Porous calcium niobate nanosheets prepared by an exfoliation–restacking route

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ABSTRACT

The single phase layered perovskite-type niobate KCa$_2$Nb$_3$O$_{10}$ was obtained by a solid state reaction of the starting materials (K$_2$CO$_3$, CaCO$_3$ and Nb$_2$O$_5$) at 1,200 °C. Then the H$^+$-exchanged form (HCa$_2$Nb$_3$O$_{10}$) was successfully exfoliated into colloidal porous single layers on the intercalating action of tetra(butyl)ammonium ion. The various characterization techniques such as X-ray diffraction (XRD), field-emission scanning electron microscopy, N$_2$ absorption–desorption and diffuse reflectance UV–visible spectrometry gave important information on the unusual structural features of the perovskite-related niobate nanosheets. XRD analysis of the exfoliated nanosheets showed a unique profile with wide peaks that represented individual molecular aspects of the nanosheets. The Brunauer–Emmett–Teller isotherm of the exfoliated coiled nanosheets showed a sharp increase in the surface area by a factor of >30 in comparison to parent layered material, which is due to the exfoliation and restacking process. The nanosheets in this study were also found to act as a semiconductor with a wide band gap that is due to the quantum size effect.

Key words | chemical synthesis, nanostructures, surface properties, visible and ultraviolet spectrometers, X-ray diffraction topography

INTRODUCTION

The recent storm of interest in nanoscale materials has been inspired, in part, by the realization that nanoscale materials often exhibit physical and chemical properties that are dramatically different from their bulk counterparts (Choi et al. 2013; Hynek et al. 2013; Jacobs-Gedrim et al. 2013; Saleem et al. 2013; Gunjakar et al. 2014).

Thanks to the steadily increasing synthetic capabilities, a so-called ‘nano-toolbox’ filled with a variety of nanocry stallites including nanoparticles/quantum dots (zero-dimension), nanotubes/nanorods/nanobelts (one-dimension), and nanosheets (two-dimension), have been explored (Jacobson 1994; Sasaki et al. 1996; Nalwa 2000; Patzke et al. 2002; Rao & Nath 2003; Xia et al. 2003).

Two-dimensional nanocrystals (nanosheets) prepared by exfoliation of layered parent materials upon interacting with bulky guests, for example, quaternary ammonium ions (Treacy et al. 1990; Keller et al. 1994; Sasaki et al. 1996; Sasaki & Watanabe 1998; Fang et al. 1999; Harada et al. 2002; Sasaki 2002) are single crystals with thicknesses on the order of molecular sizes. Nanosheets have a thickness of about 0.5–3.0 nm thick that is comparable to the dimensions of molecules (Sasaki et al. 2001), while their lateral size ranges from several hundred nanometres to several micrometres, basically depending on the dimensions of the starting layered crystals (Sasaki et al. 2001). Nanosheets with such unique structures have various potential applications such as in photocatalysis. A high crystallinity and a large surface area are critical for realizing high-efficiency photocatalysts, and nanosheets satisfy both of these requirements. In addition, the molecular size thickness of nanosheets also improves their quantum efficiency. For conventional powder catalysts with particle sizes in the range 0.5–3.0 μm, photoexcited electrons and holes generated within them have to travel a long distance to the surface to react with reactant molecules adjacent to the layers. However, electrons and holes may recombine or become trapped at defect sites during this long trip to the surface, which can reduce their photoreaction efficiency. However, photoexcited electrons and holes generated in a nanosheet can reach its surface without encountering obstructions owing to its ultrathin thickness and high crystallinity. The preparation of these nanosheet crystallites is also very...
interesting and important because they can be used as building blocks to construct a variety of nanostructured systems. The structural flexibility of nanosheets also allows one to construct multicomponent photosystems that incorporate electron donors, acceptors, catalytic nanoparticles, or photon antenna molecules (Keller et al. 1994; Kaschak et al. 1999; Choy et al. 2001, 2002; Ebina et al. 2002a, 2005; Paek et al. 2006; Kim et al. 2007; Hata et al. 2008). Moreover, formation of novel shapes such as thin flakes and hollow microspheres by using the nanosheets as building blocks has been achieved by applying freeze-drying or spray-drying processing (Sasaki et al. 1997).


A Dion–Jacobson type perovskite oxide, ACa₂Nb₂O₁₀ (A = H or K) (Dion et al. 1981; Jacobson et al. 1985; Fukuoka et al. 2000), with a layered structure and a wide band gap has been studied by several researchers as a photocatalyst and a photoelectrode for UV light-driven water splitting (Domen et al. 1990, 1993; Ebina et al. 1996, 2002a, 2005; Izawa et al. 2006; Compton et al. 2007; Compton et al. 2008; Hata et al. 2008). The structure of KCa₂Nb₂O₁₀ is schematically illustrated in Figure 1 (Nassau et al. 1969; Dion et al. 1981; Jacobson et al. 1985; Fukuoka et al. 2000). KCa₂Nb₂O₁₀ consists of negatively charged calcium niobate sheets, with each sheet made of layers of μ₂-O bridged NbO₆ octahedra and with Ca²⁺ ions filling the voids and K⁺ cations located between the triple perovskite layers (Fukuoka et al. 2000).

Acid exchange of KCa₂Nb₂O₁₀ produces HCa₂Nb₂O₁₀ as a strong solid Brønsted acid and then it can be chemically exfoliated into individual crystalline nanosheets by reaction with bulky base molecules such as TBA⁺OH⁻ (Treacy et al. 1990; Ebina et al. 2002a, 2002b, 2005; Izawa et al. 2006; Compton et al. 2007, 2008; Hata et al. 2008; Song et al. 2015) and finally flocculated by changing the ionic strength or pH of the colloidal suspension to give restacked aggregates of nanosheets that have much higher specific surface area than the parent layered material (Ebina et al. 2002a, 2005). The resulting single sheets upon ‘exfoliation–restacking’ processes can also be used to form one-dimensional structures, such as nanotubes, nanorods, nanowires and nanoscrollles through soft chemistry routes (Rao & Nath 2003; Tenne 2005).

The present study was, therefore, undertaken to demonstrate the validity of this synthetic strategy with a successful example of the preparation of niobium-based nanosheets from the parent layered perovskite niobate (KCa₂Nb₂O₁₀) based on a two-step intercalation process. The obtained layered KCa₂Nb₂O₁₀ and exfoliated nanosheet-based materials were investigated from the basic scientific viewpoint on the synthesis, structure, composition, and characterization.

The analysis was based on X-ray diffraction (XRD), field-emission scanning electron microscopy data (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), Brunauer–Emmett–Teller (BET) isotherm and diffuse reflectance UV–visible spectrometry (DRS UV-vis).

**EXPERIMENTAL SECTION**

**Reagents and materials**

Nb₂O₅, K₂CO₃, CaCO₃ with purity of 99.9% or higher and tetra(butyl)ammonium hydroxide solution (20 wt.% in H₂O), were purchased from the Merck company. All the other chemicals were of analytical grade and used as received. Milli-Q filtered ultrapure water (>18 MΩ cm) was used throughout.
Synthesis of KCa2Nb3O10

The starting layered perovskite, KCa2Nb3O10, was prepared by the conventional solid state route according to the previous literature reports (Dion et al. 1984; Jacobson et al. 1985): K₂CO₃, CaCO₃, and Nb₂O₅ were mixed at the ratio of 1.1:2:3 and calcined at 1,473 K for 10 h in air. An excess of alkali metal (K) carbonate (10 mol.%) was added to compensate for the loss due to volatilization of the alkali component.

Proton exchange of KCa2Nb3O10

The K ions in the layered KCa₂Nb₃O₁₀ (5.0 g) were exchanged with protons by acid exchange with 4 M HNO₃ (40 g) solution for 72 h. In this procedure, the HNO₃ solution was replaced by a fresh solution twice, followed by centrifugation, washing with distilled water, and drying at 333 K. The formation of HCa₂Nb₃O₁₀ was confirmed by atomic absorption spectrometry, which revealed that the percentage of K⁺ ions removed from KCa₂Nb₃O₁₀ was 98%.

Exfoliation and restacking of HCa₂Nb₃O₁₀

The resulting H⁺-exchanged phase, HCa₂Nb₃O₁₀ (0.4 g), was shaken in an aqueous solution (100 cm³) containing tetra(butyl)ammonium hydroxide (TBA⁺OH⁻, Merck, 20 wt.% in H₂O) at room temperature for 1 week in a similar manner to that reported by Ebina et al. (2002a, 2005).

During shaking, the inter-sheet spacing might also be expanded due to the increase in water contents and TBA⁺OH⁻ intercalation. The electrostatic interaction between neighboring sheets was thus significantly reduced. As a result, the turbostratic restacked nanosheets became very loosely bonded and were granted a tendency to delaminate into individual nanosheets again.

The concentration of the TBA solution was 7.3 mmol dm⁻³, which is a favorable condition for promoting delamination of layered perovskite into colloidal single layers. The bulky TBA⁺ ions were first intercalated into the galleries of the layered perovskite and then exfoliated the layered structure into nanosheets. A stable colloidal suspension of nanosheets was obtained after centrifugation and removing sediment, as shown in the photograph (Figure 2).

After removing the sediment that is unreacted HCa₂Nb₃O₁₀, the nanosheet colloids were reassembled by adding aqueous hydrochloric acid (HCl: 2.5 M, pH = 2) to form precipitates.

This resulted in a porous aggregate of fine crystallites of turbostratic layered nanosheets. At higher pHs, colloid dispersion is stable for months in respect to flocculation, due to high electrostatic repulsion among the exfoliated negative calcium niobate layers.

The resulting milky glue-like colloidal aggregates were then rinsed several times with pure water to remove residual TBA⁺Cl⁻ and HCl, followed by drying in a vacuum oven at 333 K overnight and grinding into a powder using a mortar and pestle. The architecture of these single coiled nanosheets is illustrated in Figure 5(d) (inset section). EDX spectroscopy revealed that the acid-precipitated colloids contained little residual potassium, with K/Nb ratios of <0.01. The final product is thus referred to below as exfoliated coiled nanosheets (ex-Ca₂Nb₃O₁₀).

CHARACTERIZATION AND EQUIPMENT

Powder XRD patterns were obtained with a Philips PW 3710 X-ray diffractometer using Cu-K radiation source (λ = 1.54, 056 Å). The morphologies of the samples were observed using an S4160-Hitachi Japan FE-SEM operating at an accelerating voltage of 15 kV. The nitrogen adsorption–desorption isotherm was collected on a Micromeritics ASAP 2020 surface area and porosity analyzer at 77 K after the sample had been degassed in the flow of N₂ at 180 °C for 5 h. The BET surface area was calculated from the linear part of the BET plot (relative pressure P/P₀ = 0.1–0.25). The average pore size and the pore size distribution plot were estimated using the desorption branch of the isotherm, and the Barrett–Joyner–Halenda (BJH) formula. UV–vis diffuse reflectance spectra were recorded using a Shimadzu (Mini1240) spectrometer. Chemical analysis was carried out by completely dissolving a weighed amount of sample in a 3:1 mixture of concentrated HCl and
HNO$_3$, respectively, followed by determination of alkali metal ion (K) by atomic absorption spectroscopy. Elemental analysis data by EDX analysis were obtained by a Mira II LMU, TESCAN, Czech Republic, and HV: 30 kV.

RESULTS AND DISCUSSION

During synthesis, the layered structure of the proton-exchanged form of KCa$_2$Nb$_3$O$_{10}$ exfoliates into nanosheets through the intercalation of bulky TBA$^+$ ions into interlayers. Figure 3 shows XRD patterns of restacked nanosheets (ex-Ca$_2$Nb$_3$O$_{10}$), along with the data for layered KCa$_2$Nb$_3$O$_{10}$ made by solid state method (1,473 K, 10 h) for comparison.

The observed single phase diffraction pattern for parent layered material (KCa$_2$Nb$_3$O$_{10}$) can be indexed on a tetragonal unit cell with lattice parameters ($a = 7.7270$ Å; $b = 7.7270$ Å; $c = 294660$ Å) and space group P42212. The assignment was based on the previous report (Dion et al. 1981).

The XRD pattern of the restacked nanosheets (ex-Ca$_2$Nb$_3$O$_{10}$) exhibits broad and weaker diffraction peaks, owing to a much less ordered lamellar structure as well as reduction of the crystallite size in the restacked materials. Turbostratic stacking of perovskite nanosheets is suggested since only basal diffraction series of (001) and intra-nanosheet reflections of (110) and (100) were observed. Their relatively broad nature compared to the profile of the original as-prepared layered perovskite compound and the absence of general hkl peaks are common features of flocculated aggregates of nanosheets. These observations indicate decreasing of scattering domains not only in the stacking direction but in the in-plane directions as well and the loss of three-dimensional ordering of the lamellar structure and relatively poor registry between sheets, respectively. Moreover, the two-dimensional lattice or in-plane crystalline order within the individual nanosheets was maintained, strongly suggesting exfoliation. The crystallite size, which was calculated using Scherer's equation from the (110) reflection of XRD was 46.7 and 22.1 nm for KCa$_2$Nb$_3$O$_{10}$ and ex-Ca$_2$Nb$_3$O$_{10}$, respectively. The position of the (001) diffraction peak in restacked nanosheets appears at lower 20 angles than that in the corresponding layered materials. This layer expansion relative to KCa$_2$Nb$_3$O$_{10}$ implies more hydration and intercalation of TBA$^+$OH$^-$ bulky base molecules into the interlayer gallery. These results are consistent with the previous studies (Takagaki et al. 2003; Kobayashi et al. 2007b). This strongly suggests that TBA$^+$OH$^-$ intercalation is an essential step in the nanosheet synthesis. TBA$^+$ cation is a large species that could be responsible for the great basal spacing enhancement once co-intercalated with H$_2$O between niobate layers.

The process of intercalation of TBA$^+$OH$^-$ into HCa$_2$Nb$_3$O$_{10}$ is commonly understood as an acid–base reaction between interlayer protons (Brönsted acid) and TBA$^+$OH$^-$. This process generally depends on the size and charge density of the guest species, and the hydration state of the layered compounds. A TBA$^+$ ion is a quaternary ammonium ion with four butyl groups attached to a positively charged nitrogen atom at the center. The diameter of a TBA$^+$ ion is 0.8 nm, which is most likely larger than the interlayer distance of HCa$_2$Nb$_3$O$_{10}$, which may have been one of the possible reasons for the current finding. Figure 4 shows a schematic drawing of H$^+$-exchange and exfoliation–restacking processes.

Figure 5 shows FE-SEM images of exfoliated HCa$_2$Nb$_3$O$_{10}$ nanosheets along with the parent lamellar materials. Parent KCa$_2$Nb$_3$O$_{10}$ presents an ordered rod-like block structure with average width 400 nm and length range of 1–5 μm and with well-defined fracture planes (Figure 5(a) and 5(b)), a common characteristic of layered compounds. The cross-sections of these rods were rectangular or polygonal.

In restacked HCa$_2$Nb$_3$O$_{10}$, individual sheets with edge lengths of several hundred nanometres are randomly restacked to form larger aggregates with very low organization when compared to the precursor phase.

This observation is consistent with the previous report by Osterloh and colleagues (Compton et al. 2007). The edge lengths of the HCa$_2$Nb$_3$O$_{10}$ nanosheets is obviously

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Figure 3 | XRD patterns of layered parent material (KCa$_2$Nb$_3$O$_{10}$) and restacked nanosheets (ex-Ca$_2$Nb$_3$O$_{10}$).
**Figure 4** | Schematic drawing of $\text{H}^+$-exchange and exfoliation-restacking processes.

**Figure 5** | FE-SEM images of parent lamellar material ($\text{KCa}_2\text{Nb}_3\text{O}_{10}$) (a), (b) along with the exfoliated nanosheets ($\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}$) (c), (d) (inset of Figure 5(d): Illustration of calcium niobate sheets containing coiled opposite edges, based on Shiguihara et al. (2007)).
smaller than that reported for the parent material made by
the solid state reaction of the binary oxides and carbonates
(typically, a few micrometres) (Compton et al. 2007, 2008;
Carroll et al. 2008). Because the ex-Ca$_2$Nb$_3$O$_{10}$ sheets do
not have mirror symmetry (i.e., the individual sheet is asym-
metric), there is an intrinsic tension in the sheet, which leads
to spontaneous scrolling and lateral coiling in order to
release the strain energy (Saupe et al. 2000).

It is also possible to observe that some particles are con-
stituted of two parallel tubes, forming something like a
parchment scroll with one roll to the left and one roll to
the right. Particles are thought to be calcium niobate
sheets containing coiled opposite edges as illustrated in
the inset of Figure 5(d).

Unfortunately the mechanism of the coiling process of
flat inorganic particles is not yet completely understood.
Maybe neutralization of excess negative charges on
HCA$_2$Nb$_3$O$_{10}$ exfoliated flat particles favors sheet coiling
and diameter shrinkage.

The typical EDX measurements confirmed the nearly
stoichiometric ratio of the precursor layered perovskite,
that is, K:Ca:Nb = 1:2:3 (Figure 6(a)). This analysis also
showed that there is no residual K$^+$ (detection limit 2%) in
restacked nanosheets (Figure 6(b)).

N$_2$ adsorption–desorption isotherm and pore-size distri-
bution of exfoliated nanosheets are displayed in Figure 7.
The isotherm revealed stepwise adsorption and desorption
shapes (type IV isotherms), showing the characteristic of
mesoporous materials. All the textural properties of the exfo-
liated sample such as the BET surface area and average
mesopore size calculated by the BJH method and specific
surface area of parent layered KCA$_2$Nb$_3$O$_{10}$ are listed in
Table 1, together with the energy band gaps discussed as
follows.

The specific surface area of exfoliated edge-coiled
nanosheets (65 m$^2$/g) was greatly enhanced in comparison
with that (<2 m$^2$/g) of the starting bulk material,
KCA$_2$Nb$_3$O$_{10}$, before exfoliation. This should be favorable
for their use as photocatalysts.

The high surface area of exfoliated sample compared to
parent niobate is mainly due to particle topography as coiled
nanosheets that precludes an organized re-stacking.

UV-vis diffuse reflectance spectra for the exfoliated and
parent layered samples are shown in Figure 8. Both samples
exhibit absorption bands in the UV region (<400 nm). A
strong absorption at a wavelength above 300 nm is charac-
teristic of semiconducting KCA$_2$Nb$_3$O$_{10}$ layered material
that corresponds to the excitonic or interband (valence to
conduction bond) transition.

The nanosheet and the parent compound had absorp-
tion edges at 375.8 nm and 413.3 nm, respectively. The
position of the absorption edge moves to shorter wave-
lengths in the ex-Ca$_2$Nb$_3$O$_{10}$ nanosheets. The band-gap
energies of the materials were estimated using the following
equation (Mott & Davis 1979):

$$\alpha h \nu = (h \nu - E_g)^n$$

where $\alpha$, $E_g$, and $n$ are, respectively, the absorption coeffi-
cient (Kubelka–Munk function), band gap, and an
exponent that is 2 for indirect-gap semiconductors and $1/2$
for direct-gap semiconductors. From the plot of $(\alpha h \nu)^{1/n}$
vs. $h \nu$, $E_g$ can be obtained by extrapolating the linear portion
to the $h \nu$ axis intercept. Assuming that the materials are
indirect band-gap semiconductors ($n = 2$), one can estimate
the band-gap energies of the exfoliated nanosheets
(ex-Ca$_2$Nb$_3$O$_{10}$) and parent layered material (KCA$_2$Nb$_3$O$_{10}$)
to be 3.3 eV and 3.0 eV, respectively. The decrease in the

Figure 6 | EDX spectra of parent layered material (KCA$_2$Nb$_3$O$_{10}$) (a) and the H$^+$-exchanged form (HCA$_2$Nb$_3$O$_{10}$) (b).
adsorption edge or increase in the band-gap energy may be due to the one-dimensional size-quantization effects peculiar to the molecularly thin nanosheets, which has been reported for exfoliation of layered parent oxides, suggesting that exfoliated particles be in nanoscale range. Comparable increases in the band gap have previously been observed between bulk and exfoliated (TBA,H)Ca₂Nb₃O₁₀ sheets prepared by an alternative method by Han & Choy (2001) and in restacked sheets of a related perovskite, K₂Nb₆O₁₇, by Furube et al. (2002).

**CONCLUSIONS**

The layered perovskite KCa₂Nb₃O₁₀ was successfully synthesized by the solid state reaction of the starting materials (K₂CO₃, CaCO₃ and Nb₂O₅) at 1,200 °C and showed to have interlayer reactivity under mild conditions both in proton exchange reactions and also in intercalation of large organic base, TBA⁺OH⁻, as exfoliating agent for the preparation of calcium niobate nanosheets by an exfoliation–restacking process. Formation of an interesting class of niobate nanosheets with a molecular thickness and other unusual structural features was demonstrated by various characterization techniques such as XRD, FE-SEM, N₂ adsorption–desorption and DRS UV–vis spectroscopy. The XRD profile containing broad peaks confirmed the individual molecular aspects of the nanosheets. FE-SEM images of exfoliated nanosheets (ex-Ca₂Nb₃O₁₀) represented lateral coiling in order to release the intrinsic tension in the sheet. The specific surface area of exfoliated coiled nanosheets was 65 m²/g, which is much larger than that of the parent layered solid prior to exfoliation (<2 m²/g). The nanosheets in this study were also found to act as a semiconductor with a wide band gap as a result of quantum size effect.

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