F-4-01 (Invited)
Extended Abstracts of the 2019 International Conference on Solid State Devices and Materials, Nagoya, 2019, pp273-274

2D Oxide and Hydroxide Nanosheets: Synthesis, Layer-by-Layer Assembly and Function Design

Takayoshi Sasaki, Yasuo Ebina, Nobuyuki Sakai, Renzhi Ma and Minoru Osada

International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS)
1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
Phone: +81-29-860-4313 E-mail: sasaki.takayoshi@nims.go.jp

Abstract

We have synthesized a variety of oxide and hydroxide nanosheets by delaminating layered compounds into single layers. Then solution-based processes were applied to organize resulting colloidal nanosheets layer-by-layer into nanofilms and bulk-scale composites. Useful functions associated with superior electronic, magnetic, optical and catalytic properties were developed through the selection of suitable nanosheets and nanostructure design from them.

1. Introduction

Atomically or molecularly thin two-dimensional (2D) materials have attracted enormous attention due to their unique structures and physicochemical properties. Intensive investigations in the last two decades have succeeded in isolation and production of a wide variety of 2D materials as exemplified by graphene, transition metal chalcogenides, oxides, hydroxides, MXenes and CONASHs and so on.

Our group has developed a unique class of 2D oxide and hydroxide nanosheets from appropriate layered compounds as a precursor by inducing their massive swelling and subsequent exfoliation [1,2]. Through such soft-chemical processes, we obtain a colloidal suspension, in which 2D nanosheets are monodispersed. These nanosheets can be synthesized in wide varieties of composition and structure, leading to a range of attractive properties. Thus, these nanosheets are useful as a building block to construct "artificial lattice systems" with a tailored nanoarchitecture by applying various solution-based processes. In this presentation, the recent progress of our study on oxide and hydroxide nanosheets is overviewed.

2. Synthesis of 2D Oxide and Hydroxide Nanosheets

We synthesized layered metal oxides and hydroxides as a precursor of nanosheets via various synthetic techniques such

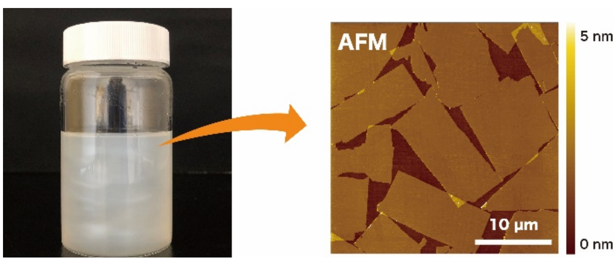

Fig. 1 Colloidal suspension of nanosheets and the AFM image for $Ca_2Nb_3O_{10}$ as an example

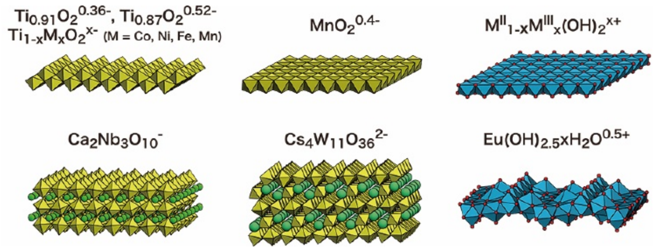

Fig. 2 Typical oxide and hydroxide nanosheets

as solid-state calcination, flux-growth and homogeneous precipitation. The layered compounds were treated with aqueous amine solutions or organic solvents, which induces enormous interlayer expansion. Permeation of a large volume of the solutions or solvent props open the interlayer gallery to over one hundred folds of the initial spacing [3]. With mechanical agitation, such highly swollen layered crystals could be disintegrated into individual single layers, or molecularly thin 2D crystals, extending laterally up to several tens of micrometers (Fig. 1). Figure 2 depicts typical 2D oxide and hydroxide nanosheets reported so far, having a diverse range of composition and structure. Ti or Nb oxide nanosheets of $Ti_{1-\delta}O_2$ and $Ca_2Nb_3O_{10}$ work as a wide-gap semiconductor, showing photocatalytic and dielectric properties, while Mn- or W-based nanosheets such as MnO_2 and $Cs_4W_{11}O_{36}$ show redox activity and chromic property. Hydroxide nanosheets also show various useful properties, depending on their composition and structure.

2. Layer-by-Layer Assembly of Nanosheets

The oxide and hydroxide nanosheets are negatively and positively charged colloidal 2D crystals, respectively, that are monodispersed in solutions. Thus, we can apply solution-based processes such as electrostatic self-assembly and Langmuir-Blodgett (LB) deposition to assemble the nanosheets onto a substrate [1,2]. Monolayer coverage of neatly tiled nanosheets could be attained under optimized conditions and its repetition yielded highly organized multilayer films (Fig. 3). In addition, we recently demonstrated that spin-coating of DMSO suspension could produce monolayer and multilayer films of various nanosheets, providing a facile and scalable route [4]. These techniques enable to tailor complex nanostructures such as superlattice films via layer-by-layer deposition of multiple nanosheets, which is effective to design advanced and sophisticated functionalities.

Besides the nanofilms, we could produce superlatticelike

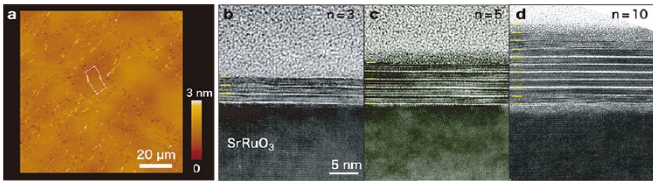

Fig. 3 a: AFM image of a monolayer film of $Ca_2Nb_3O_{10}$ nanosheets fabricated on a $SrRuO_3$ substrate by LB method, b-d: cross-sectional TEM images of multilayer films (n =3, 5, 10)

composites of two nanosheets at bulk-scale by controlling their surface charges and subsequent mixing. Opposite charged nanosheets spontaneously underwent alternately restacking to yield a flocculate-like superlattice material [5].

3. Function Design

Various functions can be designed with nanofims and flocculate composites of nanosheets. We assembled Ti- or Nb-based oxide nanosheets into multilayer films on a $SrRuO_3$ substrate by LB method and then deposited gold on top of the film. The fabricated MIM device showed superior dielectric properties even at a very small film thickness of ~10 nm (Fig. 4) [6], where other high-k materials do not show good performance. The room-temperature deposition without need of post annealing realized very sharp and clean interface between the nanosheet film and the substrate, contributing to this superior high-k property..

Superlattice films of two kinds of nanosheets can produce sophisticated and advanced functions through the synergistic interaction between them [7]. We have shown that ferroelectric response was evolved by depositing two dielectric nanosheets, e. g., $LaNb_2O_7/Ca_2Nb_3O_{10}$ and $Ti_{0.87}O_2/Ca_2Nb_3O_{10}$. Furthermore, combination of dielectric $Ca_2Nb_3O_{10}$ and ferromagnetic $Ti_{0.8}Co_{0.2}O_2$ nanosheets brought out unique multiferroic function at room temperature [8].

The flocculated superlattice composites were found to work as superior active materials for energy storage and efficient electrocatalysts. The superlattice flocculate of MnO_2/rGO showed a very large electrochemical capacity of 1325 $mAhg^{-1}$ at a current density of 0.1 A g^{-1} and 370 $mAhg^{-1}$ even at a fast discharging of 12.8 A g^{-1}[9]. Furthermore, the material showed excellent cycling stability over 5000 times. Confinement of MnO_2 nanosheets between the carbon network of rGO enables the stable cycling of the conversion reaction of the oxide to metal. Similarly, hydroxide nanosheets showed superior electrochemical and catalytic properties when combined with rGO into a superlattice material [7]. The composite of $Co_{2/3}Ni_{1/3}(OH)_2$/rGO showed high energy storage performance, which is the combination of double layer capacitance from rGO and redox process from the hydroxide. On the other hand, the heteroassembly of $Ni_{2/3}Fe_{1/3}(OH)_2$/rGO showed highly efficient OER activity with a very small overpotential of 0.21 V, which is comparable to noble metal electrodes.

4. Conclusions

Delamination of layered metal oxides and hydroxide

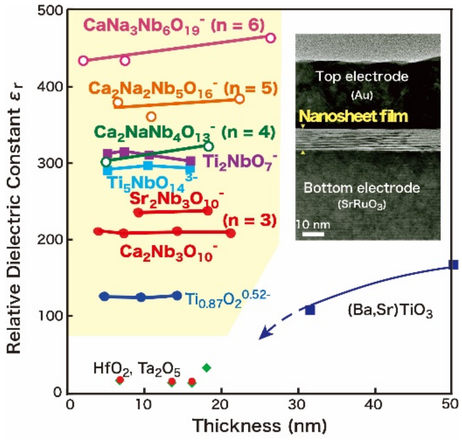

Fig. 4 Relative dielectric constant of oxide nanosheets

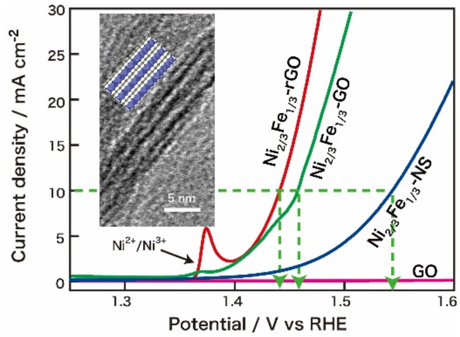

Fig. 5 OER activity of superlattice composites of hydroxide nanosheets and GO or rGO

could produce molecularly thin 2D nanosheets monodispersed in a solution. These nanosheets could be assembled layer-by-layer into precisely organized multilayer and superlatticelike assemblies. A range of useful functionalities have been designed based on the nanosheets as a building block and the nanoarchitectures from them. We have a number of nanosheets and their combination is practically limitless. Thus we expect that we can develop more advanced materials and devices through nanoarchitectonics with 2D nanosheets.

References

[1] R. Ma and T. Sasaki, *Adv. Mater.* **22**, (2010) 5082.
[2] L. Z. Wang and T. Sasaki T. *Chem. Rev*. **114**, (2014) 9455.
[3] F. Geng, R. Ma, Y. Ebina, Y. Yamauchi, N. Miyamoto, T. Sasaki, *J. Am. Chem. Soc*. **136**, (2014) 5491.
[4] K. Matsuba, C. Wang, K. Saruwatari, Y. Uesusuki, K. Akatsuka, M. Osadam Y. Ebina, R. Ma, T. Sasaki, *Sci. Adv*. **3**, e1700414 (2017).
[5] X. Cai, T. C. Ozawa, A. Funatsu, R. Ma, Y. Ebina, T. Sasaki, *J. Am. Chem. Soc*. **137**, (2015) 2844.
[6] M. Osada and T. Sasaki, *Adv. Mater*. **24**, (2012) 210.
[7] R. Ma and T. Sasaki, *Acc. Chem. Res.* **48**, (2015) 136.
[8] B. W. Li, M. Osada, Y.-H. Kim, Y. Ebina, K. Akatsuka, T. Sasaki, *J. Am. Chem. Soc*. **139**, (2017) 10868.
[9] P. Xiong, R. Ma, N. Sakai, T. Sasaki, *ACS Nano* **12** (2018) 1768.