Morphological evolution of sol-gel synthesized Ag-TiO$_2$ nanocomposite

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Abstract. Addition of silver to titanium dioxide particles are known to increase its photocatalytic activity. Despite the numerous researches that has studied the mechanism of photocatalytic activity of Ag-TiO$_2$ nanocomposite, there are only a few papers that discuss the formation mechanism of this material. In this research, Ag-TiO$_2$ nanocomposite was successfully synthesized through sol-gel method. The morphology of nanocomposite was determined through the synthesis procedure and calcination temperature. Characterization results showed that at the solution phase, crystallization was slowed down by the presence of acid. However, after the drying process, rapid increase in titanium dioxide crystallization rate was observed due to the presence of silver particles. As a result, a transition from anatase to rutile was observed at a lower temperature.

1. Introduction

Due to its exceptional photocatalytic capabilities, titanium dioxide has been a research interest for more than two decades [1, 2]. It has been commonly used in the dye-sensitized solar cell (DSSC), water treatment technology and even anti-bacterial uses. [3-7] However, titanium dioxide has a quite large bandgap of 3.2 eV that hinders its capabilities as a photocatalyst [8]. Fortunately, several researches have shown that through introduction noble metals to the material, it is possible to reduce the bandgap and increase its properties [8-11]. Among the noble metals used to improve titanium dioxide, silver is one of the mostly used. Addition of silver reduces the material bandgap into 2.8eV and enhances its photocatalytic activity. Moreover, the reaction between silver and titanium dioxide under irradiation at a specific wavelength works as a potent anti-bacterial agent [12].

Over the decade, lots of research has been done to improve the capability of silver-titanium dioxide composite. One of the most commonly used is to reduce the materials crystalline size into nanometer scale [8, 12, 13]. However, aside from the crystallite size, the morphology of the composite plays an essential part to its photocatalytic activity [14, 15]. To the best of author’s knowledge, there have been only a few studies conducted to investigate the structure of Ag-TiO$_2$ nanocomposites. Therefore, this paper was done to investigate the morphological evolution of Ag-TiO$_2$ nanocomposite.

This paper will focus on the morphology of silver-titanium dioxide nanocomposite synthesized through the sol-gel method. Sol-gel synthesis is one of the most commonly used methods due to produce nano-sized metallic oxide due to its cost-effectiveness and natural controllability environment [8, 16].
2. Experimental Methods

2.1. Materials
Titanium tetraisopropoxide (TTIP, Sigma-Aldrich, 97%) used as a base material for the synthesis of titanium dioxide powder. The solvent used for the sol-gel synthesis is a mixture of ethanol (96%) and distilled water. Silver nitrate solution (Merck, Titripur 0.1M) will be used as a source for the silver particles, and Nitric Acid (Merck, 65%) will be used to control pH level.

2.2. Materials synthesis
The synthesis of silver-doped titanium dioxide through sol-gel method started with synthesizing the precursor. TTIP was added drop-wise to a mixture of water and ethanol while being stirred with a magnetic stirrer; then the mixture was kept under constant stirring for 45 minutes. The mixture has a mole ratio of 4:14:82 for TTIP, distilled water and ethanol respectively. The hydrolyzation ratio is determined by reference to a synthesis procedure of silver-doped titanium dioxide using a mixture of ethanol and water as precursor [5, 16]. Silver nitrate was added drop-wise to the mixture kept being stirred. The acidity level was set to 2 with the help of nitric acid. Next, the mixture was kept under constant stirring for 12 hours and finally aged to form the gel for 15 hours under atmospheric condition. Then, the gel was washed with a mixture of solution distilled water and ethanol (1:1 volumetric ratio). After the filtration process, the gel was dried at 60°C for 5 hours. Finally, the dried powder was calcined to the designated temperature with a heating rate of 5 °C/minute and kept at holding temperature for two hours. Figure 1 shows the schematic of the Ag-TiO₂ nanocomposite synthesis procedure.

2.3. Characterization method
The morphology of powder that has been synthesized will be observed with JEOL FIB 4610-F FESEM after the drying and calcination process. Phase analysis of the powder will be done with Rigaku X-ray diffraction instrument in 2θ range of 20°-85° and crystallinity of the powder will be calculated through Scherrer’s equation. Also, a TEM observation will be done to characterize the morphology of Ag-TiO₂ nanocomposite.

3. Results and Discussion

3.1. Materials synthesis
Hydrolysis reaction occurred when titanium isopropoxide was added into the mixture of distilled water and ethanol, followed by condensation and precipitation that forms the TiO₂ particles according to the simplified equation (1) [16-18].

![Figure 1. Schematic of material synthesis and characterization procedure](image-url)
\[ Ti(OR)_{n} + \frac{n}{2} H_2O \rightarrow TiO \frac{n}{2} + \frac{n}{2} ROH \]  

This process depends significantly on the ratio of water and titanium alkoxides used. An excess of water to titanium alkoxides ratio would cause the reaction to go faster and cause agglomeration of the precipitates [17]. Therefore, to promote the formation of the nano-sized composite by reducing the hydrolyzation ratio a mixture of water and ethanol was used in this research.

After the aging process, the gel was found to exhibit a change in color from white into dark brown color, which proves that silver particles were formed through a reduction of silver nitrate [12, 20]. The final product of the synthesis procedure is a brown colored powder which will change color into grey under UV irradiation. The color change phenomenon was caused by the reduction of silver particles with the help of titanium dioxide [2].

3.2. Phase and Crystallite size analysis

From the XRD analysis result in figure 2, it can be observed that amorphous titanium dioxide was present before the calcination process. The amorphous phase was formed as a result of rapid hydrolysis process of titanium alkoxides [20]. After the 500 °C calcination process, amorphous titanium dioxide formed anatase phase which has the best photocatalytic activity among the other titanium dioxide phases [14, 21]. Due to the presence of silver, crystallization of titanium oxide will occur at a lower temperature. Therefore, at 500 °C brookite crystal peak are less observable [16, 19]. However, no amount of silver peak was detected in the XRD result because of the overlapping of silver with anatase peak.

After calcination to 650°C it is found that there is an absence in the anatase phase and a significant amount of rutile phase. It is opposed to what commonly observed that anatase to rutile transition has only started between 650°C - 700°C, which means that a phase of anatase should still be in present. The lack of anatase phase at 650°C proves that the presence of silver did enhance the crystallization rate of titanium dioxide [10, 12, 17, 20]. At the 800°C calcination temperature, the increase in rutile peak intensity means that further crystallization occurs. Which is in accordance with the morphology images in figures 4 (a) – (d).

Through Scherrer's equation calculation, it can be found that there is an exponential growth of titanium dioxide crystallite size as shown in figure 3. At 500°C calcination temperature, the size of crystallite is observed to be around 10.95nm which is similar to what can be observed in HRTEM images in figure 5 (b). The crystallite sizes in titanium dioxide at 650 °C and 800 °C calcination temperature are 70.55 nm and 81.75 nm respectively. The rapid increase of crystallite size at 650°C was caused by the transition of anatase to rutile phase [19, 20, 24].

3.3. Morphological observation

The evolution of synthesized Ag-TiO₂ nanocomposite morphology can be observed in figure 4. The nanocomposite powder started as amorphous spherical structure of 137 μm size that forms an irregularly shaped aggregate. These unique shapes were formed due to the addition of H⁺ ion to the sol when titanium alkoxides undergo hydrolysis. The addition of silver nitrate caused the pH level to decrease, which means an increased presence of H⁺ ion. The positive ion promotes the breakdown of particles to a smaller size and prevents early crystallization, where it will interact with each other to form an amorphous aggregate [20, 24]. However, after the drying process, the lack presence of H⁺ was replaced by the presence of silver, which will promote the crystallization of titanium dioxide as stated before.

During the calcination process to 500°C, crystallization of the amorphous aggregate occurred and resulted in rougher shaped particle aggregate with silver particles of 9.5nm size on its surfaces. The rough feature comes from the formation of anatase from the amorphous shape [24]. Figure 4 (e) shows a magnification of anatase phase titanium dioxide with silver particle on top of its surfaces (white colored). TEM images on figure 5 (a) also depict the structure of anatase with silver particles (black colored) distributed on top of its surfaces.

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Figure 2. XRD characterization of (a) uncalcined, (b) 500°C, (c) 650°C, and (d) 800°C calcined Ag-TiO$_2$ nanocomposite.

Figure 3. Crystallite size of titanium dioxide at different temperatures

HRTEM result on figure 5 (b) shows a magnification on Ag-TiO$_2$ particle surfaces. The detailed image on the lattice fringe shows that the particle has excellent crystallinity. Dark spot on the surfaces was observed as silver particle with the $d$ spacing of 0.11 nm corresponds with the XRD result of Ag (222) plane, while the light-colored surface is proven to be titanium dioxide with $d$ spacing of 0.35 nm that is in accordance to anatase (101) plane [21, 24-25].

The polycrystalline surface of the particle on the HRTEM images are indicated through the SAED pattern in figure 5 (c). However, most of the ring pattern observed through the pattern shows the plane of Anatase phase. Silver pattern is not observable through the pattern, due to the overlapping with anatase phase.

Calcination process beyond 650°C causes the transition of anatase to rutile phase. The transition creates a significant change in crystallite shape, where rutile materials are more densely packed. Which means several anatase particles will form an interaction on the edge to form denser and massive structure [25]. Further calcination to the 800°C continues the rapid agglomeration of rutile structure as shown in figure 4 (d). Postulated Ag-TiO$_2$ nanocomposite morphological evolution process in this research could be observed in figure 6.
Figure 5. (a) TEM images, (b) HRTEM and (c) SAED pattern of Ag-TiO₂ nanocomposite calcined at 500°C

Figure 6. Postulated morphological evolution of Ag-TiO₂ nanocomposite

4. Conclusions
Silver-titanium dioxide nanocomposite has been successfully synthesized through the sol-gel method. The morphology of the nanocomposite was determined through the synthesis procedure and calcination process. While on the solution forms, crystallization of titanium dioxide was slowed down due to the presence of positive ion charge. However, after the drying process, the lack of H⁺ and the presence of silver particles instead promote the rapid crystallization of titanium dioxide. The rapid crystallization causes the anatase transitioned into rutile at 650°C.

At 500°C calcination temperature, the structure of anatase phase is observed through high-resolution SEM and TEM images. It is shown that titanium dioxide is formed through an agglomeration of smaller amorphous phases. Thus, creating a polycrystalline structure with silver particles located on its surfaces.

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References
[1] Lind J Effect of synthesis duration and HCl acid concentration on the formation of hydrothermally synthesized TiO₂ nanoparticles 2015 (CPUT: Cape Town)
[2] Chen X and Mao S S 2007 Chem. Rev. 107 2891
[3] Yang H G, Liu G and Liu G Q 2011 Synthetic Chemistry of Titanium Dioxide (The Chemistry of Nanostuctured Materials vol 2) ed Yang P (Berkeley: World Scientific Publishing) pp 281-
328.

[4] Chamber C et al 2017 Dental mater., 33 no 3 115
[5] Cozmuta A M et al 2014 Packag. Technol. Sci. 28 vol 4 271
[6] Jalali S A H, Allafchian A R, Banifatemi S S and Tamai I A 2016 J. of Taiwan Inst. of Chem. Eng. 000 1
[7] Khan S et al 2013 J. of Nanomaterials 2013 (ID: 531010)
[8] Harikishore M et al 2014 Proc. Mater. Sci. 6 557
[9] A. Padmanaban et al 2017 Mech. Mater. Sci. and Eng. J. 9 no 1 (DOI: 10.2412/mmse.97.67.748)
[10] Seery M K, George R, Floris P and Pillai S C 2007 J. of Photochem. and Photobiology 189 258
[11] Bahadur J et al 2015 Mater. Foc. 4 134
[12] Zhang H and Chen G 2009 Environ. Sci. Technol. 43 no. 8 2905
[13] Niguissie G Y et al 2017 Int. J. of Photoenergy 2018 (ID: 5927485)
[14] K Hayashi et al 2011 Mat. Let. 65 3037
[15] Zhang H et al 2017 Chem. Select 2 3282
[16] Araoyinbo A O et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 343 012011
[17] Sayilkan F et al 2005 Turk. J. Chem. 29 697
[18] Wetchakun N et al 2012 Mat. Letters 82 195
[19] Hanaor D A et al 2012 Adv. in Appl. Ceram. 111 no 3 149
[20] Termnak S, Triampo W and Triampo D 2009 J. of Ceram. Processing Res. 10 no 4 491
[21] Dai S et al 2010 Nanoscale Res. Let. 5 1829
[22] Esfahani M N and Habibi M H 2008 Int. J. of Photoenergy 2008 (ID: 628713)
[23] A Ahmad et al 2007 J. Phys.: Conf. Ser. 61 11
[24] Gopal M, Chan W J M and Jonghe L C D 1997 J. of Mater. Sci. 32 6001
[25] Chowdhury I H, Ghosh S and Naskar M K 2016 Ceram. Int. 42 2488
[26] Rehan M, Lai X and Kale G M 2011 CrystEngComm 11 2011 (DOI: 10.1039/c0ce00781a)
[27] Klein S M and Choi J H 2003 J. Mater. Res. 18 6 1457