MORPHOLOGY-CONTROLLED SYNTHESIS OF $SrTiO_3$ NANOCUBE BY CAPPING AGENT-ASSISTED SOLVOTHERMAL METHOD

SINTESIS NANOKUBUS $SrTiO_3$ DENGAN PENAMBAHAN *CAPPING AGENT* SEBAGAI PENGONTROL MORFOLOGI PADA METODA SOLVOTERMAL

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ABSTRACT

The synthesis of $SrTiO_3$ nanocubes have been carried out by solvothermal process using cetyl trimethyl ammonium bromide (CTAB) as capping agent to control the particles morphology. The condition of the synthesis was obtained at 160 ºC for 24 hours with molar ratio of $SrTiO_3$ and capping agent was 1 : 1. The X-ray diffraction (XRD) pattern shows that $SrTiO_3$ adopts a perovskite structure with a higher intensity of 110 at 2θ:32.33º and the crystallite size calculated from FWHM was found to be 41 nm. Fourier transform infrared (FTIR) spectrum shows a shift in particular absorption band attributed the interaction between $SrTiO_3$ particles surface and the head group of CTAB molecules. Transmission electron microscopy (TEM) image shows the cubic-like particles of $SrTiO_3$, this indicates that CTAB successfully functions as capping agent on the synthesis of $SrTiO_3$.

Keywords: capping agent, nanomaterials, nanocube, solvothermal, transmission electron microscope (TEM)

ABSTRAK

Nanokubus $SrTiO_3$ telah disintesis melalui proses *solvothermal* menggunakan setil trimetil amonium (CTAB) sebagai agen pembentuk (*capping agent*) yang berfungsi untuk mengontrol morfologi partikel. Kondisi sintesis diperoleh pada suhu 160 ºC selama 24 jam dengan rasio molar $SrTiO_3$ dan *capping agent* adalah 1:1. Pola difraksi sinar-X (XRD) menunjukkan bahwa $SrTiO_3$ mengadopsi struktur perovskit pada intensitas yang lebih tinggi di bidang 110 dengan 2θ:32.33º, dan ukuran kristal adalah 41 nm yang dihitung dari FWHM. Spektrum fourier transform infra red (FTIR) menunjukkan adanya pergeseran pada pita serapan spesifik terkait interaksi antara permukaan partikel $SrTiO_3$ dengan gugus kepala molekul CTAB. Gambar mikroskop elektron transmisi (TEM) menunjukkan bahwa partikel $SrTiO_3$ berbentuk seperti kubus, hal ini menunjukkan bahwa CTAB telah berfungsi sebagai *capping agent* pada sintesis $SrTiO_3$.

Kata Kunci: agen pembentuk, nanomaterial, nanokubus, solvothermal, mikroskop elektron transmisi (TEM)

INTRODUCTION

The research in nanotechnology describes the creation and exploitation of materials with structural features in between those of atoms and bulk materials and advanced functional application. Properties of materials of nanometric dimensions are significantly different from those of atoms as well as those of

bulk materials (Hussein, 2015; Pearce, 2012).

Appropriate method and suitable control during synthesis can lead to the formation of novel materials with special function, thus the creation of new science as well as new devices and technologies will thrive. The effort of many researchers to find the new strategies for the synthesis of nanomaterials and new tools for characterization and manipulation of its functions have created an explosive growth of nanoscience and technology in the last few years. Therefore, several methods of synthesizing nanoparticles, nanocube, nanoplate, nanowires and nanotubes, and their assemblies, have been discovered and were found to be appicable (Laocharoensuk et al., 2013; Smith, Ray, Carlson, Sarma, & Misra, 2013).

The recent research on nanostructured materials have attracted considerable interest because of their unique physical and chemical properties. It has been revealed that the morphology and structure of the inorganic materials strongly influence their properties (Aricò, Bruce, Scrosati, Tarascon, & van Schalkwijk, 2005). Therefore, great effort has been carried out to synthesizing various inorganic materials with controlled shape and size as well as multivarious structural engineering, which are expected to offer superior properties for various applications (Hicks, L. D, Harman, & Dresselhaus, 1993; Poza et al., 1998).

One of inorganic materials that provides a fundamental stepping-stone for the development of functional nanomaterials is metal oxides. These materials represent the most common, most diverse, and probably the richest class of materials in terms of physical, chemical, and structural properties so that it demonstrates a promising future in various applications and devices. The diversity of metal oxide originates from the more complex crystal and electronic structures as the result of the variety of oxidation states, coordination numbers, symmetry, crystal-field stabilization, density, stoichiometry, surface properties and etc. In addition, they truly are fascinating compounds, capable of insulating, semiconducting, metallic, and magnetic behaviors with continuous or sudden transitions between these states (Cañas-Carrell, Li, Parra, & Shrestha, 2014; Patzke, Zhou, Kontic, & Conrad, 2011).

Strontium titanate ($SrTiO_3$), well-known as STOis one of an important member of binary oxide with indirect band gap of 3.25 eV and a direct gap of 3.75 eV. It is a promising material with tunable compositions whichhas been extensively studied due to its functional properties both scientific importance and application in electronics (Hu, Tan, Pan, Huang, & Cao, 2005; Wang, Han, He, Park, & Koumoto, 2011). It adopts a perfect cubic perovskite structure where Sr^{2+} cations are at the cornersof the cube and each is coordinated by twelve O^{2-}, and a Ti^{4+} cation in the centre of the cube occupies the centro-symmetric position surrounded by six oxygen anions, forming the TiO_6 octahedron. This structurehas created a wide variety of structural instabilities such as rotation and distortion of the TiO_6 octahedron which explains for the rich variety of properties of this compound (Van Benthem, Elsässer, & French, 2001). Moreover, the site selective doping from its ideal position for both strontium and titanium sites have created favorable feature in the development of advance functional materials. In addition, the studies in the past few years have demonstrated that the size and shape of $SrTiO_3$ nanocube profoundly affect its electrical and thermal properties (Erdman et al., 2002; Syha et al., 2012; Wang et al., 2010).

Research on nanomaterials with low-dimensionality make the studies of STO nanostructures become a very important issue of research and

development from both fundamental and industrial standpoints. It can be applied in the thermoelectric energy conversion generator, gas sensors, solar cell electrodes, photocatalysis under UV irradiation and manufacture practical nanodevices. Koumoto et al reported that the formation of 3D nanocube superlattice (magic cube) gives a significant influence on the improvement of thermoelectric properties of STO, in particular the power factor due to energy filtering effect and quantum confinement. Furthermore, the surface of the cubes are also crucial in controlling the lattice thermal conductivity which is significantly decreased through boundary scattering (Ohta et al., 2007).

Development of a strategy to reach the rational design of nanomaterials with modelled and controlled particles size, morphology, orientation, and crystal structure have become a challenge. Many efforts have been deployed to build nanomaterials with tunable physical and chemical properties by controlling its morphology. Size and shape are one of the many aspects that influence the properties of nanomaterials. The size is determined by the ability to segregate the nucleation and the growth stages, so as the mono dispersity of nanoparticles can be controlled. Therefore, aqueous precipitation can be applied by performing precipitation far from the typical point of zero charge (PZC) to enhance the control of the nucleation, growth, and ageing processes. On the other hand, the shape as well as the crystallographic structure may be controlled by manipulating and controlling the interfacial tension enabling to grow nanoparticles with shapes tailored for their applications. Applying the appropriate solution chemistry can reach the ability to develop purpose-built crystal morphology (Kimijima, Kanie, Nakaya, & Muramatsu, 2014).

In this work, we report on the synthesis of $SrTiO_3$ nanocubes via solvothermal method using cetyltrimethyl ammonium bromide (CTAB) as capping agent. The use of capping agent intended for controlling the interfacial tension by reducing the surface energy which enables to grow STO nanocubes.

EXPERIMENTAL

Material and Instruments

Titanium tetraisopropoxide (Sigma-Aldrich), Ethanol (Merck), NaOH (Merck), $SrNO_3$ (Merck), CTAB (Merck), distilled water, X-ray Diffraction (XRD, PAN analytical X-pert Pro), Fourier Transform Infrared (FT-IR, JEOL JSM-6390) and Transmission Electron Microscopy (TEM, JEOL JEM 1400).

All chemicals were analytical grade and used without further purification. The solutions were prepared by dissolving 1,480 mL titanium tetra isopropoxide (TTIP) into 25 mL of ethanol and stirred for about 10 minutes. Then, the pH value was adjusted to13 by adding an aqueous solution of1 M NaOH and white suspension was formed. Strontium nitrate was added into the white suspension placed in the ice bath with a molar ratio of Sr:Ti, 1:1. The CTAB was added into the homogeneous solution with the molar ratio of starting material and capping agent (CA) was 1:1. After that, the final mixture was poured into a stainless steel autoclave filled to 2/3 of its capacity. The autoclave was sealed and put into a pre-heated oven at 160 °C by 18h and 24 h. Finally, the autoclave was naturally cooled to room temperature, and the products of the reaction were centrifugally separated, washed with distilled water, then dried at 105 °C for about 5 h. The obtained powders were characterized by X-ray Diffraction (XRD, PAN analytical X-pert Pro), Fourier Transform Infrared (FT-IR, JEOL JSM-6390) and Transmission Electron Microscopy (TEM, JEOL JEM 1400).

RESULTS AND DISCUSSION

The diffractogram of the samples are shown in **Figure 1**. The pattern in **Figure**

1(a) indicates high crystallinity of STO prepared at 160 °C for 24 hours without using capping agent. The diffraction peaks are well-defined at 2θ: 22.03° (100), 32.33° (110), 39.92° (111), 46.40° (200), and 57.81° (211) that can be indexed as a cubic perovskite $SrTiO_3$.The present of impurity peaks in all samples refer to $SrCO_3$. We suggest that the presence of $SrCO_3$ in the sample because of two reasons. First, titanium hydroxide ions were not totally formed at the time of dissolution TTIP with ethanol with the addition of NaOH. Therefore, pH adjustment effects on the formation of titanium hydroxide ions whichwould react with strontium. Second, titanium hydroxide ions did not react completely with strontium, so that the excess of strontium reacted with carbon dioxide present in the autoclave during the synthesis forming $SrCO_3$ (Demirors & Imhof, 2009).

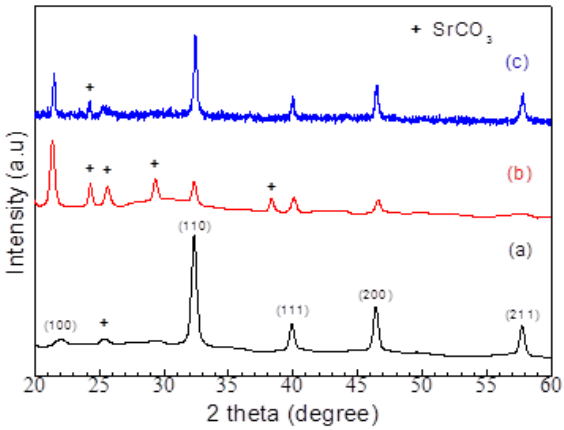

Figure 1. Powder XRD pattern of the $SrTiO_3$: (a) STO prepared without capping agent (b) STO prepared at 160 °C for 18 h using capping agent and (c) STO prepared at 160 °C for 24 h using capping agent.

Figure 1(b) shows that the intensity of XRD peaks are comparably weak due to the lower crystallinity of STO prepared at 160 °C for 18 hours using capping agent. On the other hand, **Figure 1(c)** shows the effect of growth temperature which has resulted the STO product with higher crystallinity, and the crystallite size calculated from FWHM (2θ:32.33°) was found to be 41 nm. Therefore, the time-dependent crystallization has shown an effect on the degree crystallinity of the final product (Hanzig et al., 2011; Langer, 1980; Rabuffetti et al., 2008).

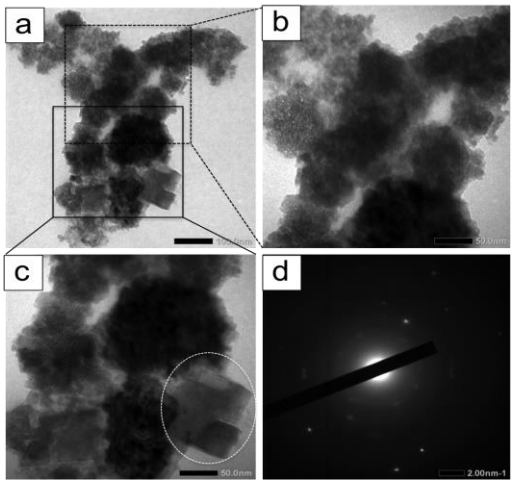

Figure 2. (a) TEM images of $SrTiO_3$ products, (b and c) TEM images of $SrTiO_3$ products in particular area and (d) corresponding SAED pattern.

Transmission electron microscopy (TEM) was used to investigate the morphology of the synthesized $SrTiO_3$. **Figure 2 (a)** shows that the $SrTiO_3$ synthesized with solvothermal method using CTAB as capping agentwas successfullyto be nanocube particle with the size of 100 nm. However, it can be observed clearly in **Figure 2 (c)** that the STO nanocube particles were formed from the agglomeration of some smaller nanocube particles. These particles form self assembly cube on cube through the three coordinate planes, so that the resulting cubes develop into a bigger volume. The adhesion caused by the presence of CTAB on the surface of the smaller cubes, as a result the whole surface enclosed with CTAB, as illustrated in **Figure 3**.

Therefore, in the next work we will try to find the suitable solvent to prevent agglomeration during the synthesis, so as

the resulting particles disperse in a fine particle in the form of a perfect cube shape.

SAED pattern as shown in **Figure 2 (d)**, explains that the ring pattern is diffuse which indicates that the observed selective area occurred agglomeration, hence affecting the shape of the particles. In addition, the pattern also reveals that the product has a polycrystalline structure (Yang, Yan, Wang, Zhang, & Yang, 2014; Zhan et al., 2015).

FTIR measurement in the region of 600-4000 cm^{-1} was carried out to obtain further information about the interaction of CTAB with STO nanocubes. The vibration bands of CTAB can be grouped into two categories: those associated with methylene tails and those with alkylammonium head groups. As shown in **Figure 4** the broad bands around 3200-3700 cm^{-1} is due to asymmetric and symmetric O-H stretching of water and the band at around 1600 cm^{-1} is ascribed to the bending mode of hydroxyl groups of adsorbed water for CTAB, those the same as for STO-CTAB. The simultaneous presence of these bands are associated with the lattice of water molecule due to the physical absorption. The two intense bands at 2918 and 2849 cm^{-1} of the spectrum are assigned to asymmetric and symmetric stretching vibrations of the CH_2 in the methylene chains of CTAB. The unchanged frequency positions for STO-CTAB suggest that the conformation of methylene chains is maintained and there is no interaction between STO and the tail of molecular CTAB. The sharp band at 1400 cm^{-1} is an instrumental artifact. The obvious difference for symmetric C-H scissoring vibrations and C-N stretching mode of the head group CH_3-N^+ moiety is observed between CTAB and STO-CTAB. The band at 1487 cm^{-1} for pure CTAB is attributed to the C-H scissoring modes of vibrations, and that for STO-CTAB it is 1489 cm^{-1}. The weak band in the region of 1100-1250 cm^{-1} is ascribed to the C-N stretching band for pure CTAB, which is broad with lesser intensity and shifted to lower wave numbers in the STO-CTAB. The shifted clearly indicates the interaction between the N-containing group of CTAB and the surface of STO nanoparticles. All these experimental observations explain the fact that CTAB molecules capped $SrTiO_3$ via their polar head group (George et al., 2009; Li et al., 2012).

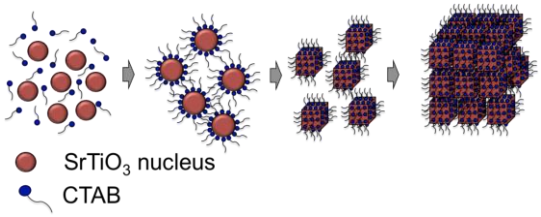

Figure 3. Schematic illustration of the formation process of the cube-like $SrTiO_3$ nanostructure.

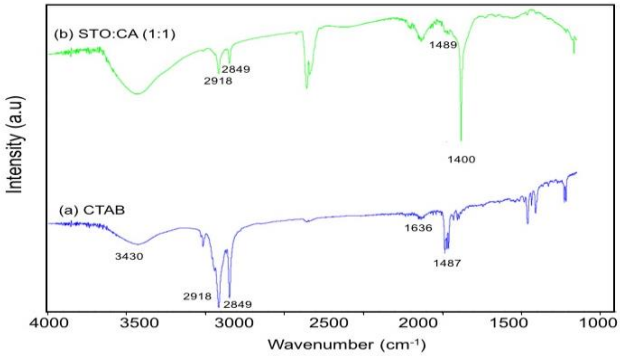

Figure 4. (a) FT-IR spectrum of CTAB and (b) FT-IR spectrum of STO-CTAB nanocubes.

CONCLUSION

We have successfully synthesized $SrTiO_3$ nanocube via solvothermal method. XRD analysis confirms the synthesized material to be a cubic perovskite structure with higher crystallinity and the crystallite size calculated from FWHM (2θ:32.33°) was found to be 41 nm. TEM images show that the morphology of $SrTiO_3$ particles are nanocube with size of 100 nm. The role of CTAB on the STO nanoparticles was assigned by shifts of the band in FTIR spectra and it was found that the CTAB molecules were attached to the nanoparticle surface and capped the particles via their polar head group.

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