

Reverse Micelle Synthesis of Brownmillerite-type Oxide Ultrafine Particles on Titania

Kei Hira_o, Ryosuke Nanbu, Etsushi Tsuji,
Satoshi Suganuma, Naonobu Katada

Tottori Univ., Tottori, Japan

*E-mail: M16T4019M@edu.tottori-u.ac.jp

Photocatalytic water splitting has attracted much attention as producing of clean hydrogen. However, the efficiency of the reaction is not yet high enough to actual utilization. One of the reasons for low conversion efficiency is large overpotential for oxygen evolution reaction (OER). Thus, some researchers have improved OER activity by combination of semiconductors including photocatalysts and active OER catalysts as cocatalysts. It is well known that noble metal oxides such as RuO₂ and IrO₂ show high catalytic activity for OER [1]. On the other hand, more recently we found that brownmillerite (BM)-type Ca₂FeCoO₅ showed much higher OER activity than the noble metal oxides [2]. However, the Ca₂FeCoO₅ nanoparticles synthesized by the conventional method were too large to use as cocatalysts. Therefore, in this study BM-type Ca₂Fe_{2-x}Co_xO₅ (0 ≤ x ≤ 1) ultrafine particles were synthesized by reverse micelle method [3] on anatase TiO₂ nanoparticles.

Precursors of Ca₂Fe_{2-x}Co_xO₅ were synthesized in the reverse micelles using hexaethyleneglycol nonylphenyl ether as a surfactant. Then, the precursors were loaded on anatase-type TiO₂ nanoparticles and calcined at 600 °C for 5 h in the air.

Fig. 1 shows XRD patterns of resulting samples with various Co/Fe ratios. All samples showed XRD patterns of BM-type Ca₂Fe_{2-x}Co_xO₅ and anatase TiO₂. Inset figure in Fig. 1 shows enlarged main peak of Ca₂Fe_{2-x}Co_xO₅. A shoulder peak at 32.8 ° shifts into a higher angle with increasing cobalt (x), implying that the Co/Fe ratio contained in the products increased with increasing that in the starting solutions. SEM-EDS analysis showed that the ratios in all samples were almost consistent with those of the starting solutions. Fig. 2 shows a TEM

image of 10 wt% Ca₂FeCoO₅/TiO₂. There are spherical Ca₂FeCoO₅ ultrafine (about 5 nm) particles on TiO₂ nanoparticles. In contrast, in the case of calcination without TiO₂, Ca₂FeCoO₅ particles were grown up to about 30 nm because of aggregation. These results suggest that interaction between the precursors and TiO₂ nanoparticles established before calcination was effective to keep the extremely small particles of Ca₂FeCoO₅.

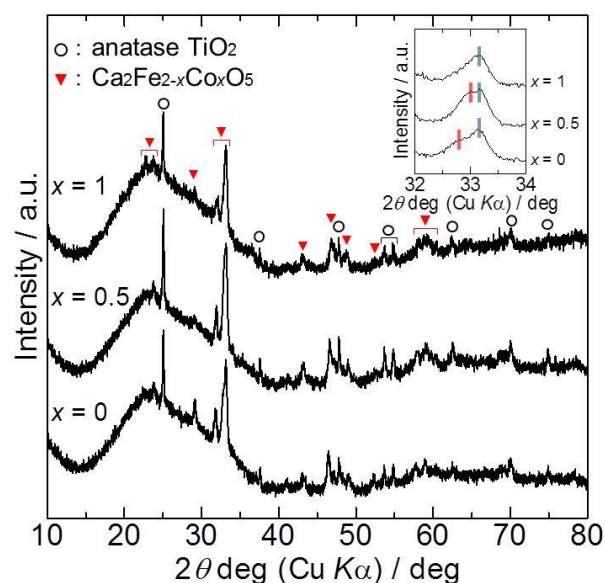


Fig. 1 XRD patterns of Ca₂Fe_{2-x}Co_xO₅/TiO₂ (0 ≤ x ≤ 1).

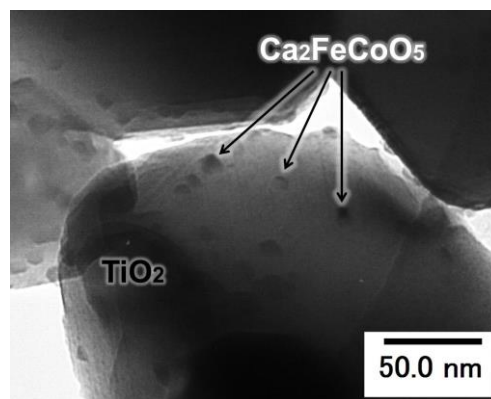


Fig. 2 TEM image of Ca₂FeCoO₅/TiO₂.

A part of this study was funded by the Iwatani Naoji Foundation and JSPS Grants-in-Aid for Young Scientists (B) (No. 16K17968).

REFERENCES

- [1] J. Yang, D. Wang, H. Han and C. Li, *Acc. Chem. Res.*, **46**, 1900 (2013).
- [2] E. Tsuji, H. Motohashi, H. Habazaki, H. Noda and T. Takeguchi, PCT/JP2015/52649 (2015).
- [3] M. Yuasa, N. Yamazoe and K. Shimano, *J. Electrochem. Soc.*, **158**, A411 (2011).