CHAPTER VII

HIERARCHICAL ARCHITECTURE OF $Bi_{12}TiO_{20}$ VIA ETHYLENE GLYCOL-MEDIATED SYNTHESIS ROUTE

7.1 Abstract

Hierarchical architecture of cubic sillenite bismuth titanate ($Bi_{12}TiO_{20}$) is successfully synthesized using simple ethylene glycol-mediated self-assembly; followed by calcination under air at 600 °C for 30 min. The products are characterized using field emission scanning electron microscopy (FE-SEM), fourier transform infrared spectroscopy (FT-IR), thermogravimetric-differential thermal analysis (TG-DTA), and X-ray diffraction (XRD). The reaction time has an effect on the product morphology, which changed from a leaf- and circular plate-like structure to a completely formed hierarchical structure within 2 h. The hierarchical structure of $Bi_{12}TiO_{20}$, having a size around 3 μm, is composed of 2D twist nanoplates, and each twist nanoplate has a thickness around 10–30 nm.

7.2 Introduction

In recent years, hierarchical structures have been extensively studied due to their unique properties. A number of three-dimensional architectures have been explored to expand potential applications in advanced nanotechnology.[1-3] For instance, flower-like bismuth oxide shows better ion conductivity than a rod-like structure,[4] while 3D iron oxide has a superior ability to remove heavy metal ions in water treatment[5]. The hierarchical architecture can be synthesized by various techniques, such as hydrothermal method[6], electrodeposition,[7] or addition of a foreign metal to mediate the nucleation.[8]

Ethylene glycol was widely used as a solvent to synthesize metal and metal alloy owing to its strong reducing agent and high boiling point.[9-10] This method involves heating metal salt ormetal oxide in ethylene glycol media to form 1D nanowire, 2D disk-shaped or 3D metal oxide.[11-12] Recently, Ma et al.[13] also obtained

hierarchical structure of bismuth oxide in ethylene glycol media via a microwave-assiste synthesis route.

Sillenite structure (I23 space group) of $Bi_{12}TiO_{20}$, one of bismuth titanium oxide phases composed of two structural units of BiO_5 polyhedra and TiO_4 tetrahedra, promises a number of uses in such applications as electro-optic devices, photovoltaic cells and photocatalysts.[14-16] In this work, we illustrate how to synthesize hierarchical architecture of $Bi_{12}TiO_{20}$ via a simple ethylene glycol-mediated route.

7.3 Experimental

7.3.1 Preparation of $Bi_{12}TiO_{20}$

Bismuth nitrate pentahydrate 3.08 g (≥98% purity, Fluka) was dissolved in 100 ml of ethylene glycol (99.9% purity, J.T.Baker) in a round-bottom flask. The stoichiometric amount of titanium butoxide (97% purity, Aldrich) was slowly dropped into the bismuth nitrate pentahydrate solution and stirred for 1 h. The mixture was heated under nitrogen atmosphere at 150 °C for 30 min, 1 h, and 2 h to precipitate out. The obtained powder, denoted as bismuth titanate precursor, was washed with acetronitrile three times and dried in a vacuum dessicator at room temperature for further calcination in a carbolite muffle at 600 °C for 30 min to achieve bismuth titanate.

7.3.2 Characterization

Fourier transform infrared spectroscopy was carried out on Bruker-EQUINOX55 instrument (FT-IR) using KBr pellets and a spectral resolution of 4 cm−1. Thermal-decomposition behavior of the powder before calcination was determined using Perkin Elmer-Pyris Diamond thermogravimetry-differential thermal analyzer (TG-DTA) anda heating rate of 10 °C/min at a temperature range of 30°–750 °C. Crystallinity of the samples was analyzed on a Rigaku-RINT-2200 X-ray diffractometer system (XRD) using CuKα radiation (1.5406 Å) at a generator voltage of 40 kV, and a generator current of 30 mA. Field emission scanning electron

microscope (FE-SEM, Hitachi-S4800) was carried out to determine morphology of samples.

7.4 Results and Discussion

FT-IR spectrum of the bismuth titanate precursor is shown in Figure 7.1a. The bismuth titanate precursor showed two strong absorption bands at 3376 and 2879 cm^{-1}, attributed to -OH stretching of H_2O and C-H stretching of $-CH_2$, respectively. The band at 1385 cm^{-1} was assigned to N-O stretching of free NO_3^-.[17-18] The peak at 1619 cm^{-1} was assigned to a bending of absorbed H_2O. Peaks at 1321, 1084–1042, and 882 cm^{-1} were referred to C-C-O stretching vibration of ethylene glycol whereas the position at 534 cm^{-1} was belonged to metal-O bond.[19-20] TG curve of bismuth titanate precursor in Figure 7.1b shows two steps of decomposition. The first step at 30–200 °C with around 2% weight loss was attributed to the removal of adsorbed water together with nitrogen-containing materials and un-reacted ethylene glycol[21], while the other, exhibiting a sharp weight loss of around 30% at 263 °C, was assigned to the decomposition of chelating ethylene glycol.[21] The crystallinity of bismuth titanate precursor and bismuth titanate is shown in Figure 7.1c. As can be seen, the precursor showed a strong peak at low angle (around 11 2theta degree), assigning to the coordination of ethylene glycol with the metal ion. This characteristic is a typical feature of metal alkoxides from the polyol-mediated process.[10,11,19,22] After calcining the precursor at 600 °C for 30 min, the bismuth titanate precursor was transformed to a cubic sillenite structure, as confirmed by the obtained XRD result matched with the sillenite phase of $Bi_{12}TiO_{20}$, as recorded in the JCPDS 34-0097.

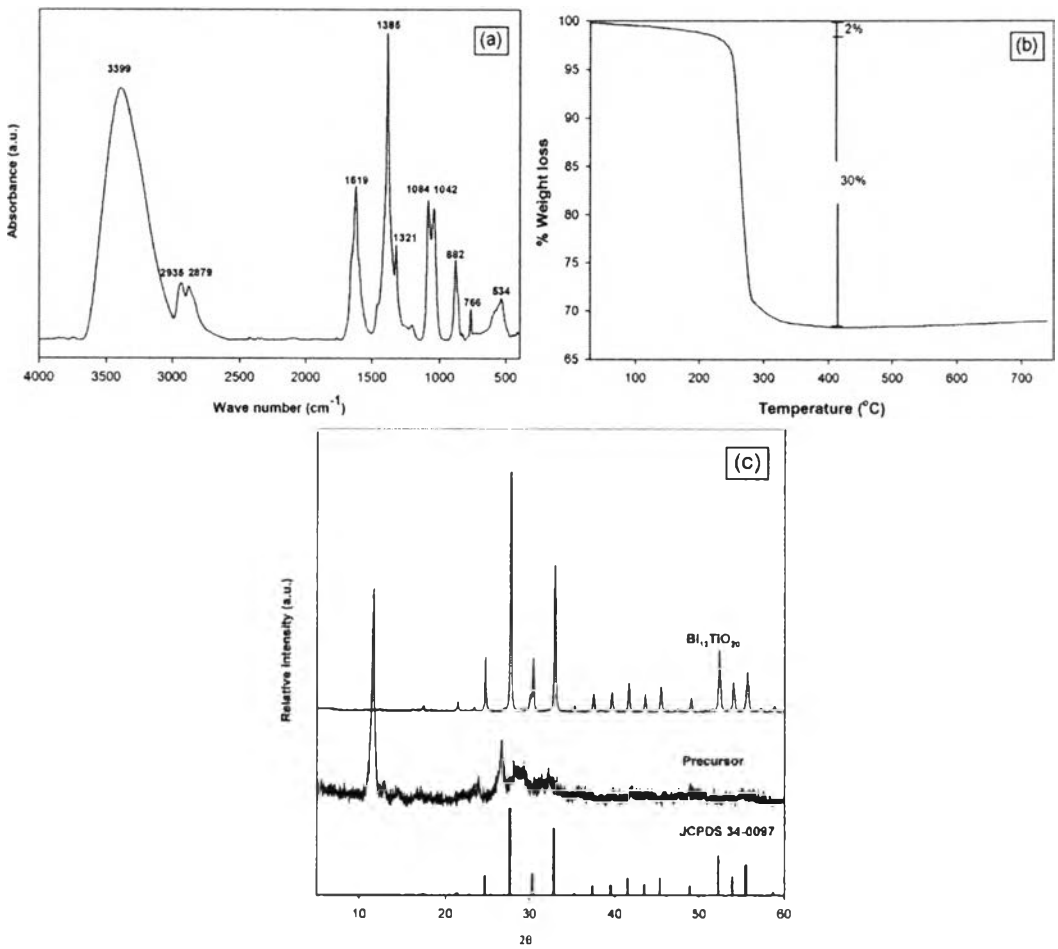

Figure 7.1 a) FT-IR spectrum and b) TG curve of the bismuth titanate precursor, c) XRD patterns of the bismuth titanate precursor and $Bi_{12}TiO_{20}$ product, comparing to JCPDS database.

The morphology of the bismuth titanate precursor is shown in Figure 7.2. Figure 7.2a shows uniform hierarchical structures while Figure 7.2b illustrates an individual hierarchical structure, composed of twist nanosheets with a diameter of approximately 3 μm hierarchical structures. The detail of each nanosheet was observed using a higher magnification in Figure 7.2c. It can be seen that the twist nanosheets have thicknesses around 10–30 nm. Figure 7.2d, illustrating the architecture of the sphere, indicates that the nanosheets joined to form a hierarchitecture through self-assembly process.

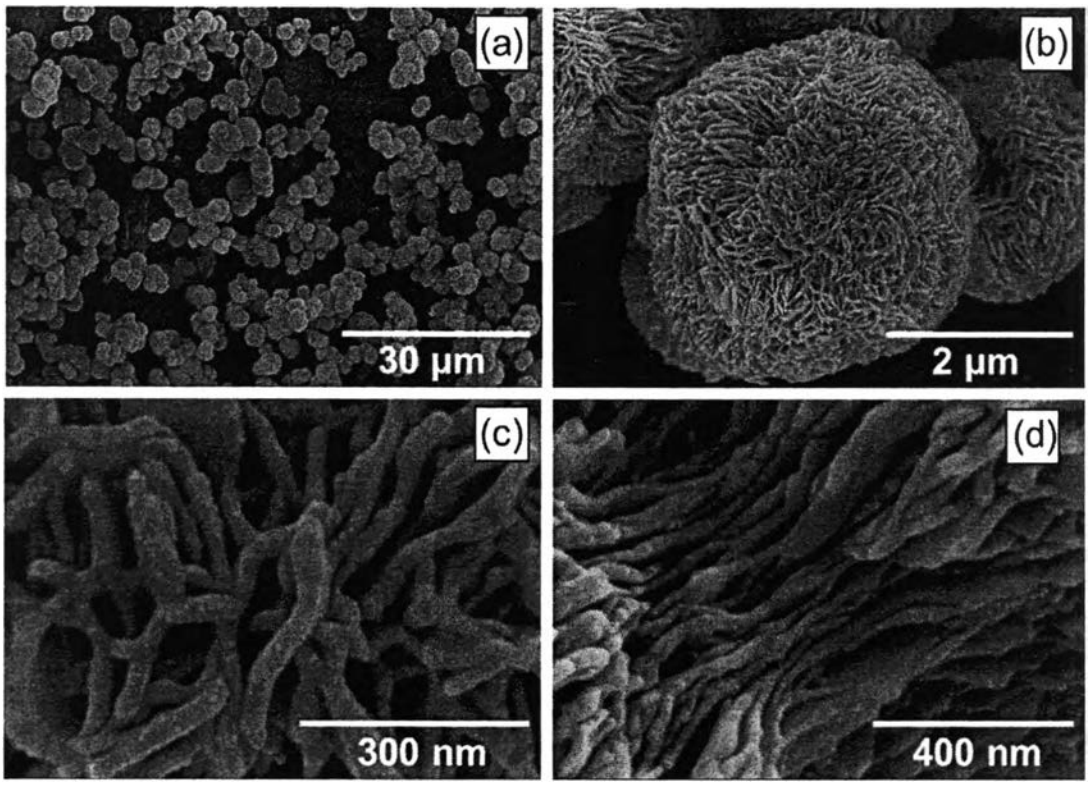

Figure 7.2 Morphology of the bismuth titanate precursor synthesized at 150 °C for 2 h: a) Uniform hierarchical structure, b) An individual sphere, composed of c) twisted nanosheets, d) assembled nanosheets taken at high magnification.

To follow the transformation process of the precursor to the hierarchical structure, we carefully carried out time-dependent experiments by keeping the other synthesis parameters constant. The mixture solution of bismuth nitrate and titanium butoxide was heated at 150 °C for 30 min, 1 h, and 2 h. The morphological results observed by FE-SEM are shown in Figure 7.3. The 30 min reaction time resulted in a leaf-like and circular plate-like morphology (Figure 7.3a). The length of the leaf-shaped structure was around 8–12 μm. As the reaction proceeded to 1 h, the leaf and the circular-plate particles were partially re-crystallized to form three dimensional hierarchical structures, having a size around 1–2 μm, as illustrated in Figure 7.3b. Under these conditions, the leaf-like particles had a length as short as ca. 7 μm, and the flower-like structure was completely formed in 2 h reaction time, as seen in Figure 7.3c. 123

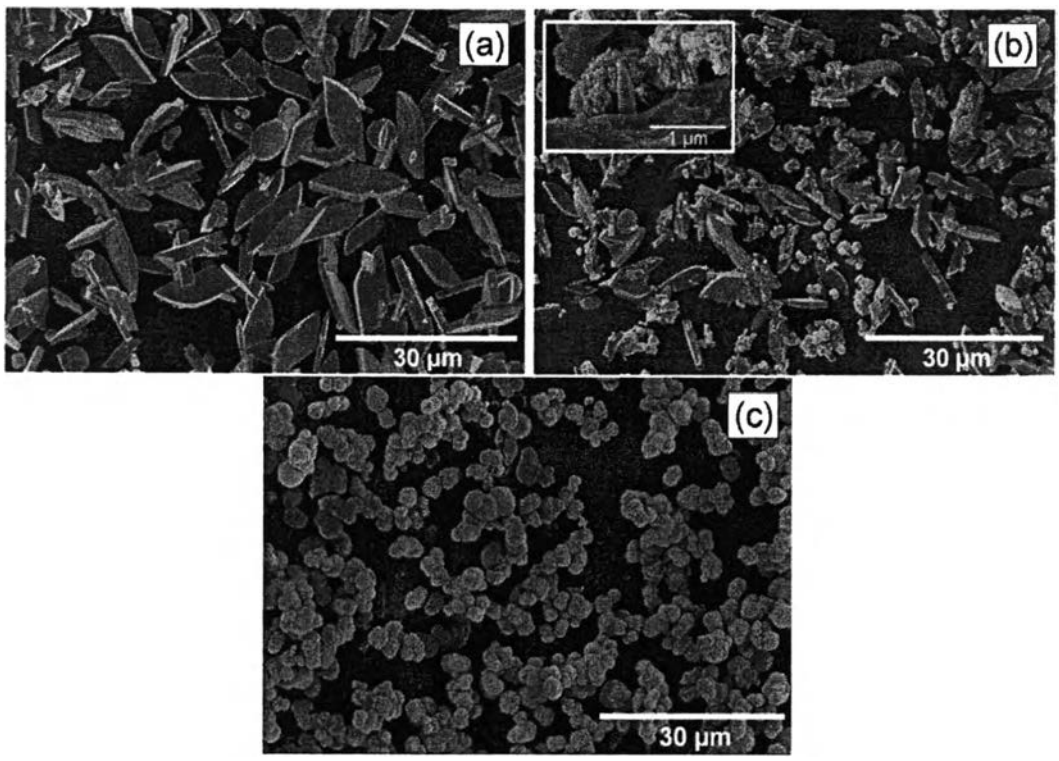

Figure 7.3 Morphology evaluation of the bismuth titanate precursor obtained from heating the mixture at 150 °C for reaction times of a) 30 min, b) 1 h, and c) 2 h.

In this experiment, ethylene glycol acted not only as a media for the self-assembly process, but also as the complexing agent with metal ions for consequent polymerization.[23-24] In the ethylene glycol medium, bismuth and titanium were separately chelated with ethylene glycol to form a single complex, and both bismuth and titanium complexes polymerized to form a polymeric network, as also observed by Lee *et al.*,[25] who synthesized $BaTiO_3$ and Ba_2TiO_4, using ethylene glycol to capture the metal ions to form a complex-polymerization mechanism, and found that ethylene glycol content affected the crystallization behavior of the nanostructure. Moreover, Zhou *et al.*[26] synthesized hierarchical $FeWO_4$ and found that ethylene glycol played an important role in directing growth and self- assembly of the unique structure. Slab-like nanoparticles of $FeWO_4$ were quickly formed before stacking to form small sheet-like microcrystals via oriented attachment and self-assembly processes. Yang *et al.*[27] also proposed a similar functionality of ethylene glycol on the formation of 3D flower-like Lu2O3. They explained that the nuclei of lutetium

oxide precursor seeds were first formed through a homogeneous nucleation process, and it subsequently recrystallized to grow into nanoflakes. In the presence of ethylene glycol, acting as surfactant, the ethylene glycol could be absorbed onto the flakes, leading to the self-assembly process. In our work, it can thus be concluded that the bismuth titanate precursor nuclei was first formed via ethylene glycol complex with bismuth and titanium ions. The nuclei were then further recrystallized to form the leaf- and circular plate-like shapes. Extending the reaction time, the leaf-like particles transformed to hierarchical structures through self-assembly process.

As mentioned by Yang *et al.*[27], the self-assembly process was very complicated, although a number of 3D structures have been reported,[2-4,12,28] due to the various effects on this process by crystal-face attraction, electrostatic and dipolar fields associated with the aggregates, the hydrophobic interaction, a hydrogen bond, and van der Waals forces.[5,27-29]

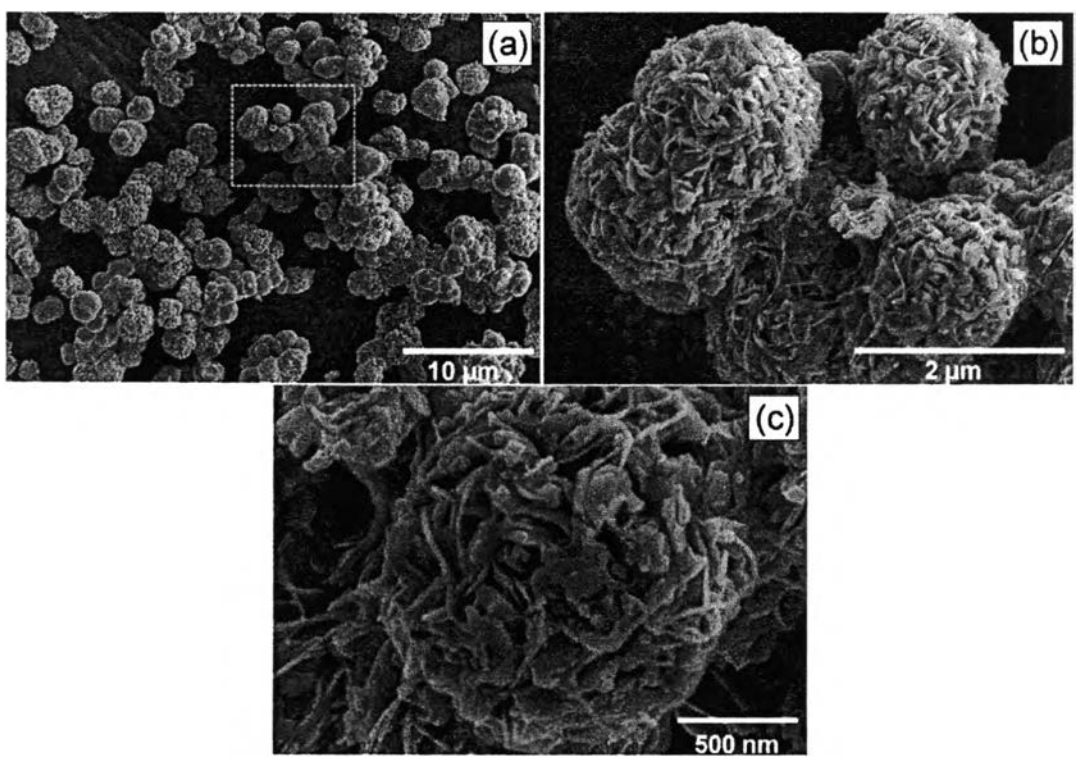

Figure 7.4 Synthesized $Bi_{12}TiO_{20}$ calcined at 600 °C for 30 min and taken at low (a–b) and high (c) magnifications.

After the calcination process, the hierarchical structure was still capable of maintaining its morphology, as seen in Figure 7.4. The energy dispersive X-ray (EDX) analysis confirmed the existence of bismuth, titanium, and oxygen in the $Bi_{12}TiO_{20}$ hierarchical structure.

7.5 Conclusions

Hierarchical architecture $Bi_{12}TiO_{20}$ was easily synthesized via ethylene glycol mediated route. The uniform hierarchical structures were obtained by heating the mixture of bismuth nitrate and titanium butoxide in ethylene glycol at 150 °C for 2 h. The morphology evaluation of the transformation of the precursor to the hierarchical architecture was found before calcination at 600 °C for 30 min. The synthesized hierarchical architecture $Bi_{12}TiO_{20}$ can be used as a catalyst in which its study is being investigated.

7.6 Acknowledgments

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7.7 References

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