Nd³⁺-Doped Perovskite Nanosheets with NIR Luminescence

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Abstract

Exfoliation of layered materials into ultrathin nanosheets introduces a new cost-effective and environmentally safe fabrication method for novel nanostructured devices. In the present study, we have developed for the first time inorganic **oxide** nanosheets with near-infrared (NIR) luminescent properties. KLa_{1-x}Nd_xNb₂O₇ (x = 0.025, 0.05, 0.1, 0.2, or 0.3) powders obtained by a solid state reaction were exfoliated into single-layer metal oxide nanosheets with approximately 1.7 nm thickness by osmotic swelling with tetrabutylammonium cations, followed by the protonation of KLa_{1-x}Nd_xNb₂O₇. We observed strong coupling of high-energy OH vibration with the Nd³⁺ energy levels upon protonation and exfoliation steps because of the extremely thin nature of **oxide** nanosheet-layers. Colloidal **oxide** nanosheets with an optimized Nd-doping concentration yielded detectable NIR luminescence due to ⁴F_{3/2}–⁴I_{11/2} (Nd³⁺) radiative transitions, which opens

possible application of these **oxide** nanosheets as bioimaging probes and bioanalytical sensors.

Keywords nanosheet; near-infrared; Luminescence; perovskite; Nanocomposites

1. Introduction

Nanosheets have been extensively investigated for the fabrication of ultrathin devices. For example, graphene is a potential nanosheet material^{[1],[2]} that can replace Si devices in the near future. In addition, metal oxide nanosheets,^{[3]-[14]} which are prepared by exfoliating layered metal oxides, have attracted considerable interest as building blocks for the fabrication of advanced devices using soft-chemical strategies.^{[11] and [14]} Their properties are largely tunable by doping heterometallic ions into the structure, thus affording a variety of unique features, including optical,^{[14]-[11]} catalytic,^[12] electrical,^[13] and dielectric^[14] properties.

Trivalent rare-earth (Re) ion-doped **oxide** nanosheets with well-characterized 4f–4f luminescence are potential next-generation nanophosphors.^{[4]-[5] and [7]-[9]} For example, layer-by-layer assembly of nanosheets enables the fabrication of optically transparent films with improved luminescent properties.^[11] As another application, luminescent nanosheets are highly suitable materials for bioanalytical devices. Owing to the extremely ultrathin nature of nanosheets (ca. 1 nm in thickness), their luminescence can be strongly influenced by surface adsorbed components, such as ions and molecules, enabling potential applications as bioimaging probes and bioanalytical sensors that are sensitive to external fields and various stimuli.^[15]

To date, luminescent **oxide** nanosheets with blue,^[5] green,^[4] and red^{[4],[7] and [8]} emissions have been synthesized; however, these **oxide** nanosheets are often impractical for biochemical applications as they require

ultraviolet light excitation, which may damage the target system or produce interfering background luminescence. In fact, much effort has been devoted to finding novel organic and inorganic bioprobes that can be excited by an 800–1700-nm light source in the range of the biological window.^{[16]–[18]}

In this framework, we have attempted to the synthesis of Nd³⁺-activated **oxide** nanosheets with NIR luminescence by exfoliation of KLa_{1-x}Nd_xNb₂O₇ layered perovskite. Colloidal **oxide** nanosheets with 1.7 nm thickness and microscale width yield well-defined NIR luminescence due to ⁴F_{3/2}–⁴I_{11/2} (Nd³⁺) radiative transitions. The effects of Nd³⁺ concentrations as well as inter-lamellar and surface spices on the PL properties are investigated to provide general importance for development of **oxide** nanosheet-based luminescent materials.

2. Experimental

2.1. Synthesis of KLa_{1-x}Nd_xNb₂O₇ powder by solid state reaction.

Layered KLa_{1-x}Nd_xNb₂O₇ were prepared as follows. The synthesis of KLa_{1-x}Nd_xNb₂O₇ (x= 0.025, 0.05, 0.1, 0.2, 0.3) was carried out using a conventional solid-state procedure. The starting material was a stoichiometric mixture of K₂CO₃ (99.5 %, Wako Chemicals), La₂O₃ (99.5 %, Wako Chemicals), Nd₂O₃ (99.5 %, Wako Chemicals), and Nb₂O₅ (99.5 %, Wako Chemicals). The mixture was heated at 900°C for 4h and 1100° C for 40h.

2.2. Protonation of KLa_{1-x}Nd_xNb₂O₇ powder

Protonation was carried out by stirring 1.0 g of KLa_{1-x}Nd_xNb₂O₇ powder in 300mL of 1M aqueous HCl

(35.0~37.0 %, Wako Chemicals) solution for 7days at room temperature. After reaction, obtained solid product was centrifuged and washed with deionized Milli-Q water.

2.3. Exfoliation of $\text{HLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$.

The exfoliation of the $\text{HLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ was carried out as follows. The $\text{HLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ (1.0 g) was exfoliated in 0.1M tetrabutylammoniumhydroxide (TBAOH)(40.0 %, Kanto Chemicals)(300 mL) for 7days. The subsequent centrifugation of the solution under 3000 rpm for 30 min yielded colloidal suspension of $\text{KLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ nanosheets.

2.4. Characterization and Equipment.

The crystal structure was analyzed using X-ray powder diffraction (XRD) patterns (using Cu $K\alpha$ radiation, Rigaku RINT-2500VHF). The concentration of the **oxide** nanosheets in the solution was analyzed by an inductively coupled plasma (ICP) spectrometer (Seiko Instruments, SPS7800). The concentration of $\text{La}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ nanosheet suspension was $1.2 \times 10^{-3}\text{M}$. FT-IR spectra were recorded on a Perkin-Elmer spectrometer using a KBr method. The chemical composition analysis of $\text{KLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ was Electron probe microanalyzer (EPMA, Shimadsu EPMA-1720H). The thickness of the exfoliated **oxide** nanosheets was confirmed by atomic force microscopy (AFM, Veeco Nanoscope-V) measurements.

NIR emission spectra were recorded using a Horiba Fluorolog-3 spectrofluorometer at room temperature. The luminescence spectra of the sample were measured under excitation by a 808-nm continuous wave (cw) laser diode (LD) (L9418-04, Hamamatsu Photonics) equipped with a temperature controller (TED200, Thorlabs).

3. Results and Discussion

The synthesis of $\text{KLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ ($x = 0.025, 0.05, 0.1, 0.2, \text{ or } 0.3$) was carried out using a conventional solid-state procedure. The synthesized $\text{KLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ contained single-layered perovskite blocks (see Fig. 1(a)) with intercalated K^+ . The A and B sites in the perovskite blocks can accommodate Ln (La^{3+} and Nd^{3+}) and Nb cations, respectively. Fig. 1(b) and (c) show XRD patterns of KLaNb_2O_7 and $\text{KLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ ($X = 0.30$, the maximum Nd^{3+} doping concentration investigated in the present study). Both patterns correspond well to the KLaNb_2O_7 structure, indicating the successful substitution of Nd^{3+} for La^{3+} even at a very high concentration; this is mostly due to the similar ionic radii of these ions. The sharp peaks demonstrate the highly crystalline nature of the sample. SEM-EDX analysis of as-synthesized $\text{La}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ -microplates confirmed that all the metallic elements were distributed uniformly in the products (see Fig. 1(d)).

The mechanism for the NIR luminescence of the Nd^{3+} ions is described as follows. (see Fig. 2(a)). First, an 808-nm photon excites Nd^{3+} ions to the $^4\text{F}_{5/2}$ level, after which they decay nonradiatively to the lower $^4\text{F}_{3/2}$ level to produce NIR emission with radiative transitions. Fig. 2(b) shows the photoluminescence (PL) spectra of the starting material ($\text{KLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$) at various La/Nd ratios (Nd is 2.5%, 5%, 10%, 20%, and 30%) resulting from excitation at 808 nm. All samples yielded NIR luminescence as a result of the Nd^{3+} radiative transitions corresponding to $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ (880nm), $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ (1060nm), and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$ (1350nm)^{[6]and[19]}. The sample with 2.5-mol% Nd^{3+} produced the strongest emission. The decrease in the emission intensity for the samples with higher concentrations of Nd^{3+} resulted from concentration quenching due to the cross-relaxation process accompanying the change in the relative band intensities. Because they had the highest emission

intensity, the 2.5-mol% Nd^{3+} -doped samples were studied in the following investigations.

Intercalated K^+ ions were exchanged with protons by treatment with 1 M HCl. Protonation was carried out by stirring $\text{KLa}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ powder in a 1 M aqueous HCl solution at room temperature. Fig.3(a) shows the XRD patterns of $\text{HLa}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ as protonated layered oxides, which shows that the inter-lamellar distance decreases by proton exchange. Fig. 3(b) shows PL spectra for $\text{KLa}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ and $\text{HLa}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ resulting from excitation at 808 nm. The figure indicates that proton exchange decreases the PL intensity. In the cation exchange process, the proton is intercalated as an oxonium ion (H_3O^+). It is presumed that the high-energy OH vibration of the intercalated H_3O^+ is coupled with the Nd^{3+} energy levels. As a result, the rate of nonradiative transition increased significantly. Notably, we observed a decrease in the relative intensity of the high - energy stark component of the $^4\text{F}_{3/2}$ doublet to low-energy one, where they were observed at 1050 nm to 1070 nm, respectively. A decrease in the relative band intensity was also detected with an increase in the Nd^{3+} concentration (Fig. 2). These results revealed that the relative intensity of these peaks is strongly influenced by inter-lamellar and intra-lamellar structures.

We performed exfoliation of the host layer to prepare single layer oxide nanosheets. Fig. 4(a) shows typical atomic force microscopy (AFM) images of $\text{La}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ nanosheets obtained by exfoliation of $\text{HLa}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ with a tetrabutylammonium hydroxide aqueous solution. Cross-sectional analysis of the AFM data demonstrated that the thickness of the oxide nanosheets was approximately 1.7 nm, a value that corresponded well to that of the perovskite layers in the initial materials. SAED patterns from single oxide nanosheets displayed well-defined square spots, indicating that each sheet is a single crystal (see Fig. 4(b)).

Fig. 4(c) shows PL spectra for the aqueous colloidal $\text{La}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ nanosheets. The colloids yielded NIR-PL bands at ca. 1060 nm corresponding to the well-defined $^4\text{F}_{3/2}-^4\text{I}_{11/2}$ (Nd^{3+}) transitions. We observed that PL bands of $\text{La}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ nanosheets were broadened and weakened in comparison with protonated powders. This is presumably because unlike those of the protonated layered structure, the OH ligands in the perovskite **oxide** nanosheet layers were directly coordinated with metal ions. These surface hydroxyl groups should more strongly couple with the Nd^{3+} energy levels than those from intercalated H_3O^+ in the protonated layered structure, resulting in remarkable quenching effects. Furthermore, considering the single layer thickness, all the luminescent Nd^{3+} centres might interact with OH such that surface quenching occurs more in the **oxide** nanosheets than in conventional nanoparticles. The strong coupling between Nd^{3+} and hydroxyl group also might introduce disordered crystal fields around Nd^{3+} , resulting in the significant broadening of PL bands. Although, so far, luminescent **oxide** nanosheets have been reported, no works have addressed on the effects of inter-lamellar or surface species on the PL properties. Strong surface effects on the PL properties demonstrated in the present study indicates that the luminescence properties of the **oxide** nanosheets would be highly sensitive to changes in the surface environment, such as surface modifications, which opens potential applications as bioimaging probes and bioanalytical sensors.

4. Conclusions

In this study, we successfully synthesized NIR luminescent metal oxide nanosheets for the first time by the exfoliation of $\text{KLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ layered perovskite. The colloidal oxide nanosheets afford 1060-nm

luminescence resulting from $^4F_{3/2}$ – $^4I_{11/2}$ (Nd^{3+}) transitions upon excitation at 808 nm. Our study demonstrated that Nd^{3+} -doped nanosheets exhibit NIR luminescent properties with their large tunability depending on surface states, which will lead to the development of smart bioimaging probes and bioanalytical sensors.

Acknowledgments

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Figure Captions

Fig. 1(a) Structural model of layered $\text{KLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$.

(b) XRD patterns of layered KLaNb_2O_7 and $\text{KLa}_{0.7}\text{Nd}_{0.3}\text{Nb}_2\text{O}_7$. All peaks correspond to KLaNb_2O_7 phase, strong peaks are indexed with (h, k, l) .

(c) FE-SEM image and EDX analysis of the layered $\text{KLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$.

Fig. 2(a) Energy level diagram of Nd^{3+} .

(b) PL spectra of starting material ($\text{KLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$) with various La/Nd ratios (97.5/2.5: Nd-2.5%, 95/5: Nd-5%, 90/10: Nd-10%, 80/20: Nd-20%, 70/30: Nd-30%) (λ_{ex} :808nm).

Fig. 3 (a) XRD patterns of $\text{KLa}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ and $\text{H La}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$. Symbols $\blacktriangledown$ and $\times$ indicate expected diffraction peak positions of KLaNb_2O_7 and HLaNb_2O_7 , strong peaks are indexed with (h, k, l) , respectively.

(b) PL spectra of $\text{K La}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ and $\text{H La}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ (λ_{ex} :808nm).

Fig. 4 (a) AFM image of $\text{La}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ nanosheets, (b) TEM images of $\text{La}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ nanosheets, and (c) PL spectra of $\text{La}_{0.975}\text{Nd}_{0.025}\text{Nb}_2\text{O}_7$ nanosheet solutions (λ_{ex} : 808nm).

Fig. 1

Fig. 2

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