



Anodic hybridization of fluorinated layered perovskite nanosheet with polyaniline for electrochemical capacitor



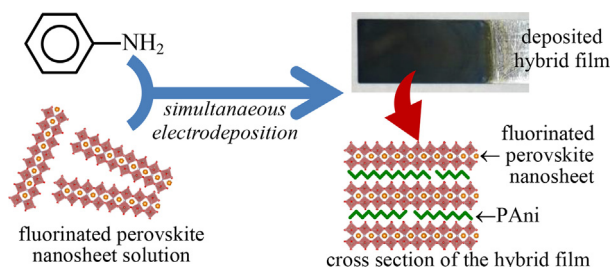
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HIGHLIGHTS

- The fluorinated layered niobate perovskites can be exfoliated in the acetonitrile solution.
- Oriented hybrids with polyaniline are electrodeposited from fluorinated perovskite nanosheet.
- The XRD patterns confirm that the polyaniline molecules can be intercalated between nanosheets.
- Fluorination of perovskite increases electrochemical capacitances steeply to around 230–250 F/g.

GRAPHICAL ABSTRACT



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ABSTRACT

A layered perovskite was fluorinated by polytetrafluoroethylene (PTFE) and then exfoliated to prepare a solution of fluorinated-perovskite nanosheets. Dion–Jacobson-type layered perovskites, $\text{RbLaNb}_2\text{O}_7$ and $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, were prepared in solid-state reactions at 950 and 1100 °C, respectively. The perovskites were fluorinated using PTFE at 400 °C, upon which their color changed from white to gray or black and their electrical conductivity increased to the order of 10^{-4} – 10^{-5} S/m. The tetrabutyl ammonium cations (TBA^+) in each fluorinated layered perovskite were first intercalated by tetrabutylammonium hydroxide (TBAOH) in H_2O and then exfoliated in an acetonitrile solution for electrodeposition. Aniline was added to the solution as a monomer and electrodeposition was carried out in the acetonitrile solution for formation of a hybrid film. X-ray diffraction patterns confirmed that the polyaniline molecules could be intercalated within the interlayer space. Despite the fluorination, the volumetric filling fractions of polyaniline in the interlayer space were around 0.4 and 0.2 for the respective samples from $\text{RbLaNb}_2\text{O}_7$ and $\text{KCa}_2\text{Nb}_3\text{O}_{10}$. The electrochemical specific capacitances of the deposited hybrid films increased steeply from below 50 F/g to above 230–250 F/g owing to the fluorination.

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1. Introduction

Layered materials with negative layer charge, such as smectites, layered niobate, titanate, manganate, layered perovskite, and layered phosphates, have soft chemical reactivities in ion exchange, intercalation, and exfoliation. Inorganic nanosheets can be prepared from exfoliation of the layered compounds, which can be

used for preparation of the film by processes such as sequential adsorption, the Langmuir–Blodgett method, and electrodeposition. These techniques have been reported by many researchers [1–7] for deposition of layered titanate, manganate, and most of the layered compounds, and some results have been reported [8–13] for electrodeposition of films of various types of nanosheets. In our group, layered phosphate and manganate nanosheets were used for the formation of electrodeposited films [9–12]. For metal-phosphate nanosheets in particular, preparation of the hybrid on a conductive polymer or metal-phosphate nanosheets were reported, and the obtained films showed relatively high

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electrochemical specific capacitance of around several hundred farads per gram [9,10]. In addition, these hybrid films did not decompose in the range from -2 to 2.5 V vs. $\text{Ag}|\text{Ag}^+$, at which a pure polyaniline film is prone to decompose completely. Thus, this type of hybrid has high electrochemical durability [14], and these metal phosphates exhibit ionic conductivity that affect attempts to improve their electrochemical properties. No electronic conductivity has been observed in the metal phosphates, however. The nanosheets that exhibit electronic conductivity may affect the electrochemically capacitive behavior in the hybrid formed with a conductive polymer. Actually, some researchers reported extremely high values of several hundreds or over half a thousand farads per gram for the electrochemical specific capacitance of polyaniline through hybridization with carbon nanotubes (CNTs), graphite, or a conductive metal [15–17]. Layered perovskites have become strong candidates for starting materials of electronically conductive nanosheets because their electronic structures are relatively controllable owing to the wide compositional variety. Therefore, we decided to investigate layered perovskites for the production of inorganic-nanosheet-conductive-polymer hybrids.

In general, a layered perovskite is composed of alternately stacked perovskite block layers and cationic layers. A perovskite block consists of n layers of corner-shared octahedral and slab-occupied cations. The cationic layer between the perovskite slabs compensates the negative charge electronically. Layered perovskites are divided into three types according to their structures: Ruddlesden–Popper (e.g., NaYTiO_4 and $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$), Dion–Jacobson (e.g., $\text{RbLaNb}_2\text{O}_7$ and $\text{RbCa}_2\text{Ta}_3\text{O}_{10}$), Aurivillius phase (e.g., $\text{Bi}_2\text{O}_2(\text{Bi}_2\text{Ti}_3\text{O}_{10})$). When alkali cations intercalate compounds as a cationic layer, they can be exchanged with protons. In the case of a layered perovskite, a soft-chemical reaction such as ion exchange, intercalation, or exfoliation may occur [18–20]. For a layered perovskite of the Dion–Jacobson phase, its general formula can be expressed as $A^zA^a_{n-1}B^bX_{3n+1}$, where the A' cation is the interlayer charge-compensated cation, and A and B form the perovskite block layer. The electronic properties such as conductivity and dielectric constant are significantly affected by the B cation. For oxide-type layered perovskites, the B cation valence can be determined by $b = ((6 - a) + (2 + a - z)/n)$. When A' is an alkali cation ($z = 1$), the possible valences of B are 3, 4, 5, and 6 for n values of 1, 2, 3, and 4, respectively. However, if the valence of A exceeds that of B , it may not be favorable for formation of the perovskite block owing to its tolerance factor. Consequently, 4, 5, and 6 are acceptable for the valence of B ; in these cases, Ti^{4+} , Nb^{5+} , Ta^{5+} , and W^{6+} , each of which has a closed d-electron shell, are candidates for the B cation. With these constraints, it is difficult to form an electronically conductive layered perovskite with ion exchangeability. Kobayashi et al. had a different approach: by controlling the electronic structure through fluorination of the Dion–Jacobson-type layered niobate or titanate perovskite [21], an electronically conductive layered perovskite with ion exchangeability could be obtained.

In the study reported here, two fluorinated layered perovskites, $\text{RbLaNb}_2\text{O}_7$ and $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, were exfoliated for the formation of nanosheet–conductive-polymer hybrid films. The electrochemical properties of the prepared hybrid films were examined to evaluate their suitability as an active material for the electrode of an ultracapacitor.

2. Experimental

2.1. Preparation of layered perovskites

The layered perovskites were prepared via conventional solid-state reactions with heating at high temperature. $\text{RbLaNb}_2\text{O}_7$ was prepared by heating a mixed powder composed of Rb_2CO_3 , La_2O_3 ,

and Nb_2O_5 in a molar ratio of 1.2:1.0:2.0 at 950 – 1200 °C for 48 h. $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was also prepared via a solid-state reaction, where a mixture of K_2CO_3 , CaCO_3 , and Nb_2O_5 with a molar ratio of 1.2:4.0:3.0 was heated at 950 – 1200 °C for 48 h. The heated samples of $\text{RbLaNb}_2\text{O}_7$ and $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ were designated the abbreviations RL and KC, respectively.

Next, some of the heated samples were fluorinated in a heating process with a fluorine source, which has been reported in the literature. It proceeded as follows [21]. The prepared layered perovskites were mixed thoroughly with polytetrafluoroethylene (PTFE) powder and then pressed under a pressure of 64 MPa to form pellets with increased reactivity. The pressed pellets were heated at 400 °C under a N_2 flow to reduce pentavalent Nb. After heat treatment, PTFE was added again and mixed with the crushed pellets. New pellets were formed from the mixture and then heated; the heat treatment was carried out three times. The sample color changed from white to black during the fluorination. The RL and KC samples that received fluorination treatment are designated as RLF and KCF, respectively. Both RL and KC powders with and without fluorination (RL, RLF, KC, and KCF) were then added to individual 2 M HNO_3 solutions for protonation; the Rb and K ions were exchanged with H ions by stirring the mixtures for 5 days, with the acid solution for each mixture replaced daily. The protonated samples are referred to as H-RL, H-RLF, H-KC, and H-KCF hereafter.

2.2. Formation of TBA^+ cations: intercalated phase and exfoliation

An aqueous solution of tetrabutylammonium hydroxide (TBAOH) was reacted with the protonated layered perovskites (with and without fluorination). The protonated perovskites, H-RL, H-RLF, H-KC, and H-KCF, were added to separate TBAOH solutions and stirred for 1 week to intercalate TBA^+ cations. The ratios of TBA^+ to H-RLF and H-KCF were both 1:8. After stirring, the solutions containing the samples were filtered to separate the reacted samples, which were then dried at room temperature (RT). The resulting TBA^+ -intercalated samples are referred to as I-RL, I-RLF, I-KC, and I-KCF in this paper. The intercalated compounds were then placed in acetonitrile and the two mixtures were stirred for several days. The consequent solutions were ultrasonicated (at 28 kHz) for 30 min and then centrifuged at 2000 rpm to separate unwanted particles that were not exfoliated. The exfoliated samples are referred to as E-RL, E-RLF, E-KC, and E-KCF hereafter.

2.3. Preparation of perovskite-nanosheet–polyaniline hybrids

The hybrid films consisting of layered perovskite nanosheets (with and without fluorination) and polyaniline were prepared by electrodeposition. Nanosheet–acetonitrile solutions were first obtained and used as the mother solutions for the preparation of the hybrid films. Tetrabutylammonium chloride was added at a concentration of 4 mmol/L to the individual solutions of acetonitrile with E-RL, E-RLF, E-KC, and E-KCF to improve their electrical conductivity as low conductivity of a solution would yield a film of poor quality. A monomer, aniline, was then added at a concentration of 8 mmol/L to the solutions and stirred for 30 min before electrodeposition began. The electrodeposition was then carried out at a constant current (typically 2.0 mA for 15 min) supplied by a DC source (7651, Yokogawa) with a monitoring voltage and current. Platinum plates (50 mm \times 10 mm \times 0.1 mm) were used for both electrodes in the electrodeposition set-up. After electrodeposition was completed, each sample was picked up very gently from the solution to avoid collapse of the deposited film. The samples were then dried at RT.

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