Preparation and microstructure of titanate nanowire thin films by spray Layer-by-Layer assembly method

Yoshikazu SUZUKI,*±,***,** Benoit P. PICHON,**±,*** Daniela D’ELIA,**± Christian BEAUGER*** and Susumu YOSHIKAWA

*Institute of Advanced Energy, Kyoto University, Uji 611-0011
**Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 ULP-CNRS, 23 rue du Loess, F67034, Strasbourg, France
***Ecole Européenne de Chimie, Polymères et Matériaux de Strasbourg (ECPM), Université Louis Pasteur, 25 rue Becquerel, F67087, Strasbourg, France

©2009 The Ceramic Society of Japan. All rights reserved.

Key-words: Layer-by-Layer (LbL) method, Titanate nanowire, Thin film, Spray technique, TALH, Hydrothermal synthesis, High-temperature X-ray diffraction (HT–XRD), Self assembly

[Received November 17, 2008; Accepted January 15, 2009]

Titanate and titania one-dimensional (1D) nanomaterials obtained by the hydrothermal method have attracted much attention since the innovative works by Kasuga et al. in 1998–1999. Titanate nanowires, with typically 10–50 nm in diameter and 300–10000 nm (or more) in length, can be also prepared by hydrothermal method similarly to titanate nanotubes, but at slightly higher temperatures (~150–170°C, whereas typically ~110–130°C for nanotubes) and/or within stronger basic conditions (in 10 M KOH or 15 M NaOH, whereas typically 10 M NaOH for nanotubes). At higher hydrothermal temperatures and/or stronger basic (corrosive) conditions, nanosheet-like intermediate (which form scrolled nanotubes) cannot exist stably, and hence, intrinsic one-dimensional oriented crystal growth of layered titanates becomes preferential. Titanate nanowires can be further converted into TiO2 (B) (a tunnel-structured TiO2 polymorph related to a bronze structure, Na2Ti6O13) nanowires or TiO2 anatase nanowires by ion-exchanging and post-heat treatment. The formation of titanate nanowires can be recognized as the “downsizing” of titanate microfibers, which were reported by Watanabe et al. in late 1970’s. These titanate and TiO2 nanowires generally have smaller specific surface area than titanate nanotubes; e.g., ~150 m²/g for hydrogen titanate nanowires, 30–80 m²/g for TiO2 nanowires and ~300 m²/g for hydrogen titanate nanotubes. However, the titanate and TiO2 nanowires have higher crystallinity (i.e., less defects) and higher thermal stability of 1D nanostructure. Hence, the titanate and TiO2 nanowires are suitable for photo-electro conversion applications, such as dye-sensitized solar cells (DSC) and photo-catalysts. Our recent study revealed that TiO2 nanowires (obtained from the post-heat treatment of hydrogen titanate nanowires) showed much better hydrogen production ability due to their higher crystallinity. In order to extend the application fields of these nanowires and other 1D nanomaterials, e.g., for electrodes, sensors, heterogeneous catalysts and so on, thin-film processing technologies must be established. In general, thin-film processing technologies tend to be required as rapid, precise (in nanometer order thickness), wide-area, homogeneous, low cost, and low environmental impact. Since the titanate and TiO2 1D nanomaterials are temperature-sensitive, an ambient temperature process is favored. Aqueous solution processes have high potential to fit these demands.

Layer-by-Layer self-assembly method (or LbL method) is a versatile coating process using aqueous solutions (or suspensions) with nanometer-scale controllability, which was firstly reported by Decher et al. in 1991. The LbL method, oppositely charged thin layers are alternately coated on a substrate. As for ambient aqueous solution processes, thin-films obtained by LbL method are generally strong due to the strong coulomb interaction. The LbL method was initially applied to charged molecules, and then, it was extended to polyelectrolytes and charged nanoparticles. The conventional LbL method is a kind of multilayer “dip-coating” in beakers, where spontaneous adsorption of charged materials is taking place, without using an external electromagnetic field. Thus, a disadvantage of the conventional LbL method could be a slow coating speed compared with other solution processes such as spin-coating. To solve the speed problem, an automated LbL method and a spray LbL method are recently developed. The spray LbL method uses alternate spraying (instead of alternate dipping) of aqueous solutions or suspensions. In this study, we have attempted to prepare titanate nanowire thin films by the spray LbL method. For the
For spray LbL instead of titanate nanowire suspension. A TiO2 anatase nanoparticle suspension was also prepared and used is much faster than the conventional LbL method. As a reference, each operation were 2 min, i.e., 1 cycle corresponds to 8 min. It approximated as (Na,H)2Ti3O7·H2O. After it was cooled down to room temperature, the precipitate stainless autoclave. The autoclave was heated at 150°C for 72 h. After it was cooled down to room temperature, the precipitate (approximately as (Na,H)2Ti3O7·H2O) was ion-exchanged with HCl aqueous solution, washed by distilled water repeatedly and then mildly dried, to obtain hydrogen titanate nanowires (approximated as H2Ti3O7·xH2O). H2Ti3O7 hydrogen trititanate, is one of the layered titanate family. Crystal structure of titanate nanowires was evaluated by powder X-ray diffraction. In order to know their thermal behavior and to compare with previous reports, a high-temperature X-ray diffractometer (Multiflex, Rigaku Co., Tokyo) operated at 40 kV and 40 mA (Cu Kα) up to 1000°C was used. The spray LbL method in this study was based on the report by Kim et al. on the colloidal TiO2 film processing via conventional LbL method. Hydrophilic, negatively charged glass substrates were obtained by 1 wt% KOH aq. treatment for 5 min and then rinsed with Milli-Q water (hereinafter, water). Titanate nanowire aqueous suspension (0.1 wt%, pH 2, adjusted by HCl) was sprayed on the negatively charged glass substrate, and then, rinsed with water. The titanate nanowire suspension was whitish, but rather stable. Then, similar spraying was carried out for titanium (IV) bis (ammonium lactato dihydroxide) aq., (TALH, 1 wt%, diluted from 50 wt% solution by Aldrich) and then rinsed with water. These coating procedures were repeated to prepare multilayer thin films up to 20 cycles. TALH is a stable double negatively charged inorganic precursor, having TiO6 octahedra structure similarly to layered titanate and TiO2 anatase, and it decomposes at > 100°C to form amorphous-like TiO2. Figure 1 depicts a schematic illustration of the spray-LbL method (modified from that of Izquierdo et al.). Intervals of each operation were 2 min, i.e., 1 cycle corresponds to 8 min. It is much faster than the conventional LbL method. As a reference, TiO2 anatase nanoparticle suspension was also prepared and used for spray LbL instead of titanate nanowire suspension. A commercial TiO2 colloidal sol (STS-01, Ishihara Sangyo Kaisha Ltd., ~30 wt% TiO2 in H2O) was diluted by water (0.1 wt%, pH 2, adjusted by HCl). This suspension was very stable and translucent, which indicates the homogeneous dispersion of TiO2 nanoparticles. The microstructure of thin films was evaluated by FE–SEM (JSM6500F, JEOL Ltd., Tokyo). Optical absorbance spectra of thin films was obtained by UV-Vis spectrometry (UV-2450, Shimadzu Co., Kyoto).

**Figure 2** demonstrates high-temperature X-ray diffraction patterns taken for as-synthesized titanate nanowires with elevating temperature. As can be seen in the as-synthesized pattern, a broad peak at around 2θ = 10° was found, which corresponds to the interlayer distance of a layered titanate structure. Furthermore, with increasing the heating temperature, the crystal structure changed into TiO2(B), anatase, and then rutile. Judging from the HT–XRD behavior, the as-synthesized nanowire (prepared in Mines ParisTech) can be identified as a layered titanate, the same as previous reports.

Hereinafter, the microstructure of spray-LbL thin films is described. At first, microstructure of TiO2 anatase thin films (reference) is shown in **Fig. 3**. Well-dispersed and homogeneous TiO2 nanoparticle thin films were obtained by the spray LbL method, in a similar manner as the conventional LbL method reported by Kim et al. The good dispersion and homogeneity in the films (even for a short processing time) are attributable to the narrow particle-size distribution and homogeneous dispersion of spherical-like TiO2 nanoparticles in the spray suspension, which facilitated the rearrangement of the nanoparticles on the substrate.

Then, microstructure of titanate nanowire thin films is shown in **Fig. 4**. As for the 1 cycle film, some short nanowires (with several hundred nm in length) were attached on the substrate, however, long nanowires were not frequently observed. With increasing LbL cycles, long nanowires (with several micrometers in length) can be frequently observed. This phenomenon is attributed to (1) increased opportunity of nanowires contacting to the substrate, and (2) TALH layers acting as nanometer order “glue” of the nanowires. Actually, small nanoparticles are also found in increased cycles, and they can be thought as the decomposition product of TALH (most probably as amorphous-like TiO2 or poorly crystallized anatase TiO2).

**Figure 5** shows optical absorbance spectra of (a) TiO2 nano-

---

**Fig. 1.** Spray Layer-by-Layer process in this study (modified form Ref. 18 by Izquierdo et al.). Intervals of each operation were 2 min, i.e., 8 min for 1 cycle.

**Fig. 2.** High-temperature powder X-ray diffraction patterns of titanate nanowire prepared by hydrothermal method. (Pt peaks were from sample stage).
particle and (b) titanate nanowire thin films. For both samples, absorbance at UV region increased with increasing spray cycles. The difference of absorbance between nanoparticles and nanowires can be attributable to the difference of coverage, which is in good agreement with SEM observation given in Figs. 3 and 4. Up to now, reports on nanowire coating by LbL methods are...
rare, because the spontaneous interaction between substrate and nanowires is not strong for “large” particles (dimensions of nanowires are nanometer scale in diameter, but typically micrometer scale in length). An exception is, for example, natural cellulose nanowire, which has highly flexible structure and plenty of surface OH groups. In this study, the titanate nanowires had linear shapes (see in Fig. 4) and a rather good dispersion state in a suspension. Once the titanate nanowires in this study adsorb on the substrate contacting on their side surface, due to their high linearity, contacting (adsorbing) area becomes large compared to curved nanowires. That is why the titanate nanowires can be coated even by rapid spray LbL method in this study. To facilitate the understanding, a schematic drawing of adsorption processes of nanoparticles and nanowires is given in Fig. 6. Detail properties of the titanate nanowire thin films will be reported in a forthcoming work.

In our preliminary study on titanate nanotubes (to form large secondary particles by strong agglomeration/aggregation), it is difficult to coat them by rapid spray-LbL method, even though the primary nanotube size is much smaller than that of titanate nanowires. For such nanomaterials, surface modification by surfactants or dendrimers might be effective to improve the dispersion state in spray suspensions.

Fig. 6. Schematic illustration of the adsorption of (a) nanoparticles and (b) nanowires.

Conclusion

1) Homogeneous thin films of TiO₂ anatase nanoparticles were obtained by rapid spray LbL method.

2) Titanate nanowires thin films were successfully prepared by spray LbL method. The adhesion of titanate nanowires to substrate under a rapid spray process was attributed to their linear morphology and good dispersion in the aqueous suspension.

Acknowledgments: A part of this work was financially supported by Grant-in-Aid for Scientific Research No. 19685020 For Young Scientist: Category A, French National Research Agency (ANR), and M.I.N.E.S Carnot Institute. This study was also supported by the Collaboration Agreement between Kyoto University and Université Louis Pasteur. The authors wish to thank Professor Yoichi Nakatani and his colleagues of JSPS Strasbourg Office and to the ULP–JSPS Joint Forum for starting up the collaboration study.

References

22) Y. Suzuki, B. P. Pichon, M. Grandcolas, N. Keller, V. Keller-Spitzer and S. Yoshikawa, unpublished work.