Preparation and Characterization of XRD Nano Cu-TiO₂ using Sol-Gel Method

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Abstract. One of the reported doping agent to increase TiO₂ activity is Cu. In this research, TiO₂ was prepared by So-Gel method. Preparation was performed by calcination at the temperature range of 400, 500, 600°C for 2 hours with a corresponding dopant concentration of 0%, 1%, 3%, 5% mol of TiO₂. The nanoparticle materials was characterized using XRD. It is found that anatase phase occur in the calcinations temperature of 400°C and transform to rutile phase at 500°C. The crystallite size of Cu-doped TiO₂ with dopant concentration of 5% are found 4.63 nm, 8.70 nm, 6.09 nm respectively at 400°C, 500°C, 600°C.

1. Introduction

Modification of semiconductor structures is a potential research, especially in the field of photocatalysts[1-3]. One of the prospective materials to study is Titania. Titanium dioxide is one of metal transition oxide which has three main crystal structures, those are; rutile, brookite, and anatase with band gap range between 3.0 – 3.2 eV[4]. Rutile phase is the most stable form of TiO₂. Rutile formed at high temperature and pressure. Anatase and brookite reported can be transformed into rutile phase at particle size above 14 nm. The photocatalytic activity of rutile phase is lower than anatase phase owing to the crystallite structure[5]. TiO₂ brookite has orthorhombic crystal structure with the lowest density and rarely applied as semiconductor. Another metastable phase of TiO₂ is anatase. Anatase has tetragonal crystal structure and can transform to rutile phase under certain annealed temperature and preparation condition. Anatase perform good optical properties and widely used as semiconductor and photocatalyst [6].

Titanium dioxide (TiO₂) is one of the most popular photocatalyst that has been devoted to the preparation of many industrial products such as white pigment in paint manufacture, cosmetics as well as semiconductor material [7]. Modification of TiO₂ has been one of the important task due to its various application. Pristine TiO₂ is naturally active under UV radiation. It is important to modify and optimize TiO₂ photocatalytic activity, thus can be applied under visible light radiation. Many methods have been widely explored in order to improve photoefficiency of TiO₂[8]. One of the well-known method to improve TiO₂ photoefficiency is using doping agent to decrease band gap. TiO₂ doping with the transition metal doping act as trapping charges carriers and interceding in the interfacial transfer[9]. The various applications of semiconductor has been reported for energy conversion, include photo-splitting water[10], transformation of humic acid[1,11] and Indoor lights photovoltaic[2,12-14]. In the future, in the absorption of heavy metal waste, so far the adsorption system is often used such as the use of algae[15] and various organic agents[16], then the photocatalyst system allows for the reduction of heavy metals through load transfer reactions by placing heavy metals as scavenger.

In this research, copper (Cu) act as the doping agent and reported increase the photocatalytic activity of the TiO₂. Cu²⁺ ionic radius (0.68 Å) is close to Ti⁴⁺ radius (0.74 Å) therefore, the dispersion of Cu²⁺ in TiO₂ lattice is naturally happen by substitute the Ti⁴⁺ [17]. This situation contributes to modify

the electronic density of states inside the band gap of pristine structure. This recent work would focused on the physical properties of the crystallite structure and it's alteration as the function of calcinations temperature in Cu-doped TiO₂ because it is strongly affect to the photocatalytic activity of semiconductor [18].

2. Experimental Section

2.1. Preparation of Cu-doped TiO₂

Cu-doped TiO₂ was prepared by sol-gel method using Titanium tetraisopropoxide as the precursor (8,4 mL TTIP) in 10 mL isopropanol. The solution was stirred at room temperature for 30 minutes with 300 rpm. Forced hydrolysis of TTIP solution was achieved by adding solution consist of 8 mL isopropanol, 1 mL bidistilled water and 1 mL HNO₃ p.a. The solution was kept under room temperature and was stirring for 2 hours until viscous and homogenous solution was obtained. This sol-gel process occur under acidic condition by adding amount HNO₃ p.a. HNO₃ p.a also act as the acid catalyst to enhance the hydrolysis and condensation rate. In this paper, Cu doped were obtaining by dissolving corresponding amount of Cu precursor; CuCl₂.2H₂O in 2 mL isopropanol and was added to the TTIP + isopropanol solution. The concentration of dopan were obtained to be 0%, 1%, 3%, 5% mol. The Cu-doped TiO₂ gel was calcinated in temperature range between 400°C, 500°C, 600°C for 2 hours and then characterized using XRD.

2.2. Characterization

Sample of Cu-doped TiO₂ with different calcination temperatures were characterized using X-Ray Diffraction (XRD), Siemens D-501 diffractometer, Ni filter and graphite monochromator. The X-Ray source came from Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with scanning angle between 10° and 100°. The XRD patterns were recorded at room temperature.

XRD is performed to determine the nature of TiO₂ crystallinity. XRD widely used to characterize crystalline material because of it's non destructive method. XRD gives information about structure, phase, texture, crystallinity and crystallite size of the compound. Crystallite size of material was calculated using Scherrer equation [19].

$$d = \frac{k \lambda}{\beta \cos \theta}$$

Where d is crystallite size, λ is the wave length of X-ray radiation, β is full width of half maximum and θ is the diffraction angle [20].

3. Results and Discussion

The diffraction pattern of Cu-doped TiO₂ with concentration of 5% in various temperature shown in Figure 1. Cu-doped TiO₂ with calcination temperature of 400°C (A) shows peak of anatase phase (101) (004) (200) (105) at 2θ values 25.35°, 38.11°, 48.12°, 54.77° and match index data of JCPDS 00-001-0562[21]. Anatase is the metastable phase of TiO₂ and usually formed at low temperature. The diffraction pattern of Cu-doped TiO₂ with concentration of 5% at 500°C (B), shows rutile phase (110) (101) (111) (211) at 2θ values 27.4°, 36°, 41.1, 54.34° (JCPDS 01-078-4189). Diffraction pattern of Cu-doped TiO₂ with concentration of 5% at 600°C shows similar trend to B, but the intensity of peaks in the C pattern is higher than B. At calcination temperature of 500°C and 600°C, no diffraction peaks belonging to anatase phase was observed. It can be assume that anatase phase of TiO₂ completely transform to rutile phase at 500°C.

The crystallite size of Cu-doped TiO₂ with dopan concentration of 5% are found 4.63 nm, 8.70 nm, 6.09 nm respectively at 400°C, 500°C, 600°C. According to the starting precursor; CuCl₂.2H₂O, Cu²⁺ should be formed in the solution. By comparing the ionic radius of Cu²⁺ (86 nm) and Ti⁴⁺ (74.5 nm), it is clear that a possible substitution of a small amount of Ti⁴⁺ by Cu²⁺ would be accompanied by a weak lattice expansion, due o the relatively small difference between their respective ionic radius, so that the Cu²⁺ can be dissolve into TiO₂. In the higher concentration f Cu dopan, the CuO can be obtained, but in the XRD data there is no peak belonging to Cu species are observed. It is believes that Cu species

might exist in very small quantity and well dispersed in TiO_2 crystallite; bellow the detection limit of XRD method .

Figure 1. XRD pattern of Cu-doped TiO_2 at calcination temperature of 400°C (a), 500°C (b), 600°C (c)

The higher intensity diffraction peak of rutile phase in Figure 1. c) indicate the enhancement of structural quality or gain of TiO_2 crystallinity.

4. Conclusion

Cu-doped TiO_2 was successfully prepared by sol-gel method with different calcinations temperature and was characterized with XRD. It is found that anatase phase occur in the calcinations temperature of 400°C and transform to rutile phase at 500°C. It also considerably found that alteration of crystallite phase of Cu-doped TiO_2 affected by the temperature and doping concentration.

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6. References

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