Preparation and characterization of XRD nano Cu-TiO$_2$ using sol-gel method

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Abstract. One of the reported doping agent to increase TiO$_2$ activity is Cu. In this research, TiO$_2$ was prepared by So-Gel method. Preparation was performed by calcination at the temperature range of 400, 500, 600$^\circ$C for 2 hours with a corresponding dopant concentration of 0%, 1%, 3%, 5% mol of TiO$_2$. The nanoparticle materials was characterized using XRD. It is found that anatase phase occur in the calcinations temperature of 400$^\circ$C and transform to rutile phase at 500$^\circ$C. The crystallite size of Cu-doped TiO$_2$ with dopant concentration of 5% are found 4.63 nm, 8.70 nm, 6.09 nm respectively at 400$^\circ$C, 500$^\circ$C, 600$^\circ$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, brokite, and anatase with band gap range between 3.0 – 3.2 eV[4]. Rutile phase is the most stable form of TiO$_2$. 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]. TiO$_2$ brookite has orthorhombic crystal structure with the lowest density and rarely applied as semiconductor. Another metastable phase of TiO$_2$ 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 (TiO$_2$) 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 TiO$_2$ has been one of the important task due to it’s various application. Pristine TiO$_2$ is naturally active under UV radiation. It is important to modify and optimize TiO$_2$ photocatalytic activity, thus can be applied under invisible light radiation. Many methods have been widely explored in order to improve photoefficiency of TiO$_2$[8]. One of the well-known method to improve TiO$_2$ photoefficiency is using doping agent to decrease band gap. TiO$_2$ doping with the transition metal doping act as trapping chargers carriers and interceding in the interfacial transfer[9]. The various applications of semiconductor has been reported for energy conversion, include photosplitting 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 scavanger.

In this research, copper (Cu) act as the doping agent and reported increase the photocatalytic activity of the TiO\(_2\). Cu\(^{2+}\) ionic radius (0.68 Å) is close to Ti\(^{4+}\) radius (0.74 Å) therefore, the dispersion of Cu\(^{2+}\) in TiO\(_2\) lattice is naturally happen by substitute the Ti\(^{4+}\) [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 TiO\(_2\) because it is strongly affect to the photocatalytic activity of semiconductor [18].

2. Experimental Section

2.1. Preparation of Cu-doped TiO\(_2\)

Cu-doped TiO\(_2\) 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 bidistillated water and 1 mL HNO\(_3\) 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 HNO\(_3\) p.a. HNO\(_3\) 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; CuCl\(_2\).2H\(_2\)O 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 TiO\(_2\) 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 TiO\(_2\) 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\(\alpha\) radiation (\(\lambda=1.5406\) Å) with scanning angle between 10° and 100°. The XRD patterns were recorded at room temperature.

XRD is performed to determine the nature of TiO\(_2\) 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].

\[
d = \frac{k\lambda}{\beta\cos\theta}
\]

(1)

Where \(d\) is crystallite size, \(\lambda\) is the wave length of X-ray radiation, \(\beta\) is full width of half maximum and \(\theta\) is the diffraction angle [20].

3. Results and Discussion

The diffraction pattern of Cu-doped TiO\(_2\) with concentration of 5% in various temperature shown in Figure 1. Cu-doped TiO\(_2\) with calcination temperature of 400°C (A) shows peak of anatase phase (101) (004) (200) (105) at 20 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 TiO\(_2\) and usually formed at low temperature. The diffraction pattern of Cu-doped TiO\(_2\) with concentration of 5% at 500°C (B), shows rutile phase (110), (111) (211) at 20 values 27.4°, 36°, 41.1, 54.34° (JCPDS 01-078-4189). Diffraction pattern of Cu-doped TiO\(_2\) 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 TiO\(_2\) completely transform to rutile phase at 500°C.
The crystallite size of Cu-doped TiO\textsubscript{2} with dopant concentration of 5\% are found 4.63 nm, 8.70 nm, 6.09 nm respectively at 400\degree C, 500\degree C, 600\degree C. According to the starting precursor; CuCl\textsubscript{2}.2H\textsubscript{2}O, Cu\textsuperscript{2+} should be formed in the solution. By comparing the ionic radius of Cu\textsuperscript{2+} (86 nm) and Ti\textsuperscript{4+} (74.5 nm), it is clear that a possible substitution of a small amount of Ti\textsuperscript{4+} by Cu\textsuperscript{2+} would be accompanied by a weak lattice expansion, due to the relatively small difference between their respective ionic radius, so that the Cu\textsuperscript{2+} can be dissolve into TiO\textsubscript{2}. In the higher concentration of Cu dopant, the CuO can be obtained, but in the XRD data there is no peak belonging to Cu species are observed. It is believed that Cu species might exist in very small quantity and well dispersed in TiO\textsubscript{2} crystallite; below 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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