Exfoliation of Layered Transition Metal Oxides:
Formation of Functional Oxide Nanosheets and Their Applications

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ABSTRACT

Unilamellar two-dimensional crystallites of transition metal oxides, $\text{Ti}_{0.91}\text{O}_2$, $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ and $\text{MnO}_2$, have been derived by delaminating layered host precursors via intercalation of quaternary ammonium ions. The nanosheets are characterized by their high two-dimensional anisotropy with a molecular thickness, and this structural feature yields novel physicochemical properties. A range of useful nanostructured materials can be fabricated by organizing these nanosheets as a building block through various wet processes. Flocculation induced by the addition of appropriate cationic species can produce restacked lamellar aggregates, through which functional materials, e.g. porous or fluorescent materials, can be designed by the selection of the nanosheets and combined flocculating agents. The sequential adsorption procedure via electrostatic self-assembly can be employed to deposit the nanosheets layer-by-layer with polycations, which can lead to multilayer ultrathin films and hollow nanospheres.

Key words: Exfoliation, Nanosheet, Building block, Flocculation, Layer-by-layer assembly

BACKGROUND

It is well-known that smectite clay minerals spontaneously undergo exfoliation upon contact with aqueous media.1) This peculiar reactivity has invited a wide range of applications, one of such most important which is the synthesis of clay-polymer nanocomposites. In the last decade, delamination of layered host materials other than clay minerals has attracted much interest. Various soft-chemical procedures have been successfully used to achieve the exfoliation of a number of layered compounds. Complete exfoliation produces unilamellar crystallites, which correspond to individual host layers. These nanosheets have interesting and attractive features as a new class of nanoscale materials. The thickness is generally around 1 nanometer while the lateral size is usually of micrometer order. The sheet can be regarded as a two-dimensional crystal, in which constituent atoms regularly arrange themselves. These unusual structural aspects with exceedingly high two-dimensional anisotropy lead to novel physicochemical properties, which cannot be attained with bulk materials.

Several groups including our laboratory have synthesized functional oxide nanosheets such as $\text{Ti}_{0.91}\text{O}_2$, $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ and $\text{MnO}_2$ by delaminating appropriate layered precursors.2-7) The former two materials are characterized by the semiconducting nature and the latter is by its redox capability. More interestingly, the nanosheets are obtained in the form of a colloidal suspension, and, therefore, solution-phase synthetic techniques can be applied to fabricate novel nanostructured materials using them as a building block. We have demonstrated the synthesis of various useful materials including multilayer ultrathin films and hollow oxide nanoshells. This review paper describes mainly our recent results on these nanosheets and their applications.

SYNTHESIS OF OXIDE NANOSHEETS AND THEIR CHARACTERIZATIONS

The oxide nanosheets, $\text{Ti}_{0.91}\text{O}_2$, $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ and $\text{MnO}_2$, were obtained by delaminating layered transition metal oxides of $\text{Cs}_{0.7}\text{Ti}_1.825\square_{0.175}\text{O}_4$ ($\square$: vacancy), $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and $\text{K}_{0.45}\text{MnO}_2$, respectively, the crystal structure of which are illustrated in Figure 1. These materials can be synthesized via conventional solid-state calcination at high temperatures. In the first step, the layered materials were converted into protonated forms by treating them with an acid solution. The interlayer alkali metal ions can be completely removed by repeating the treatment several times while the layered structures are preserved. In the second step, the resulting protonic oxides, $\text{H}_{0.7}\text{Ti}_1.825\square_{0.175}\text{O}_4\cdot\text{H}_2\text{O}$, $\text{HCa}_2\text{Nb}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ and $\text{H}_{0.17}\text{MnO}_2\cdot\text{H}_2\text{O}$, were reacted with a solution containing tetrabutylammonium (TBA) ions.
Figure 1. Crystal structures of layered host materials as a precursor of functional oxide nanosheets. (a) Ca₂T₂O₇[O₁₋₂(T₂O₄) (square vacancies), (b) K₄.8MnO₂, (c) KCa₂Nb₃O₁₀

Translucent colloidal suspensions were produced as a result of the reaction.

X-ray diffraction (XRD) study on a colloid centrifuged from the suspension indicated a high degree of swelling giving an intersheet separation of several nanometers or larger, as exemplified for the layered titanate, H₀.₇₇T₁₈₂O₁₇₅H₂O (Figure 2). Under a particular range of TBA concentration, sharp basal diffraction lines disappeared and were replaced by a broad profile. The other two layered materials also showed a broad pattern, which was characteristic of each host.³,⁷,⁸) The broad profiles observed were very similar to the square of structure factor calculated based on a layer architecture of each compound. This agreement can be taken as strong evidence for the complete delamination, because the square of the structure factor should represent a profile based on X-ray scattering from independent oxide sheets. The sheets are not stacked in parallel to induce interference, but they are present as individual entities.

More direct evidence can be obtained by observations by transmission electron microscope (TEM) and atomic force microscope (AFM), which visualize sheet-like objects. The thickness estimated from AFM images was ≈1.1 nm, ≈0.8 nm, ≈2.0 nm for the nanosheets of Ti₀.₈₁O₂, Ca₂Nb₃O₁₀ and MnO₂, respectively, clearly demonstrating their unilamellar nature. Their lateral size generally reflected the original size of the precursor crystals, usually in a range of micrometers. Electron diffraction data collected from one sheet was composed of sharp spots, indicating the single-crystal quality.⁹,¹⁰) The symmetry was compatible with that of the host layer in the precursors, indicating that the two-dimensional atomic arrangements remained basically unchanged.

PHYSICOCHEMICAL PROPERTIES

The nanosheets of Ti₀.₈₁O₂ and Ca₂Nb₃O₁₀ showed semiconducting properties. For example, the Ti₀.₉₁O₂ nanosheet generated photocurrent upon exposure to UV light. A detailed analysis of the action spectrum led to 3.8 eV as a bandgap energy, which is larger than that (3.2 eV) of bulk TiO₂ (anatase).¹¹) The larger bandgap may be ascribed to size-quantization effects. On the other hand, the MnO₂ nanosheet exhibited feasible redox capability. Manganese ions in the nanosheet can be electrochemically switched between 3+ and 4+ in response to a potential sweep.¹²)

FABRICATION OF NANOSTRUCTURED MATERIALS USING NANOSHEETS AS A BUILDING BLOCK

The nanosheets were obtained as molecular entities dispersed in the colloidal suspension. They can be assembled or organized in various fashion to produce nanostructured materials by applying so-called wet-process synthetic techniques. In addition, they can be mixed with a range of foreign materials at a nanometer scale range to yield nanocomposites. We have reported the synthesis of various functional materials through these synthetic routes such as flocculation and layer-by-layer assembly.

Flocculation

Addition of electrolytes into the nanosheet suspension gave rise to restacking of the nanosheets trapping cationic species present in the solution. Lamellar nanocomposite materials can be easily synthesized through this approach. For example, rare earth (RE) ions can be incorporated between the gallery of Ti₀.₉₁O₂ nanosheets simply by mixing the nanosheet suspension and a solution containing RE ions.¹³) XRD measurement confirmed the formation of a lamellar structure (Figure 3). Two basal 0k0 peaks indicated a gallery height of 1.06 nm, which is compatible with the accommodation of hydrated RE ions. Heavy doping of RE ions, ≈10 mol%, was confirmed by chemical analysis. Note that direct intercalation into the bulk layered titanate cannot attain this high level of RE incorporation. The obtained restacked material showed intense characteristic emission from RE ions by exciting Ti₀.₉₁O₂ nanosheets with UV light.

The energy absorbed by the semiconducting nanosheets is...
effectively transferred to excited states of 4f orbitals for RE ions, which relax to the ground state, emitting bright red light. The material had a higher thermal stability and mechanical strength in comparison with well-known RE complexes with organic ligands such as β-diketone.

Pillaring of layered materials with polyoxocations, e.g., aluminum Keggin ion, has been investigated extensively to convert them into microporous materials.14,15 The synthetic route usually involves intercalation of polyoxocations into a layered compound followed by calcination at 400–500°C. In contrast to this conventional route, we recently found that restacking of the nanosheets with aluminum Keggin ions resulted in a new pillared structure, in which polyoxocations were arranged in double layers.16,17 This unique structure enhanced the specific surface area and porosity in comparison with conventional materials with monolayer of pillars. The structure evolution may be understood by adsorption of polyoxocations on both sides of the nanosheets and subsequent aggregation of such a unit.

In addition to the examples above, the combination of nanosheets and cationic guest species can be designed to create a range of nanocomposites, which may be useful, for example, as a photocatalyst18 and an electrode material.19

Layer-by-Layer Assembly

One of the most important achievements among material syntheses with nanosheets is the layer-by-layer deposition of the nanosheets to fabricate nanosheet ultrathin films. A simple but powerful technique via sequential adsorption of oppositely charged species first developed by Decher for polymer films20 is applicable to the oxide nanosheets, as first demonstrated with delaminated sheets of clay minerals and α-zirconium phosphate.21,22 A multilayer assembly can be built up by alternately dipping a substrate in the colloidal suspension of nanosheets and an aqueous solution of cationic polymer, e.g., poly(diallyldimethylammonium) chloride (PDDA). Figure 4 depicts UV-visible absorption spectra in the buildup process of the nanosheets and organic polymer. Other characterizations by ellipsometry, FT-IR and AFM all provide support for the growth of ultrathin nanocomposite films. This sequential adsorption procedure can control the thickness of ultrathin films with nanometer precision. The resulting composite films can be converted into inorganic films by removing polymer via heating and UV irradiation.23 These ultrathin films are expected to have various applications depending on the constituent nanosheets and film architecture. For example, the films of TiO2 nanosheets may be useful as a UV-shielding or self-cleaning coating due to their high UV absorption capability and photochemical reactivity. Furthermore, we expect that the layer-by-layer procedure can be used to tailor superlattice-like assemblies with a complex structure, through which their function can be designed.

Recently Caruso et al. have reported the synthesis of core-shell particles by depositing nanoparticles onto micron-sized polymer beads via the LBL self-assembly procedure, and hollow shells by decomposing the polymer core.23 One of the noteworthy features of the nanosheets is their highly flexible mechanical characteristics, making them ideal for shell buildup. They can cover spherical polymer beads like a wrapping paper.24,27 Figure 5a shows scanning electron microscope (SEM) images of polystyrene beads after coating with 20 bilayers of TiO2 nanosheet and cationic polymer. Although UV-visible and XRD data indicated successful multilayer buildup, the presence of the nanosheets...
was nearly invisible by SEM observations, suggesting that they were adsorbed smoothly and replicated the spherical shape. The resulting core-shell composites can be converted into hollow nanoshells by removing the polymer core by gentle heating at 500°C. A transmission electron microscope (TEM) image shown in Figure 5b clearly demonstrates the complete removal of the core. The shell thickness was found to be nearly equal to the sum of the nanosheet thickness. In other words, the shell thickness can be controlled in step of 1 nm. These novel hollow oxide nanoshells may find application as microcapsules.

CONCLUSION

Exfoliation reactions have opened a new field for layered host materials. Bulk layered compounds are separated into individual molecular entities, nanosheets, which can be taken as a new class of nanoscale materials, exhibiting interesting properties. More importantly, a range of nanostructured materials in the form of ultrathin films, hollow nanoshells and lamellar aggregates can be fabricated by employing the nanosheets as a building block.

REFERENCES