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Oxide nanosheets and their assemblies for new ceramic joining and smart processing†

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1. Introduction

Two-dimensional (2D) nanosheets obtained *via* exfoliation of layered compounds have attracted intensive research in recent years [1]. These 2D nanosheets, which possess nanoscale dimensions only in thickness and have infinite length in the plane, are emerging as important new nanomaterials due to their unique properties. Research in such exotic 2D systems recently intensified as a result of emerging progress in graphene (carbon nanosheet) [2] and novel functionalities in transition-metal-oxide nanosheets [1]. In particular, oxide nanosheets are exceptionally rich in both structural diversity and electronic properties, with potential application in areas ranging from catalysis to electronics. Now, by using of the exfoliation approach, it is possible to investigate dozens of different 2D oxide nanosheets in search of new phenomena and applications.

Here, we present the current status of research on oxide nanosheets. Particular focus is placed on recent progress that has been made in the synthesis, characterization and properties of oxide nanosheets, highlighting new ceramic joining and smart processing for electronic applications.

2. Synthesis of functional nanosheets

A variety of oxide nanosheets (such as $Ti_{1-\delta}O_2$, MnO_2 and perovskites) were synthesized by delaminating appropriate layered precursors ($Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$, $K_{0.45}MnO_2$ and $KCa_2Nb_3O_{10}$) into their molecular single sheets (**Fig. 1**) [1].

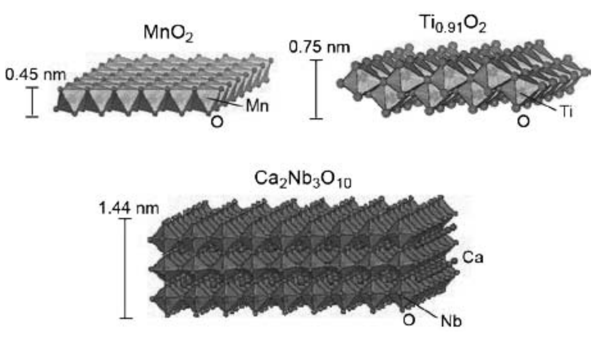

Fig. 1 Structures of oxide nanosheets.

The formation of unilamellar nanosheets was confirmed by direct observation with atomic force microscopy (AFM) and transmission electron microscopy (TEM). **Figure 2** depicts an AFM image for $Ti_{0.91}O_2$ nanosheet. This image clearly reveals a sheet-like morphology, which is inherent to the host layer in the parent compound. The thickness is ~1 nm, which is comparable to the crystallographic thickness of the host layer in the corresponding parent compounds. This supports the formation of unilamellar nanosheets. Such an exfoliation process is quite general: the exfoliation of the other layered host compounds proceeds in a similar fashion.

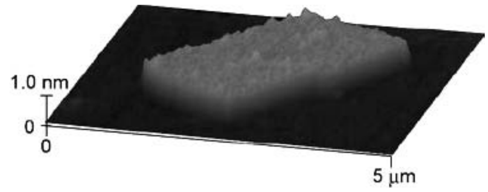

Fig. 2 AFM image for $Ti_{0.91}O_2$ nanosheet on a Si substrate.

3. Ceramic joining and smart processing using nanosheets

One of the most important and attractive aspects of the exfoliated nanosheets is that various nanostructures can be fabricated using them as 2D building blocks (**Fig. 3**) [1]. Oxide nanosheets have an extremely high 2D anisotropy of the crystallites. In addition, these nanosheets are obtained as negatively charged crystallites that are dispersed in a colloidal suspension. These aspects make the nanosheets a suitable building block for new ceramic joining technology and smart processing of nanostructured films and advanced nanodevices.

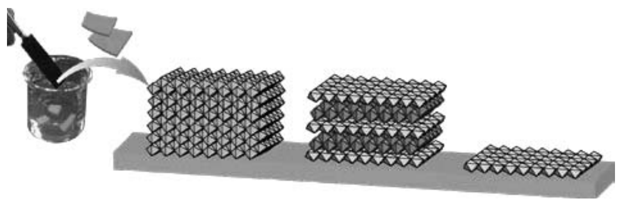

Fig. 3 Schematic illustration of ceramic joining and smart processing using nanosheets.

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One of the highlights is the fabrication of nanocomposite films of organic polymer/nanosheet materials that exhibit useful properties. The electrostatic layer-by-layer (LbL) self-assembly *via* sequential adsorption [3] and Langmuir-Blodgett (LB) procedure [4] are effective for this purpose. Sequential LbL assembly, often called "molecular beaker epitaxy", is one of the most powerful methods of fabricating nanostructured multilayer films with precisely controlled composition, thickness and architecture on a nanometer scale. **Figure 4** depicts an example of a multilayer film of perovskite nanosheets on a $SrRuO_3$ substrate. This TEM image clearly reveals a stacking structure corresponding to the LbL assembly of nanosheets.

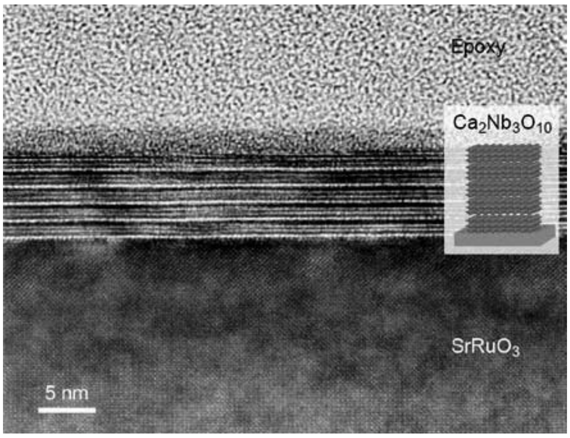

Fig. 4 Cross-sectional high-resolution TEM image of a 5-layer (7.5 nm thick) $Ca_2Nb_3O_{10}$ film on a $SrRuO_3$ substrate.

A clear benefit of these LbL approaches is the interface engineering, which appears to be a key step in the design of film properties. Physical methods such as vapor deposition and laser ablation are currently the main methods of fabricating oxide films. These techniques, however, usually require a complex and difficult deposition process involving high-temperature postannealing (>600°C), which can cause degradation in the film-substrate interface arising from both nonstoichiometry and thermal stress. The bottom-up fabrication using oxide nanosheets provides new opportunities for room-temperature fabrication of oxide thin films, while eliminating integration problems encountered in current film-growth techniques. Such LbL assembly is also expected to have great potential for advances in new ceramic joining technology.

4. Applicatioins to nanoelectronics

LbL assembly of various nanosheets allows us to tailor superlattices or heterostructures by tuning the number of nanosheets and their stacking sequences (Fig. 3) [6]. Sophisticated functionalities or nanodevices may be designed with LbL assemblies through the selection of nanosheets and combining materials, and precise control over their arrangement at the molecular scale. We utilized oxide nanosheets as a building block in a solution-based bottom-up assembly, and successfully developed various functional nanofilms such as high-*k* dielectrics [7-9], field effect transisters [1], ferromagnetic semiconductors [10,11], magneto-optical films [6,12,13], resistance switching memories [14], etc.

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