Exfoliation of Dion-Jacobson Layered Perovskite into Macromolecular Nanoplatelet

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A layered perovskite of Dion-Jacobson phase, $RbLaTa_2O_7$, was successfully exfoliated into colloidal suspension *via* successive ion-exchange and intercalation reaction. The pristine perovskite $RbLaTa_2O_7$ was synthesized by conventional solid-state reaction, and then, it was ion-exchanged with hydrochloric acid to obtain a protonic form of perovskite. The resulting proton-exchanged perovskite was reacted with ethylamine to increase interlayer spaces for further intercalation reaction. Finally, the ethylamine-intercalated form was exfoliated into nanosheets *via* an intercalation of bulky organic cations (tetrabutylammonium). According to X-ray diffraction (XRD) analysis, the TBA-intercalated form showed remarkably increased interlayer spacing (Δd = 1.67 nm) in comparison with that of the pristine material. Transmission electron microscopic image of exfoliated perovskite clearly revealed that the present exfoliated perovskite were composed of very thin layers. This exfoliated perovskite nanosheets could be applicable as building blocks for fabricating functional nanocomposites.

Key Words : Exfoliation, Intercalation, Layered material, Nanosheet

Introduction

Recently, perovskite-type transition metal oxides have attracted intense research interests due to their potential applications in the scientific and industrial fields using photocatalysis, energy storage, ferroelectricity, superconductivity, and magnetoresistance.[1-5] Conventional perovskites have three-dimensional structures with a formula of ABO_3. Meanwhile, 2-dimensional derivatives such as Dion-Jacobson and Ruddlesden-Popper phases can be also synthesized by a conventional solid-state reaction,[6] and the obtained layered perovskite oxides have a wide range of versatile intercalation chemistry for the fabrication of various hybrid materials. Especially, exfoliated nanosheet materials obtained by suitable intercalation can be used as building blocks to construct unique functional nanostructures.[7] This field is very important because the exfoliated nanosheets give rise to an unlimited set of new compounds by the hybridization with various guest materials.[8] Moreover, new hybrid materials *via* exfoliation and reassembling reaction could have large specific surface area, which is desirable for further applications.[9] In this regard, there have been tremendous research activities in the exfoliation of layered materials. For example, smectite-type clay minerals have already been used as catalysts and catalytic supports owing to their swelling properties.[10] However, most of researches in transition metal oxide systems are focused on layered titanates and manganates with their low layer charges, which readily accommodate large organic cations such as tetrabutylammonium (TBA^+) in the interlayer spaces *via* acid-base reactions.[9,11] Usually, the layer charge of perovskite-type transition metal oxide is known to be much higher than that of layered titanate and manganate, therefore, it is very challenging

research topic to exfoliate layered perovskite into colloidal suspension.[12]

In this study, we demonstrate the exfoliation of the Dion-Jacobson-type layered perovskite ($RbLaTa_2O_7$) into macromolecular nanoplatelet *via* ion-exchange and two-step intercalation reaction. The structural characterizations of samples were performed by X-ray diffraction (XRD), transmission electron microscopy (TEM), and ultraviolet-visible (UV-vis) spectroscopy.

Experimental

The pristine perovskite $RbLaTa_2O_7$ was prepared by a solid state reaction.[1,13] 50 mol % excess of rubidium carbonate was finely ground with a stoichiometric amount of lanthanum oxide and tantalum oxide. The solid mixture was pelletized and heated at 1373 K for 12 h in air. The obtained perovskite $RbLaTa_2O_7$ was briefly washed with water, and then, dried in ambient condition. The resulting $RbLaTa_2O_7$ was ion-exchanged with excess amount of 4 M HCl for 7 days under vigorous stirring. The protonic form of perovskite $HLaTa_2O_7$ was reacted with ethylamine (EA) for 3 days to prepare EA-intercalated lanthanum tantalate ($EA-LaTa_2O_7$). Finally, exfoliated $[LaTa_2O_7]^-$ nanosheet was prepared by the reaction of $EA-LaTa_2O_7$ with tetrabutylammonium hydroxide (TBAOH) for 3 days, where the molar ratio between TBA and $[LaTa_2O_7]^-$ was fixed to 1:1.

All the XRD patterns were obtained with a powder X-ray diffractometer (Bruker D2 phaser) using Ni-filtered Cu K_α radiation (λ = 1.5418 Å). TEM study was carried out with a Hitachi H-7600 at an accelerating voltage of 120 kV. UV-vis spectra of samples were recorded by Thermo Scientific Evolution 200.
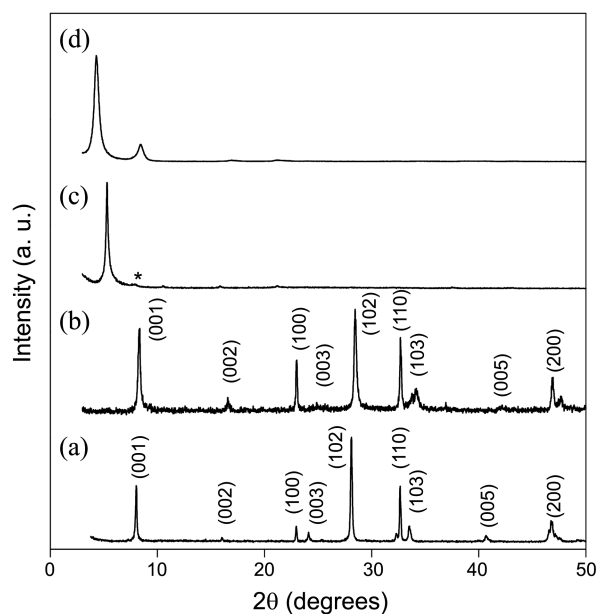
Figure 1. XRD patterns for (a) RbLaTa$_2$O$_7$, (b) HLaTa$_2$O$_7$, (c) EA-intercalated form, (d) TBA$^+$-intercalated form. (Asterisk indicates residual HLaTa$_2$O$_7$).

Figure 2. TEM images for (a) exfoliated nanosheets and (b) the self-restacked form.

Results and Discussion

Figure 1 shows the XRD patterns of RbLaTa$_2$O$_7$ and its derivatives. According to XRD analysis and cell parameter refinement, the pristine RbLaTa$_2$O$_7$ has a space group *P*4/*mmm* with cell parameters of *a* = 0.3882 nm and *c* = 1.1105 nm, which is in good agreement with the previous result.[13] The interlayer spacing between perovskite blocks was calculated to be 1.11 nm, which is same with lattice parameter along the crystallographic *c*-axis. The (001) reflection of a proton-exchanged form (HLaTa$_2$O$_7$) was observed at 2θ = 8.06°, indicating the slightly decreased basal spacing of 1.10 nm upon the ion-exchange of Rb$^+$ with H$_3$O$^+$. After proton-exchange reaction with 4 M HCl, ethylamine intercalation was successively performed to prop open the perovskite layers with longer templates. Actually, we tried direct intercalation of bulky ammonium cations (TBA$^+$) into the interlayer spaces of proton-exchanged perovskite, however, it turned out to be unsuccessful as a result of high layer charges between perovskite blocks. Direct intercalation of TBA$^+$ into HLaTa$_2$O$_7$ resulted in partial intercalation of TBA$^+$, therefore, it was impossible to obtain a single phase. Such a result suggests that EA-intercalation is essential for exfoliation of RbLaTa$_2$O$_7$. The layer charge of RbLaTa$_2$O$_7$ can be determined to be −1 per unit cell, which is much higher than that of a layered titanate with a lepidocrocite-like structure.[14] Further treatment of the proton-exchanged perovskite with ethylamine resulted in expansion of interlayer spacing up to 1.67 nm. Though very small amount of HLaTa$_2$O$_7$ (below 3%) was remained after 3 days of EA intercalation, the residual protonic perovskite could be removed by the TBA$^+$ intercalation and subsequent centrifugation. The obtained EA-intercalated lanthanum tantalum oxide was reacted
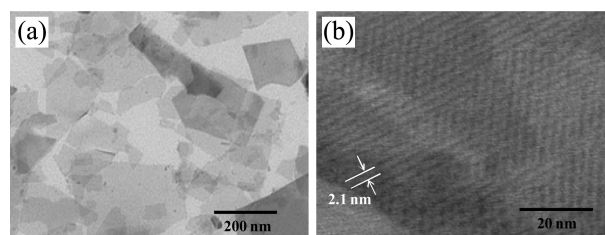
with TBAOH to prepare exfoliated macromolecular nanoplatelets. TBA$^+$ molecules were known to be a very good reagent for exfoliation because it could induce spontaneous osmotic swelling of layered compounds.[15] After 3 days of TBAOH treatment, the (001) reflection of TBA$^+$-intercalated perovskite was observed at 2θ = 4.29°, indicating remarkable expansion of interlayer spacing. The basal spacing of TBA$^+$-intercalated perovskite was determined to be 2.06 nm. The gallery height (0.95 nm) of TBA$^+$-intercalated form, determined by subtracting the thickness (1.11 nm) of the perovskite layer from the basal spacing (2.06 nm), is in good agreement with the Van der Waals diameter of TBA$^+$ molecules,[9,11] suggesting that a monolayer of TBA$^+$ molecules was formed in the intersheet region. Very broad (00*l*) reflections could be ascribed to stacking faults during the intercalation of bulky ammonium molecules. Small amount of EA-intercalated form remained even after intercalation reaction of TBA$^+$ during 3 days, however, the amount of remaining protonic form could be reduced below approximately 3%. Furthermore, EA-intercalated perovskite can be completely removed from the exfoliated solution by the centrifugation of colloidal suspension at 5000 rpm.

Clear evidence of exfoliation of layered perovskite into macromolecular nanoplatelet was directly obtained from the TEM analysis. A diluted colloid of exfoliated nanosheet was dropped on TEM grid in order to observe the morphological features. As shown in Figure 2(a), pale-colored layered platelets were detected, which suggests that the exfoliated perovskite was composed of very thin layers. The lateral sizes of nanosheets were determined to be about several submicrometers. The self-restacked perovskite nanosheets can be also obtained from forced reassembling of exfoliated phase by centrifugation at 15000 rpm. Figure 2(b) indicates the TEM image of self-reassembled form of exfoliated perovskite. The lattice fringes were clearly shown, and the interlayer spacing was approximately 2.1 nm, which is in good agreement with the basal spacing of TBA-intercalated LaTa$_2$O$_7$. Such an investigation supports that exfoliated nanoplatelet maintains its structural features even after exfoliation and restacking reaction. Also, a photograph of exfoliated perovskite suspension is shown in Figure 3, revealing that exfoliated suspension was very translucent. The estimated concentration of the as-prepared nanosheet suspension was approximately 2.7 g/L. Tyndall effect was observed by the scattering of a laser beam, highlighting colloidal nature of the present exfoliated suspension.

Figure 3. Tyndall scattering from exfoliated perovskite colloidal suspension.
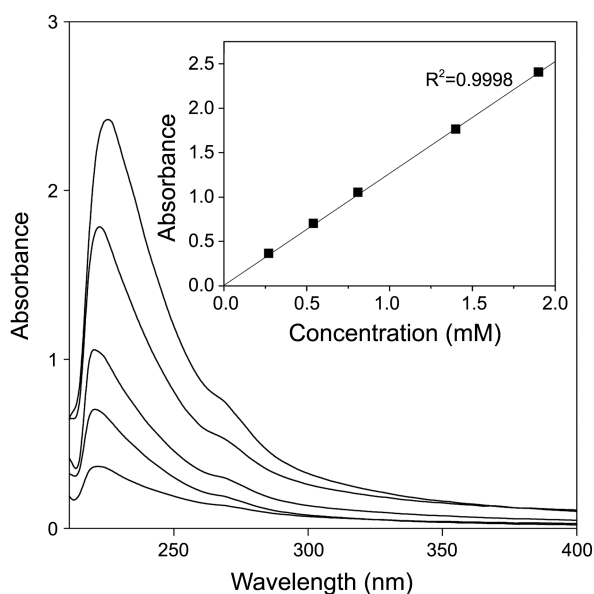

Figure 4. UV-vis absorption spectra obtained from the colloidal suspension of the perovskite nanosheets with various concentrations (Inset: plot of the absorbance at 224 nm against the concentration of a diluted suspension).

Figure 4 indicates the optical absorption spectra for exfoliated perovskite suspension with various concentrations. The colloidal nanosheet exhibited a broad peak maximum at 224 nm along with a weak shoulder at 265 nm. As the concentrations of nanosheet increase, absorbance also increases linearly. R^2 value for linear fitting was calculated to be 0.9998. Such a result is strong evidence that the bulk layered tantalate perovskite is delaminated into well-dispersed nanosheets as expected from TEM analysis. The band gap energy was also evaluated from the UV-vis absorbance. According to previous studies, bulk $RbLaTa_2O_7$ and $LiLaTa_2O_7$ had band gap energies of 3.9 and 4.1 eV, respectively.[16,17] On the other hand, band gap energy of exfoliated nanoplatelet turned out to be ~4.2 eV, which is rather blue-shifted compared to that of the bulk lanthanum tantalates. Such a blue-

shifted spectrum of exfoliated nanoplatelet is due to the quantum size effects.[18] The delaminated nanosheet could be regarded as a quantum-sized material because it has a nano-sized dimension along the crystallographic *c*-axis. The present exfoliation method could be extended for the synthesis of exfoliated perovskite with high layer charges.

Conclusion

The layered perovskite $RbLaTa_2O_7$ was successfully exfoliated into macromolecular nanosheets *via* successive ion-exchange and intercalation reaction. According to XRD analysis, the pristine perovskite could intercalate TBA^+ molecules *via* proton exchange and EA intercalation. TEM study clearly indicates that the exfoliated colloidal suspension of layered perovskite was composed of very thin nanosheets. The present exfoliated nanoplatelet could be used for the fabrication of new hybrid materials.

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