldrich, ≥99% purity (TiO<sub>2</sub> SA No.248576) without further purification.

## 3. Result and Discussion

XRD pattern in figure 1 shows that all synthesized materials have agreement with commercially anatase TiO<sub>2</sub> Sigma Aldrich (TiO<sub>2</sub> SA). Introducing vanadium (III) at 0.3 to 0.9% into TiO<sub>2</sub> lattice using sonochemical method resulted in the pure phase of anatase and does not induced the phase transformation from anatase into rutile or brukite. Further insight on XRD pattern at highest intensity peak shows that V<sup>3+</sup> doped TiO<sub>2</sub> shifted to lower value of 2θ compared to undoped TiO<sub>2</sub>. The shift of 2θ attributed to alteration of *d* spacing material caused by specific vanadium content. It was indicated that vanadium was doped in TiO<sub>2</sub> lattice.



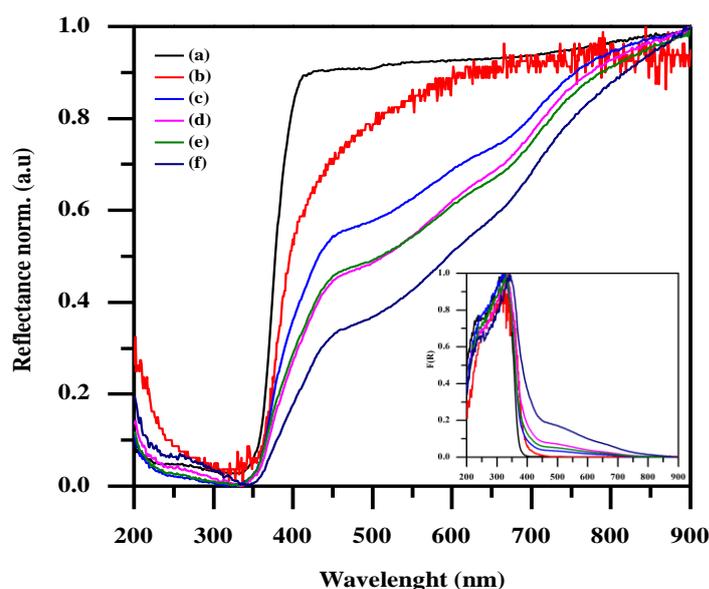
**Figure 1.** XRD Pattern for (a) TiO<sub>2</sub> SA (b) undoped TiO<sub>2</sub> and V<sup>3+</sup> doped TiO<sub>2</sub> at (c) 0.3% (d) 0.5% (e) 0.7% and (f) 0.9%.

Compared to commercially  $\text{TiO}_2$  SA, the XRD pattern of undoped and  $\text{V}^{3+}$  doped  $\text{TiO}_2$  have broadened peaks which indicated smaller particle size. Table 1 shows the average crystallite size were calculated by Scherrer's equation at the highest intensity peak (101 plane). Average crystallite size of undoped and doped  $\text{TiO}_2$  (0.3-0.7%) were smaller than  $\text{TiO}_2$  SA (53.19 nm) while 0.9% of  $\text{V}^{3+}$  was larger than  $\text{TiO}_2$  SA. Further XRD data analysis using Le Bail refinement method with anatase standart (JCPDS No. 21-1272) revealed that all materials crystallized in tetragonal lattice with  $I4_1amd$  space group and 4 asymmetric unit (Z). Unit cell parameter (a, c) and unit cell volume of  $\text{V}^{3+}$  doped  $\text{TiO}_2$  observed to decrease than undoped  $\text{TiO}_2$ . It can be affected by different size ion between  $\text{Ti}^{4+}$  and  $\text{V}^{3+}$ . Vanadium was known as multivalence ion with different ionic radii as different oxidation state. At six coordination number,  $\text{V}^{3+}$  (0.78Å) is larger than  $\text{Ti}^{4+}$  (0.74Å) while  $\text{V}^{4+}$  (0.72Å) and  $\text{V}^{5+}$  (0.68Å) is smaller ionic radii than  $\text{Ti}^{4+}$ [4]. Substitution  $\text{Ti}^{4+}$  ion with larger  $\text{V}^{3+}$  ion can result in increasing the unit cell and crystal volume. However, decreasing the unit cell and crystal volume in this research indicating that vanadium might be present at higher valence or mixed valence in  $\text{TiO}_2$  lattice. The larger decrease was obtained at 0.7% of Vanadium than another concentration.

**Table 1.** Unit Cell, Cell Volume and Average Crystallite size of undoped and doped  $\text{TiO}_2$ .

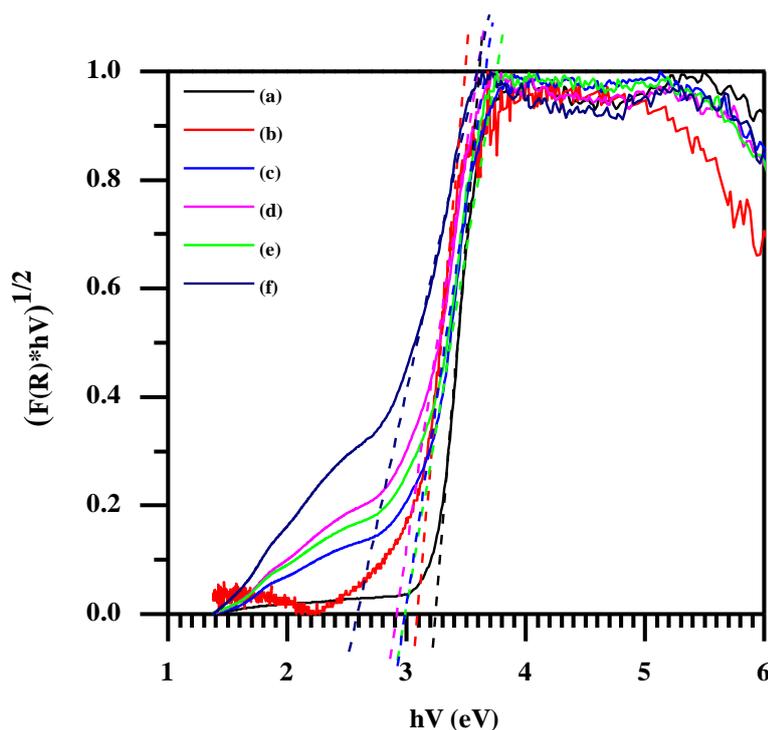
	Undoped $\text{TiO}_2$	$\text{TiO}_2$ -V 0.3%	$\text{TiO}_2$ -V 0.5%	$\text{TiO}_2$ -V 0.7%	$\text{TiO}_2$ -V 0.9%
<b>a,b (Å)</b>	3.803	3.786	3.792	3.784	3.786
<b>c (Å)</b>	9.559	9.515	9.526	9.509	9.514
<b>V (Å<sup>3</sup>)</b>	138.217	136.414	136.990	136.195	136.419
<b>Cryst. (nm)</b>	34.28	34.18	26.42	26.43	79.40

UV-Vis DRS data in figure 2 shows the reduced reflectance for all vanadium doped  $\text{TiO}_2$  materials compared to undoped  $\text{TiO}_2$  and commercial  $\text{TiO}_2$  SA at visible wavelength (400-800 nm). Reflectance tend to continuous decrease as increasing  $\text{V}^{3+}$  concentration and therefore the enhancement of absorption coefficient (F(R)) in inset figure was obtained. The reduced reflectance and enhanced absorption coefficient in visible wavelength indicated that vanadium doped  $\text{TiO}_2$  which synthesized by sonochemical method had potential to be applied under visible irradiation.



**Figure 2.** UV-Vis DRS data of (a)  $\text{TiO}_2$  SA (b) undoped  $\text{TiO}_2$  and  $\text{V}^{3+}$  doped  $\text{TiO}_2$  at (c) 0.3% (d) 0.5% (e) 0.7% and (f) 0.9%.

Determination of bandgap energy by Kubelka-Munk transformation shown in figure 3. The bandgap energy for TiO<sub>2</sub> SA, undoped TiO<sub>2</sub> and V doped TiO<sub>2</sub> 0.3%, 0.5%, 0.7% , 0.9% were respectively 3.25, 3.22, 3.05, 2.93, 3.03 and 2.40 eV. The energy tend to decrease as increasing vanadium content with the highest reduction achieved at 0.9% vanadium. 0.7% of V doped TiO<sub>2</sub> shows slightly alteration from the trend, respecting to the refinement result which showed the largest shrinkage in unit cell parameter. This evidence may contributed by the nature of vanadium state in TiO<sub>2</sub> lattice at 0.7%. Furthermore, substitution of Ti<sup>4+</sup> by vanadium at different oxidation states and different concentration may result in various spin states, oxigen vacancy, and reduction level of band gap energy as the effect of compensation method in substitutional [11] or interstitial doping.



**Figure 3.** Bandgap energy of (a) TiO<sub>2</sub> SA (b) undoped TiO<sub>2</sub> and V<sup>3+</sup> doped TiO<sub>2</sub> at (c) 0.3% (d) 0.5% (e) 0.7% and (f) 0.9%.

#### 4. Conclusion

Vanadium doped TiO<sub>2</sub> was successfully synthesized using sonochemical method. Photocatalyst materials crystallized in pure anatase structure with tetragonal lattice and *I41amd* space group. Lower shifted of  $2\theta$  and decreased unit cell parameter indicated that anatase structure distorted due to vanadium dopant. Vanadium doped TiO<sub>2</sub> shows decreased bandgap energy, lowered reflectance and enhanced absorption in visible light. As a result, it had potential photocatalytic activity under visible irradiation (400-800 nm)

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