

Generation of Highly Ordered Porous Antimony-Doped Tin Oxide Film by A Simple Coating Method with Colloidal Template

Asep Bayu Dani Nandiyanto, Asep Suhendi, Yutaka Kisakibaru, Takashi Ogi, and Kikuo Okuyama

Abstract—An ordered porous antimony-doped tin oxide (ATO) film was successfully prepared using a simple coating process with colloidal templates. The facile production was effective when a combination of 16-nm ATO (as a model of an inorganic nanoparticle) and polystyrene (PS) spheres (as a model of the template) were simply coated to produce a composite ATO/PS film. Heat treatment was then used to remove the PS and produce the porous film. The porous film with a spherical pore shape and a highly ordered porous structure could be obtained. A potential way for the control of pore size could be also achieved by changing initial template size. The theoretical explanation and mechanism of porous formation were also added, which would be important for the scaling-up prediction and estimation.

Keywords—Porous structure film; ATO particle; Ultra-low refractive index; vertical drop method; Low-density material; Polystyrene.

I. INTRODUCTION

ANTIMONY-DOPED TIN OXIDE (ATO) thin film has been important in both research and technology due to its use in various applications.[1] Many fabrication methods have been suggested by several research groups. Tsuchiya *et al.* reported the use of dip-coating method to achieve the thin ATO film with size of micrometer.[2] Ravichandran *et al.* developed the method to prepare thinner ATO film using a spray-assisted technique.[3] Although thinner film (thickness of 1.2 micrometer) could be prepared, the need of specific equipment faces a problem for industrial application. Further development to produce thin film was then reported by Lin *et al.* reported a rapid fabrication method to prepare ATO film by a spin-coating method. However, the lack of chemical/material efficiency become a problem for further application and scale-up process (spin-coating process has efficiency of 5% [4]). Tsukuma *et al.* was then reported a method to fabricate dense film with thickness of down to 100 nm using a simple dipping process.[5] However, above suggested methods reported the fabrication of dense film only, which results in the reduction of the film performance (i.e. transparency, refractive index, etc) due to its dense structure.

The common process for developing this porous material is relatively simple, which uses a self-assembly template technique that employs an organic material as the template [8]. The pore formation reflects the template shape, and easy

removal of the template is one of the main advantages of using this process [9]. However, several disadvantages of the current materials remain. When producing mesoporous materials ($D_{\text{pore}} < 50$ nm), surfactant typically used as the template [6]. Unfortunately, unordered pore structure is produced, and the surfactant could never be completely removed [9]. Further, when a small pore size was used, difficulties associated with mass transfer, diffusivity, and penetration of molecules either into or out of the pore system became a limiting factor for several applications [10]. These were the concerns that prevented further application of mesoporous materials.

In this report, we reported a simple route to fabricate the ordered porous film using dual-component colloid, based on our study in the fabrication of materials with controllable morphology in film [4,7,11] and particle forms [9, 10, 12-17]. This method could prepare porous particles by the infiltration method, in which both colloids were self-arranged on the substrate and the voids between colloidal spheres are infiltrated with other nanocolloid (i.e. ATO nanoparticles). Then, when the coated film are solidified, the porous films can be obtained by removing the colloidal templates, which could use through wet-etching or thermal decomposition. The porous ATO film with a highly ordered porous structure could be produced, in which to the best of our knowledge, it is the first method to prepare such porous ATO film in the facile process. Although many reports have been published in the preparation of porous film, the fabrication methods have multistep, time-consuming, and rigid process. [5] Here, the introduction of the simple coating method used in this paper is one of alternative ways to produce film. No additional special functional chemical was used that was typically put on the substrate to support and achieve homogeneous film in the current film fabrication. This point allowed this method as the novel method to prepare film without any supporting chemicals/materials. The other interesting result obtained from the use of present method is the ability in forming uniform spherical-shaped pore, which could not be achieved by the current development. These interesting results were believed due to use of polystyrene (PS) particles as the template. A potential way for controlling pore size was also reported in this paper by investigating the effect of PS particle size. In addition, we also added a mechanism hypothesis in how the particles were self-assembled to form porous film.

II. EXPERIMENTAL METHOD

The porous ATO film was prepared from a mixture of ATO nanoparticles and PS particles (Japan Synthetic Rubber Corp.,

All authors are with Department of Chemical Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi Hiroshima 739-8527, Japan (tel.: +81-824-24-7850; fax.: +81-824-24-7850; e-mail: ogit@hiroshima-u.ac.jp)

with a size of 136, 300, and 500 nm). These commercial particles were used to simplify the process because their preparation methods have been well-known using the current technologies[18]. Further, the other purpose from the use of commercial colloidal particles that were relatively monodispersed was to achieve our objective in the formation of highly ordered particles in the film. When monodispersed particles are self-assembled, the possibility in the formation of highly ordered particles is high; otherwise, it will be impossible.[5]

First, both commercial particles were diluted into the aqueous suspension and mixed with mass ratio of 1:1 in several minutes. The mixed colloidal suspension, namely the precursor, was then coated onto the substrate to form a composite ATO/PS film using a simple coating process (using a vertical drop spout). For the substrate, either a silicon wafer or a glass plate (microslide) was washed with a basic aqueous solution in an ultrasonic bath for several minutes. The substrate was then spouted by the precursor and dried for several hours at 40 °C. The use of a relatively low drying temperature was to allow sufficient time for the PS spheres to become arranged into an ordered structure, and to allow the ATO nanoparticles to be arranged into the voids of the template particles, which would result in self-organization of the colloidal templates [7]. After the coating process was complete, a white matrix film was produced. Finally, the coated film was then annealed in a furnace at 450 °C to evaporate PS. The template removal process left the matrix with hole and resulting porous ATO film. In addition, to minimize possibility of sintering and/or shrinking phenomenon as well as maintain its porous structure in the film, the heat treatment with a low-heating rate (5 °C/min) and short-holding time (450 °C; 15 minutes) was conducted. The porous morphology of the prepared film was then characterized using a scanning electron microscope (SEM; S-5000, Hitachi, Tokyo, Japan, operated at 20 kV).

III. RESULTS AND DISCUSSIONS

When using this simple coating method to produce a film, several factors should be determined to make a maximum coating over the film: type of substrate, precursor properties (i.e. concentration, viscosity, density, and particle size (if the precursor is a nanoparticle sol or suspension)), and coating condition (i.e. volume of dropped precursor, temperature and humidity). However, in this paper, we focused only on the development of porous film under the effect of template size to control the pore size in the film, while other parameters would be reported in our future work. Figure 1 shows the detailed experimental procedure with its mechanism during the process. In the present study, we used two steps in the fabrication of porous ATO film (Figure 1a). First, after the homogenous suspension contained ATO and PS particles were prepared, the vertical drop coating process was conducted. The prepared film was then put into the template removal process (i.e. heat treatment) to remove the PS, which allowed to the production of porous ATO film.

The porous film formation mechanism is represented in Figure 1b-e. During the coating process, a meniscus region is formed. The meniscus region is the interface region where all of the solvent can no longer be held in its liquid phase, and some of the solvent begins to release and vaporize. Solvent removal from this meniscus region induces capillary flow, and the inter-particle capillary forces, causing self-assembly of the colloid particles. All particles at the very beginning of the process are distributed homogeneously in the precursor (Figure 1b). Then, as a result of buoyancy forces and evaporation condition, the precursor (containing particles) moves from center to the edge of the substrate, covering over the substrate surface, in which the O-ring phenomenon happened.

In the initial time of process, the speed of evaporation (O-ring formation) regulates the spread of precursor over the area. This phenomenon causes the movement of the precursor onto the edge of the substrate (Figure 1c). The height of the coated precursor on the substrate, which is a function of evaporation of O-ring structure, must be considered because the thicker coating has a relatively large amount of solvent remained in the substrate, causing the lower solvent evaporation and resulting in a negative relation to the particle self-assembly process.

After several time, the continuity of the coating process allows the addition of other movement of particles and formation of complete O-ring structure (Figure 1d). The precursor (containing colloidal particles) re-moves away with the opposite direction to the center, releasing a multilayer particle formation in the center.

After the stable condition is reached (no movement of precursor contained particles from the substrate), the particles start to get a stable arrangement (Figure 1e). Self-assembly particles in the covered precursor on the substrate happen. The particles move away with opposite direction to the center; but, due to buoyancy force, they move also to the meniscus region. An attraction-repulsion phenomenon among the particles also occurs and impacts to the particle movement[7]. These particle movement parameters permit a self-assembly arrangement among the particles, producing compact and arranged particles (ATO/PS) in the film, which occurs at the same time with the solvent evaporation.

In the present case, multi-sized colloidal particles (i.e. ATO nanoparticles and PS particles) were used. The size of ATO nanoparticles is smaller than the size of PS particles, allowing this ATO to have a lower buoyancy force but higher Brownian motion effect. This circumstance makes ATO nanoparticles to move and swirl easily from one position to another. PS particles have a larger size (lower Brownian motion but higher moment inertia) that makes their movement more stable than the ATO nanoparticles. Consequently, PS particles can easily shift the arrangement of ATO nanoparticles and penetrate the interstitial channels between ATO nano-spheres. This condition allows the PS particles to organize and form equilibrium configurations in a stable pattern with the minimum energy, while the smaller ATO nanoparticles fill the spaces between the large PS particles configurations. Finally, when the template removal process was conducted to the prepared composite

ATO/PS film, the PS released and remained a porous structure in the final film product (Figure 1f). Detailed information about the self-organization kinetics of particles has been described in our previous work.[4, 7]

Figure 2 shows the SEM analysis of initial colloidal particles (ATO (a) and PS (b)) and coated film before (c) and after template removal process (d-f). The SEM results showed that the sizes of ATO particles (Figure 2a) and PS particles (Figure 2b) were relatively monodispersed and free of agglomeration, which would be effective for preparing highly ordered particles using the self-assembly process. When these colloidal suspensions were mixed and coated, the result showed the PS particles were arranged on the film, forming a dome structure-like film (Figure 2c). This confirms that a small particles (i.e. ATO) induces an attractive depletion-interaction between large templates (i.e. PS particles)[7]. A hexagonal pattern for a large PS template was observed and small ATO particles were only located in the free space between larger templates. When heat was added to remove the PS, a porous ATO film (Figure 2d). The size and the shape of pore were identical to the initial PS, in which the measurement of hole size (D_{app}) was described in our previous work[4]. From these results, it can be concluded that the PS was simply removed leaving a pore without changing the initial ATO/PS arrangement. Although there was a small difference between the pore and the initial PS sizes due to appearance of small sintering in the template removal process, the result gave a potential way for further developments (e.g. control of pore size[7]).

To confirm the possibility in the control of pore size, different PS with different sizes were used (Figure 2d-f). As expected, decrease of PS diameter allowed to the fabrication of materials with smaller pore size. Ferret analysis of pore size showed that when PS diameter of 136, 300, and 500 nm were used, the pore size could be controlled, corresponding to hole size of 98, 231, and 354nm, respectively.

Figure 3 shows the low-magnification SEM images of porous film prepared using 300nm PS. Hexagonal pore arrangements were obtained in the large area, confirming that the current method was also possible to fabricate porous film in the relatively wide area.

Although this demonstration of the preparation of highly ordered porous ATO film had been succeeded, several inadequate data and disadvantages/exceptions from our method were still found and needing further study (i.e. film homogeneity, surface area, particle order (e.g. low angle X-ray Diffraction), refractive index, etc). Material performances (e.g. XRD analysis and material composition and pattern-related characterization) were not reported in this paper because we used commercial ATO nanoparticles, and the heat treatment with a low-heating rate (5 °C/min) and short-holding time (450 °C; 15 minutes) would not change the material phase and pattern. However, we believe that further insights gained from research such as the present study should make other fabrication innovations possible due to its very relatively fast-fabrication, facile production, and possibility in the scaling-up production.

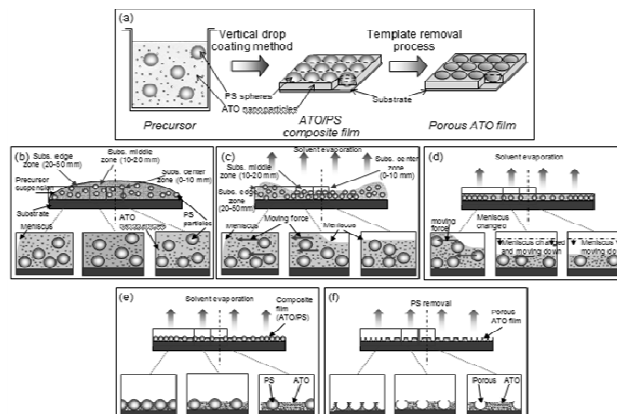


Fig. 1 Illustration of the vertical drop coating procedures (a) and its mechanism (b-d)

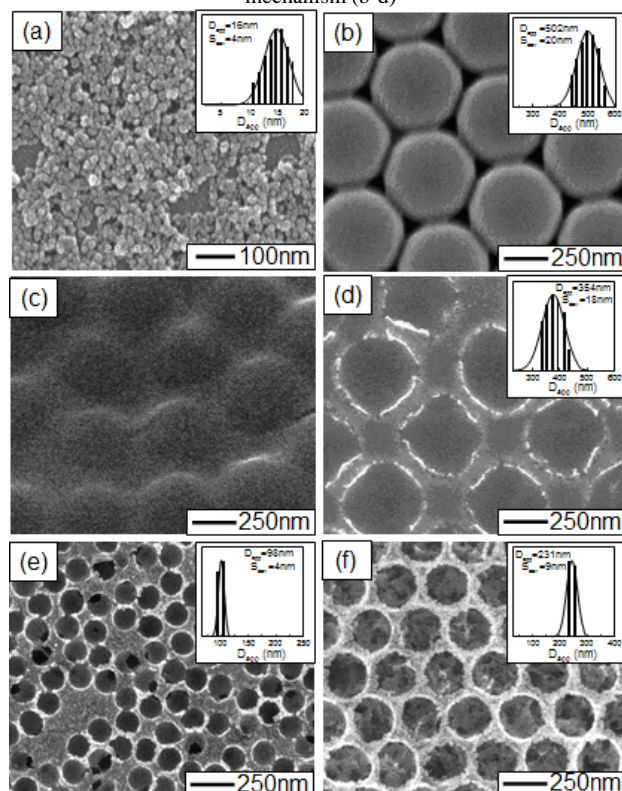


Fig. 2 SEM images of initial colloidal particles (ATO (a) and PS (b)) and coated film before (c) and after template removal process (d-f) using different PS sizes (500 (c and d), 130 (e), and 300 nm (f)). SEM images of coated film using different PS sizes: (c and d) 500, (e) 130, and (f) 300 nm.

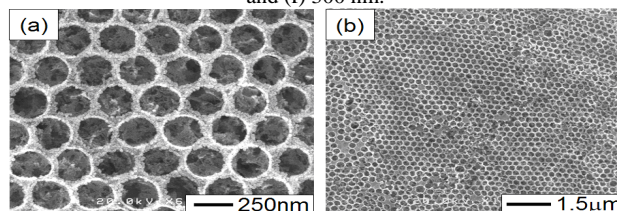


Fig. 3 SEM images of porous ATO film at high (a) and low (b) magnification. Sample was prepared from the use of ATO nanoparticles and 300-nm PS particles

IV. CONCLUSION

In summation, we developed a facile-fabrication method to produce the porous ATOfilmin therelatively large areausing thesimple coating method. The present study also demonstrated the concept and feasibility of preparing porous materials. The pore size and shape (spherical form) was identical to the initial PS. A potential way to control pore size was also reported, which could be effectively achieved by means of PS size.

ACKNOWLEDGMENT

A fellowship provided for A.B.D.N. by the Japan Society for the Promotion of Science (JSPS) is gratefully acknowledged. We acknowledged the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan for supporting this research (Grant-in-Aid for Young Researcher B, No. B-23760729).

REFERENCES

- [1] A.L. Onaogu, C.E. Okeke, "Characterization of antimony-doped tin oxide films prepared by spray pyrolysis", *Solar Energy Mater.*, vol. 20, pp.26-36, 1990.
- [2] T. Tsuchiya, A. Koizumi, "Preparation and electric properties of transparent electrically conductive tin antimonide (SnO₂/Sb₂O₃) thin films by dip coating", *J. Ceram. Soc. Jpn.*, vol. 98, pp. 1011-1016, 1990.
- [3] K. Ravichandran, G.Muruganatham, B.Sakthivel, "Highly conductingandcrystallinedoublydopedtinoxidefilmsfabricatedusing a low-costandsimplifiedspraytechnique", *Physica B*, vol. 404, pp. 4299-4302, 2009.
- [4] A.B.D. Nandiyanto, T. Ogi, F. Iskandar, K. Okuyama, "Highly ordered porous monolayer generation by dual-speed spin-coating with colloidal templates", *Chem. Eng. J.*, vol. 167, pp. 409-415, 2010.
- [5] K. Tsukuma, T. Akiyama, H. Imai, "Hydrolysis deposition of thin films of antimony-doped tin oxide", *J. Am. Ceram. Soc.*, vol. 84, pp. 869-871, 2001.
- [6] V. Müller, M. Rasp, G. Stefanic, S. Günther, J. Rathousky, M. Niederberger, D. Fattakhova-Rohlfing, "Antimony doped tin oxide nanoparticles and their assembly in mesostructured film", *Phys. Status Solidi C*, vol. 8, pp. 1759-1763, 2010.
- [7] A.B.D. Nandiyanto, N. Hagura, F. Iskandar, K. Okuyama, "Design of a highly ordered and uniform porous structure with multisized pores in film and particle forms using a template-driven self-assembly technique", *Acta Mater.*, vol. 58, pp. 282-289, 2010.
- [8] A.B.D. Nandiyanto, K. Okuyama, "Progress in developing spray-drying methods for the production of controlled morphology particles: From the nanometer to submicrometer size ranges", *Adv. Powder Technol.*, vol. 22, pp. 1-19, 2010.
- [9] A.B.D. Nandiyanto, F. Iskandar, K. Okuyama, "Macroporous anatase titania particle: Aerosol self-assembly fabrication with photocatalytic performance", *Chem. Eng. J.*, vol. 152, pp. 293-296, 2009.
- [10] A.B.D. Nandiyanto, S.G. Kim, F. Iskandar, K. Okuyama, "Synthesis of spherical mesoporous silica nanoparticles with nanometer-size controllable pores and outer diameters", *Micropor. Mesopor. Mater.*, vol. 120, pp. 447-453, 2009.
- [11] A.B.N. Nandiyanto, M. Abdullah, F. Iskandar, K. Okuyama, "Fabrication of ordered macroporous titania film using self-assembly an organic template and a simple dip-coating technique", *J. Nanosains Nanoteknologi*, vol. 2, pp. 56-59, 2009.
- [12] F. Iskandar, A.B.D. Nandiyanto, K.M. Yun, C.J. Hogan, K. Okuyama, P. Biswas, Enhanced photocatalytic performance of brookite TiO₂ macroporous particles prepared by spray drying with colloidal templating, *Adv. Mater.*, vol. 19, pp. 1408-1412, 2007.
- [13] A.B.D. Nandiyanto, F. Iskandar, K. Okuyama, "Nanosized polymer particle-facilitated preparation of mesoporous silica particles using a spray method", *Chem. Lett.*, vol. 37, pp. 1040-1041, 2008.
- [14] A.B.D. Nandiyanto, Y. Kaihatsu, F. Iskandar, K. Okuyama, "Rapid synthesis of a BN/CNT composite particle via spray routes using ferrocene/ethanol as a catalyst/carbon source", *Mater. Lett.*, vol. 63, pp. 1847-1850, 2009.
- [15] F. Iskandar, A.B.D. Nandiyanto, W. Widiyastuti, L.S. Young, K. Okuyama, L. Gradon, "Production of morphology-controllable porous hyaluronic acid particles using a spray-drying method", *Acta Biomater.*, vol. 5, pp. 1027-1034, 2009.
- [16] F. Iskandar, S.G. Kim, A. Bayu, D. Nandiyanto, Y. Kaihatsu, T. Ogi, K. Okuyama, "Direct synthesis of hBN/MWCNT composite particles using spray pyrolysis", *J. Alloy. Compd.*, vol. 471, pp. 166-171, 2009.
- [17] A.B.D. Nandiyanto, F. Iskandar, T. Ogi, K. Okuyama, "Nanometer to Submicrometer Magnesium Fluoride Particles with Controllable Morphology", *Langmuir*, vol. 26, pp. 12260-12266, 2010.
- [18] A.B.D. Nandiyanto, A. Suhendi, T. Ogi, T. Iwaki, K. Okuyama, "Synthesis of Additive-free Cationic Polystyrene Particles with Controllable Size for Hollow Template Applications", *Colloid Surf A*, submitted

Asep Bayu Dani Nandiyanto is a JSPS (the Japan Society of Promotion Science) researcher at Hiroshima University. He received his Sarjana Teknik (equivalent to B.Eng.) in 2005 in microparticle synthesis from Department of Chemical Engineering at Institut Teknologi Bandung (ITB). He received M.Eng (2008) and Dr.Eng (2011) from Department of Chemical Engineering at Hiroshima University. He received numerous awards and scholarships, including the grant and student awards by the Supersemar, the P.T. SanbeFarma, the Ministry of Education of Japan (MEXT), the Kawamura foundation, and the Hosokawa Micron Foundation. His research is in the area of particle technology focused on production of fine and ultrafine particles, starting from gas, aqueous, organic, or colloidal precursor via aerosol routes and liquid-phase synthesis, and their applications to the development materials (e.g. optical, medical, catalyst, energy, and environmental technologies).

Asep Suhendi is a PhD student at Hiroshima University supervised by Prof. Kikuo Okuyama. He received his B.Eng. and M.Eng from Department of Physics at Institut Teknologi Bandung (ITB), Indonesia. His research is in the area of particle technology focused on production of nanoparticles using aerosol spray method.

Yutaka Kisakibaru is a master student at Hiroshima University supervised by Prof. Kikuo Okuyama. His research is in the area of particle technology focused on production of nanoparticles using a spray-drying method. Now, he is working in the synthesis of magnetic nanomaterial using a liquid-phase synthesis and their functionalization (e.g. beads mill, dispersion, coating method, etc)

Takashi Ogi is an assistant professor in Chemical Engineering at Hiroshima University. He received his PhD degree in Chemistry and Chemical Engineering in 2008 from Hiroshima University. He was a JSPS researcher from 2006 to 2008 and an assistant professor at Osaka Prefecture University from 2008-2010. His current research interests include microbial synthesis of noble metal nanoparticles for catalyst materials.

Kikuo Okuyama is a Professor of Chemical Engineering at Hiroshima University. He received his doctoral degree in 1978 in chemical engineering at Osaka Prefecture University. His research has touched many aspects of aerosol science and technology, from fundamental investigations on aerosol dynamic behavior to the development of aerosol measurement equipments with a recent focus on nanomaterial synthesis. Prof. Okuyama has received numerous honors and awards, including the Fuchs Memorial Award in 2002, and KONA Award in 2007. He has coauthored more than 420 scientific papers, 120 review papers, 50 books/chapters, and 70 patents.