Incorporation of brownmillerite-type Ca_2FeCoO_5 ultrafine particles into macropores of TiO_2 nanotubular film by electrophoretic method

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Abstract: Ultrafine particles of the precursor of brownmillerite-type Ca_2FeCoO_5 were synthesized by a reverse micelle method, loaded on TiO_2 nanotubular film (TNT) by an electrophoretic loading (EPL) method in an acetone-ethanol mixture. The resultant Ca_2FeCoO_5/TiO_2 composite showed characteristic absorption band at <900 nm. The loading and hence morphology of Ca_2FeCoO_5 were controlled by the applied potential.

Keywords: Brownmillerite-type Ca_2FeCoO_5, TiO_2 nanotubular film, electrophoretic loading method.

1. Introduction

Incorporation of functional material in macroporous TiO_2 nanotubular film (TNT) has been attempted. For example, loading of CoO_x nanoparticles into TNT improved its photoelectrocatalytic activity for water splitting.[1] Also on Mn_3O_4/TNT, improved performance as a supercapacitor was observed.[2] However, most of these examples were those of incorporation of single oxides but not complex oxides. Various functions are found on complex oxides with variable compositions, but generally the complex oxide is formed in limited conditions. Therefore, it is valuable to find conditions to form complex oxide ultrafine particles in a porous material. We recently found high catalytic activity for oxygen evolution reaction on brownmillerite (BM)-type Ca_2FeCoO_5.[3] In this study, precursors of BM-type Ca_2FeCoO_5 were incorporated into the macropores of TNT by means of reverse micelle (RM) and electrophoretic loading (EPL) methods.

2. Experimental

Electropolished Ti sheets were anodized at 60 V for 22 minutes in ethylene glycol electrolyte containing 0.25 wt% NH_4F and 1 vol% H_2O. After calcination of the thus anodized substrate, anatase-type TNT with a pore diameter of about 60 nm and a thickness of about 3 μm was obtained.

RM-A solution was formed by mixing of hexaethyleneglycol nonylphenyl ether (NP-6), cyclohexane and an aqueous solution of metal nitrates (molar ratio of Ca:Fe:Co was 2:1:1). RM-B solution was formed by mixing of NP-6, cyclohexane and tetramethylammonium hydroxide (TMAH) solution. RM-A and B were mixed to obtain precursor particles of Ca_2FeCoO_5 in the RMs. Ethanol was added to the resulting RM solution to cleave the RMs, and the precursors were collected by centrifugation. Then, ethanol was added to them, stirred and centrifuged again. The treatment of ethanol was repeated 0 ~ 3 times. The obtained precursors were dispersed in ethanol containing 0.2 g/L I_2 and 2 vol% acetone, and the resultant mixture was used as the electrolyte for the EPL method. F-doped tin oxide (FTO) glass, TiO_2 nanoparticle film (TNP) coating on FTO glass and anodic TNT were used as working electrodes. The working electrode and FTO glass as a counter electrode were immersed into the precursor solution. The precursors were loaded on the working electrode at applied potentials of -2 ~ -10 V for 120 s. Finally, the resultant substrates were dried by compressed air to remove the excess solution and calcined at 600 °C in air for 0.5 hours.

3. Results and discussion

It has been reported that TaON nanoparticles were deposited on the electrode in acetone with I_2 at a negative potential; the particles were positively charged by addition of protons, which had been generated by iodoform reaction of acetone and I_2.[4] However, it was found that the precursors of Ca_2FeCoO_5 were not dispersed in the acetone-based solution. On the other hand, it was found that, in ethanol-based solution, the precursors were not loaded on the FTO substrate but kept dispersed in the solution. Therefore, we investigated the influence of mixing of acetone and ethanol. Finally, a mixture of acetone and ethanol with volume ratio of 1:49 was employed for EPL to load the precursors.

Figure 1 shows plots of electric charge density against the applied potential during EPL on a FTO substrate in the mixed solution. The charge density observed without ethanol treatment was much higher than those after the ethanol treatments of RM, implying that not only electrophoresis but also reductive decomposition of remained NP-6 occurred without the ethanol treatment. It tells us that more than twice repetition of ethanol treatment is necessary to deposit pure precursors of Ca_2FeCoO_5. The deposition of precursor on TiO_2 (TNP) was also observed.

Figure 2 shows scanning electron microscope (SEM) images of Ca_2FeCoO_5 loaded on TNT under the above established conditions. Ultrafine particles in nanometric dimension were observed not only on the surface of the TNT (Figure 2c and e) but also inside the pores, as shown by the area surrounded by red dashed line in Figure 2d and f. Increasing the applied voltage from -2 to -10 V resulted in the reasonable increase of Ca_2FeCoO_5 particles, but still the pores were not completely filled even at -10 V; the surface was covered. Thus, it has been indicated that the loading, coverage on the surface and extent of filling in the pores were controlled by the EPL voltage. Moreover, these dependences of the morphology of formed Ca_2FeCoO_5 on the voltage tell us that control of the structure is also able by adjusting the voltage.

Figure 3 shows ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectrum of Ca_2FeCoO_5/TNP (shown as a difference spectrum after subtraction of the spectrum of TNP). The Ca_2FeCoO_5/TNP showed a broad absorption band at <900 nm, whereas a mixture of Ca_2FeCoO_5 and TiO_2 showed no absorption. It is speculated that specific interaction between Ca_2FeCoO_5 and TiO_2 brought unique physicochemical nature reflected by the characteristic vis-NIR band. Thus, BM-type Ca_2FeCoO_5 should be formed on the substrates by the EPL and calcination.

4. Conclusions

Ultrafine precursors of BM-type Ca_2FeCoO_5 were loaded not only on TNP but also into the macropores of TNT by the EPL method. The composite Ca_2FeCoO_5/TiO_2 showed specific absorption of NIR and visible light. The loading and hence the morphology of Ca_2FeCoO_5 was controlled by the applied potential.

Acknowledgements

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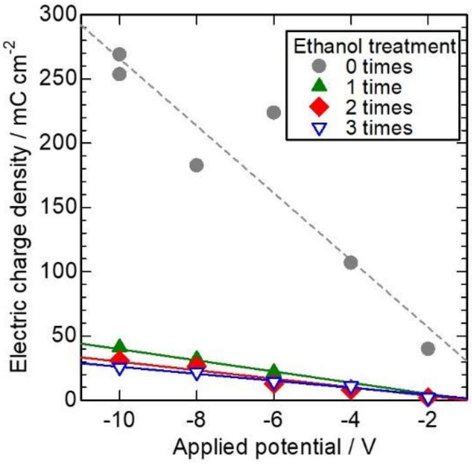

Figure 1. Plots of electric charge density against applied potential during EPL of the precursors on FTO substrate. Number of ethanol treatment of RM is shown.

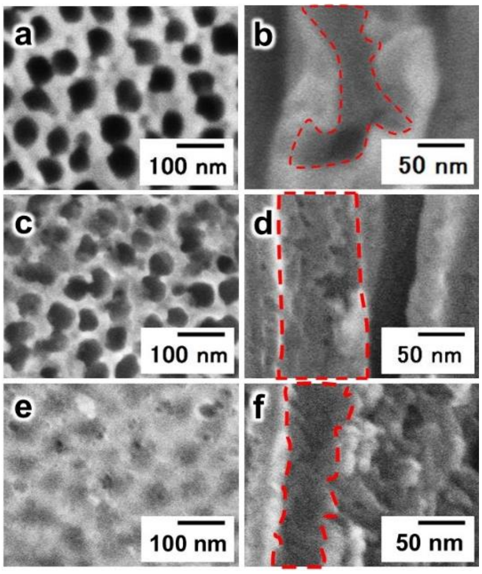

Figure 2. SEM images of the TNT before the EPL (**a**: top, **b**: cross-section) and after the EPL applied at -2 (**c**: top, **d**: cross-section) and -10 V (**e**: top, **f**: cross-section).

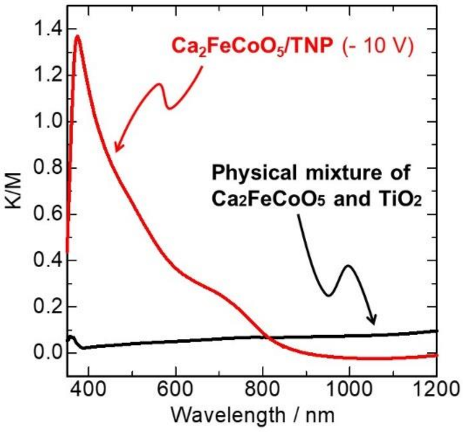

Figure 3. UV-vis-NIR absorption spectrum (difference spectrum after subtraction of spectrum of each support) of Ca_2FeCoO_5/TNP and physical mixture of Ca_2FeCoO_5 and TiO_2.