Observation of Deuterated Double-Perovskite Hydroxide CoSn(OH)6 Nanocubes

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Observation of Deuterated Double-Perovskite Hydroxide $CoSn(OH)_6$ Nanocubes

Menuka Adhikari[1], Starfari T. McClain[1], Rekha George[1], Sivasankara Rao Ede[1], Hui Wu[2], William D. Ratcliff[2], Liurukara Sanjeewa[3], Cheng Li[4], and Zhiping Luo[1,*]

[1]*Department of Chemistry, Physics and Materials Science, Fayetteville State University, Fayetteville, North Carolina, United States*
[2]*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland, United States*
[3]*University of Missouri Research Reactor, University of Missouri, Columbia, Missouri, United States*
[4]*Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States*

*Corresponding author: zluo@uncfsu.edu

Electrochemical water splitting is considered as one of the most viable, effective and eco-friendly approaches in renewable energy conversion and storage. The oxygen evolution reaction (OER) is one of the critical reactions and this reaction is kinetically sluggish because of its complex four-electron transfer. Currently, IrO_2 and RuO_2 are serving as the most effective OER catalysts; however, the cost associated with these noble-metal catalysts curtails the scalability of this technology [1, 2]. Hence, it is of great scientific and technological importance to find highly efficient catalysts from earth-abundant materials.

Perovskites possess diversified structures with tunable properties [3]. Perovskite-related transition metal-based catalysts have drawn significant interests of the scientific community because of their low cost, earth abundance, and excellent electrochemical properties. Specifically, cobalt-based catalysts such as perovskite oxide $SrCoO_3$, $CaCoO_3$, double perovskite $PrBaCo_2O_{5+\delta}$, double perovskite hydroxide $CoSn(OH)_6$, and spinel Co_3O_4 have been explored as excellent OER catalysts for electrochemical water splitting. Song et al. tuned the electrochemical property of $CoSn(OH)_6$ nanomaterials by creating nanoporous structures *via* selective electrochemical etching process [4]. They have found that initiation of etching process due to presence of crystal defects because of oxygen vacancies; while electronic doping effect of Co in this compound was not yet further identified.

In this research, we study the crystalline and electronic structures of $CoSn(OH)_6$ for high OER performance. To use neutron powder diffraction (NPD) to experimentally determine the atomic positions, it is needed to replace hydrogen (H) with deuterium (D).

The $CoSn(OH)_6$ nanocubes were synthesized by taking 1.5:2 molar mixture of $Co(NO_3)_2{\cdot}6H_2O$ and $Na_2SnO_3{\cdot}3H_2O$. The precursor sodium stannate $Na_2SnO_3{\cdot}3H_2O$ is hydrous, and its X-ray diffraction (XRD) pattern is shown in Fig. 1a. A pure product of $CoSn(OH)_6$ was obtained, and the SEM image is shown in Fig. 2a, with defined cubic shape and uniform size distribution. To synthesize deuterated sample, we could use anhydrous $CoCl_2$, while anhydrous sodium stannate is not commercially available. We calcinated the hydrous precursor at a high temperature of 800 °C for 16 h. Although it is almost thoroughly transformed to Na_2SnO_3 as shown in Fig. 1b, a small peak composed of (101)/(003) of the hydrous phase at 18.7° could not be eliminated, possibly due to the reversed transformation during cooling by absorbing moisture from the atmosphere. Further work is needed to completely eliminate the H for NPD. Using the near anhydrous sodium stannate as the precursor, the synthesized $CoSn(OD)_6$ nanoparticles are shown in Fig. 2b. They are still in the form of nanocubes, though in a smaller size [5].

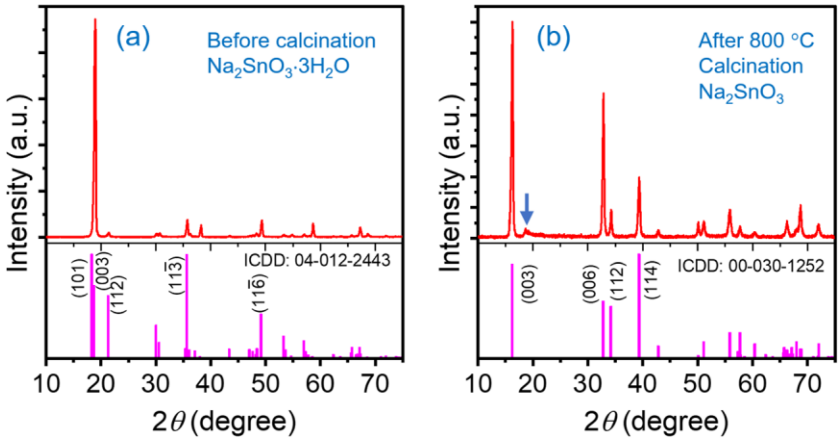

Fig. 1. XRD patterns of hydrous sodium stannate precursor before (a) and after calcination (b).

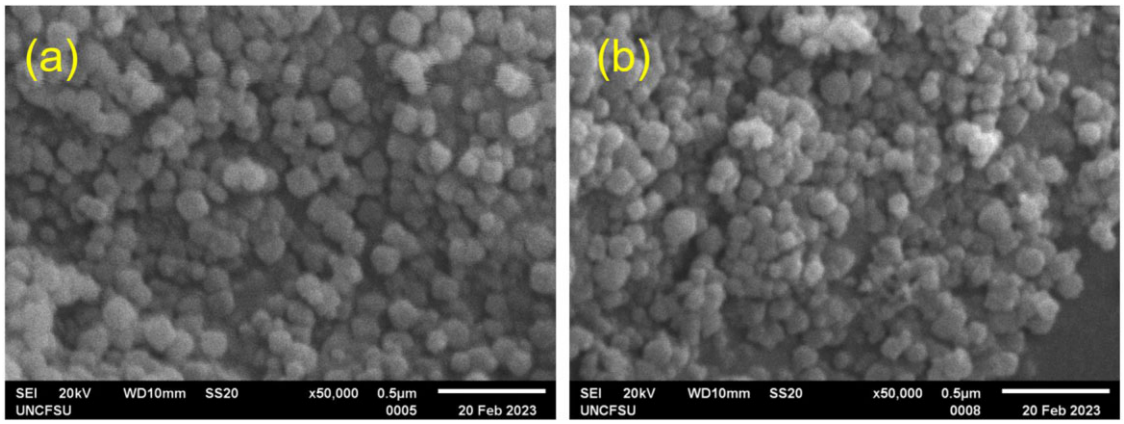

Fig. 2. SEM image of $CoSn(OH)_6$ (a) and $CoSn(OD)_6$ (b) nanoparticles.

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