



Research Article

Synthesis of Vanadium (III) Doped Anatase TiO₂ by Solid State Reaction Method

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Email: nuraini.kkfa@gmail.com**ABSTRACT**

Anatase of Titanium dioxide (TiO₂) was doped with vanadium ions (V³⁺), at doping levels ranging from 0.3, 0.5 to 0.7 atomic percentage in order to increase its photocatalytic activity under visible light irradiation. Vanadium doped TiO₂ was synthesized by solid state reaction method. Its physicochemical properties characterized by powder X-ray diffraction (XRD) and UV-Vis diffuse reflectance spectroscopy (DRS). Doping with V(III) resulted in a single phase structure of anatase TiO₂ with nanosize crystal ranging from 53.06 to 59.59 nm. Vanadium doping also resulted in a red-shift of the photophysical response of TiO₂ that was reflected in an extended absorption in the visible light between 400 and 700 nm.

Keywords: anatase, photocatalytic, vanadium, doped-semiconductor

1. Introduction

Anatase of TiO₂ (titania) has been widely used as photocatalyst due to its relatively low cost and high photocatalytic stability over water remediation and air purification. Titania has been reported as potential photocatalyst in several environmental interest such as degradation of various dyes, for example azo dye (Konstantinou & Albanis, 2004), Alizarin S, Methyl Red, Congo Red (Lachheb et al., 2002), and the degradation of Rhodamin-B (Aathi & Madras, 2007). Anatase TiO₂ is also developed as photocatalyst for solar-hydrogen production through water splitting process (Ni, Leung, Leung, & Sumathy, 2007) to support the future renewable energy. However, photocatalytic activity of anatase TiO₂ is only active under ultraviolet irradiation due to its wide band gap energy (3.0-3.2 eV). Modification of anatase TiO₂ is needed to enhance its activity under visible light irradiation.

Doping anatase with metal ion is one of strategies to enhance its activity under visible light irradiation (400-900 nm). Metal ion doping can reduce the band gap energy by new state energy level of dopant so it can be shifted the light

absorption to visible light. On the other hand, doping TiO₂ with transition metal ion also offers a way to trap charge carrier (electron and hole) during their transportation to the surface particle TiO₂. Hence, it can prevent the combination of electron-hole and enhance the efficiency of photocatalyst. The relative photocatalytic efficiency of a metal-ion dopant also depends on whether it serves as a mediator of interfacial charge transfer or as a recombination center (Choi, Park, & Hoffmann, 2010) on TiO₂ surface.

Choi et al. (2010) has been reported that incorporated 0.3% of vanadium dopant into anatase-TiO₂ lattice has induced a transformation anatase phase to rutile phase and showed higher enhancement in visible light absorption than other metal dopants such as Pt, Ni, and Cr. Thus, vanadium has potential enhancement to be studied extensively including the dopant ratio (atom percentage of vanadium) and synthesis method.

In this work, solid state reaction method was used to synthesis vanadium doped TiO₂ material. Solid state reaction method is a conventional route to synthesis a material at relatively high

temperature. However, this route has obvious advantages such as simple, high productivity, low contaminant, controllable stoichiometric reaction, no solvent needed and usually produce a high purity material with thermodynamically stable product.

2. Materials and methods

2.1. Materials

Anatase TiO₂ (Sigma Aldrich, ≥ 99% purity), V₂O₃ (Sigma Aldrich, 97%) were used as the starting materials.

2.2. Sample preparation

Vanadium (III) doped anatase TiO₂ particles were synthesized by solid state reaction method. 0.3, 0.5 and 0.7% of vanadium atom were added respectively into anatase TiO₂. Powder mixture subsequently grinded with agate mortar for 5 hours then continued with pressed into pellet and calcined at 500°C for 3 hours. Starting material of anatase TiO₂ was used as undoped anatase TiO₂ without further treatment.

2.3. Characterization of vanadium (III) doped anatase TiO₂

Powder X-ray diffraction (XRD) was used to examine the crystal structures of synthesized vanadium doped anatase-TiO₂ by using a Philips diffractometer (X'pert MPD) with Cu-Kα radiation. Collected data was refined using Le Bail Refinement method to get the information of structural data of doped material. Crystallite size of vanadium doped anatase-TiO₂ series were calculated by Debye Scerrer equation. Diffuse reflectance UV-Vis absorption spectra (DRS) of powder samples were obtained using UV-Vis spectrometer (Shimadzu UV-2101PC) equipped with a diffuse reflectance accessory. Band gap energy of materials was determined by Kubelka Munk transformation.

3. Result and discussion

X-ray diffraction pattern for doped TiO₂ (Fig. 1) showed diffraction peaks which are attributed to orientation plane of anatase phase. Those typical phase of anatase structure was confirmed by diffraction peak of miller indice (101), (103), (004), (112), (200), (005) and (211) according to undoped TiO₂. Undoped and doped TiO₂ with different vanadium level showed single phase of anatase

phase TiO₂. No detectable peaks related to secondary phase (such as rutile phase) or vanadium related peak (such as V₂O₃, V₂O₄ or V₂O₅). It was indicated that vanadium dopant up to 0.7% does not induce the formation of impurity phase and the phase transformation from anatase to rutile phase at reaction condition applied. It also indicated that vanadium ion (V³⁺) can be doped into TiO₂ lattice.

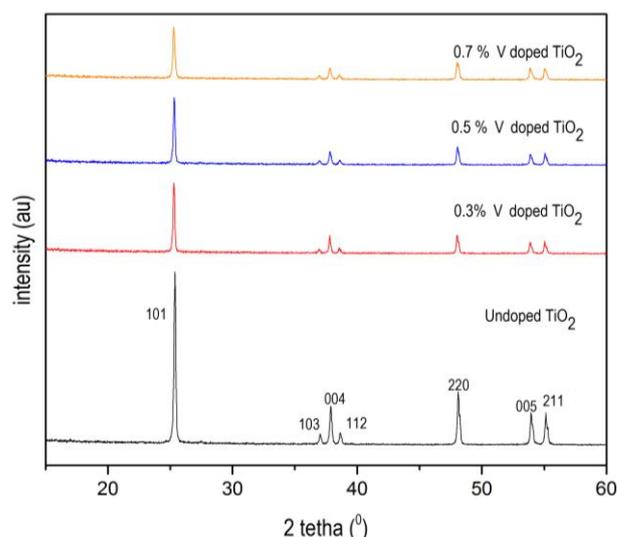


Fig. 1. Powder X-Ray Diffraction Data of Undoped TiO₂ and Vanadium Doped TiO₂ at 0.3%, 0.5% and 0.7% level of dopant

Vanadium dopant is possibly occupied in the octahedral interstitial site or substitutional position of Ti⁴⁺ ion in TiO₂ lattice. Vanadium (III) have small differences ionic radii (Coordination Number 6, *r* V³⁺ 0.64 Å) comparable to ionic radii of Ti⁴⁺ (Coordination Number 6, Ti⁴⁺ 0.61 Å) (Shiver & Atkins, 2006). So, it is energetically favorable for vanadium (III) to occupy the Ti⁴⁺ site in tetragonal lattice system. No dopant related phase observed in X-ray diffraction pattern also indicated that vanadium ion was in the substitutional position of TiO₂.

Refinement to XRD data used Le Bail Refinement method, resulted in refined spectra in Fig. 2 for 0.3% vanadium dopant. The crystallographic parameters obtained were showed in Table.1 for all various dopant concentrations. All vanadium doped TiO₂ sample crystallized in tetragonal system with space group of *I4₁amd*.

The vanadium dopant might distort the crystal lattice of anatase TiO₂ due to the different size of metal ion. Slightly distortion was observed for lattice parameter of *a*, *b*, *c* and unit cell volume due

to increase the dopant level. It was indicated that crystal lattice affected by different size of vanadium ion which incorporated into TiO₂ lattice. Another alternation was also observed at diffraction peak of (101) plane which shifted toward lower diffraction angle (2θ) at various dopant level (Table 2).

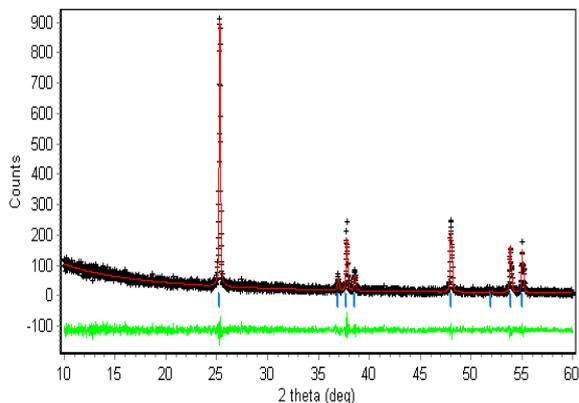


Fig 2. 0.3% vanadium doped TiO₂ refined by Le Bail Refinement methods.

Table 1. Unit Cell Parameter of Vanadium (III) Doped TiO₂ refined by Le Bail Refinement Method

Parameter	0.3% V doped TiO ₂	0.5% V doped TiO ₂	0.7% V doped TiO ₂
Space Group	I4 ₁ /amd	I4 ₁ /amd	I4 ₁ /amd
Crystal Lattice	Tetragonal	Tetragonal	Tetragonal
Asymmetric Unit (Z)	4	4	4
a, b (Å)	3.782	3.785	3.791
c (Å)	9.504	9.512	9.526
α, β, γ	90.00°	90.00°	90.00°
Unit Cell Volume (Å ³)	135.983	136.281	136.887
Rp (%)	13.50	13.71	15.41
Rwp (%)	18.55	18.83	20.30
GoF (χ^2)	1.297	1.318	1.504

Based on Full Width at Half Maxima (FWHM) of XRD pattern at 2θ shown predominance of relative intensity (Table 2), the average of crystal diameter was calculated by the Debye Scerrer's Formula. Vanadium doped TiO₂ had crystal size around 53.06 to 59.59 nm. There was no linearity effect on the crystal size related to vanadium level incorporated to TiO₂ lattice. The differences of crystallite size may induced by sintering temperature of solid state method. It can be seen through crystallite size of undoped TiO₂. This material was characterized without any further

treatment like sintering. The original phase of TiO₂ has crystallite size about 53.21 nm. When sintering process applied to doped material, the crystallite size increased to 59.59 nm for 0.3% dopant and 59.53 nm for 0.7% dopant. However the crystallite size of 0.5% doped material slightly unchanged comparing to undoped material. This varied crystallite size probably also contributed by unhomogenous of manual grinding in solid state method.

Table 2. Crystallite size of doped and undoped TiO₂ calculated by Debye Scerrer's Formula

Material	$2\theta(^{\circ})^*$	Crystallite Size (nm)
Undoped TiO ₂	25.388	53.21
0.3% V-TiO ₂	25.291	59.59
0.5% V-TiO ₂	25.341	53.06
0.7% V-TiO ₂	25.263	59.53

*Calculated from (101) orientation plane of anatase

Fig.3 showed all the UV-Vis Diffuse Reflectance Spectra for undoped and doped TiO₂. Based on Fig.3, all material showed relatively closed reflectance in ultraviolet region but different in visible regions. Undoped TiO₂ has the highest reflectance (lowest absorbance) in visible spectrum. In other hand, the vanadium doped samples showed lowered reflectance in visible region. It was indicated that incorporating vanadium dopant resulted in increasing absorption over the visible range (400-700 nm) whereas 0.7% vanadium showed the highest enhancement.

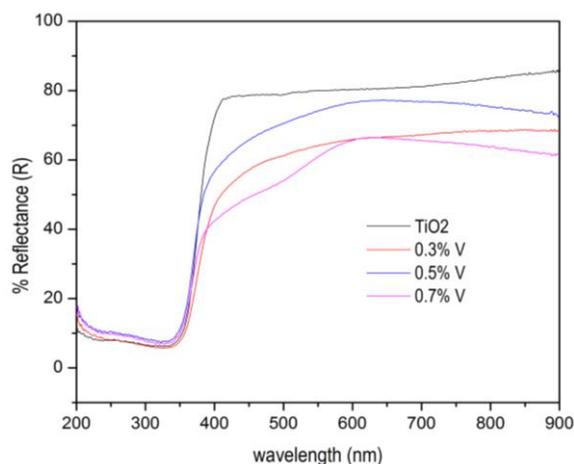


Fig. 3. The UV-Vis Diffuse Reflectance Spectra for undoped TiO₂ and vanadium doped TiO₂ at 0.3, 0.5 and 0.7% of dopant levels.

Enhancement in visible light absorption may respective to new state energy level of vanadium dopant incorporated into anatase lattice. On the other suggestion, introducing a lower charge dopant (V^{3+}) as substituent for Ti^{4+} will generating two ways of charge compensation mechanism which may induce absorption in visible region. First possibility, the defect associated with oxygen vacancies might be created in order to maintain the neutral charge. Another possibility, V^{3+} can be oxidized into higher oxidation state, such as V^{4+} and V^{5+} . Zhang, Shao, Zhang, Li & Liu (2010) has been reported the existence of V^{4+} and V^{5+} ions in nanofiber vanadium doped TiO_2 revealed by X-Ray Photoelectron Spectroscopy (XPS). It was confirmed that charge compensation might be one of the reason that contribute for extended absorption of vanadium doped TiO_2 in visible region.

Band gap energy of undoped and doped TiO_2 was determined by plotting photon energy ($h\nu$) versus $(K-M.h\nu)^{1/2}$. K-M is kubelka-Munk transformation which determined from UV-Vis diffuse reflectance data. Band gap energy obtained at $h\nu_0$ (threshold frequency) value for doped and undoped TiO_2 (Fig.4). Band gap energy for undoped TiO_2 was 3.307 eV. Vanadium doped TiO_2 at 0.3, 0.5 and 0.7% vanadium level, respectively resulted in 3.158, 3.208 and 3.184 eV.

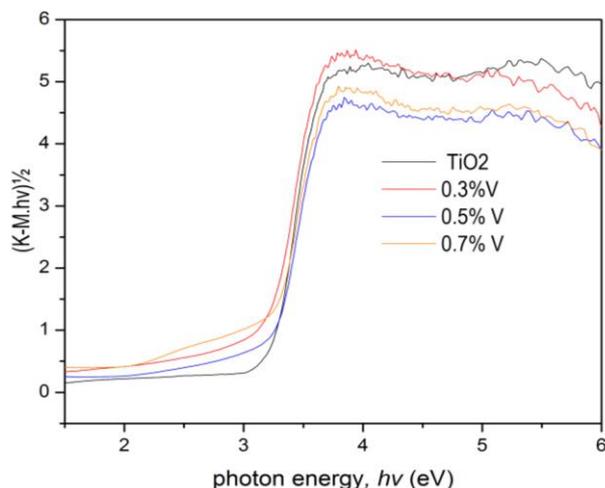


Fig. 4. Plotting $h\nu$ Versus $(K-M.h\nu)^{1/2}$ from The UV-Vis Diffuse Reflectance Spectra for undoped TiO_2 and vanadium level doped TiO_2 at 0.3, 0.5 and 0.7% of dopant level.

Among those dopant level, 0.3 and 0.7% dopant, have lower band gap energy than 0.5% vanadium level. Agreement to this result was confirmed by Fig. 3 that showed 0.3 and 0.7% have

higher lowering reflectance in visible region than 0.5% vanadium. It was indicated the alternation of visible light absorption related with specific vanadium concentration. However, in general, all band gap energy value decreased with vanadium dopant incorporated into TiO_2 . It was indicated that generation of hole and electron will be raised by introducing vanadium dopant. It could be expected that photocatalytic activity will be raised respective to raising generation of electron and hole as reducing and oxidizing agent.

4. Conclusion

Crystalline and single phase of vanadium doped anatase TiO_2 was successfully synthesized by solid state reaction method. Vanadium dopant incorporated into TiO_2 lattice induce a distortion in crystal lattice of anatase phase and shifting peak of (101) plane. Photocatalytic activity in visible region could be expected from vanadium doped TiO_2 due to its extended absorption in visible region than undoped TiO_2 . Further research in photocatalytic activity of those materials should be determined to study the mechanism of photocatalytic degradation.

5. Acknowledgement

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6. References

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