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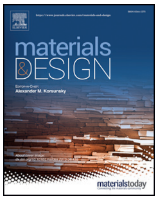

Changes in cell parameters and improvement in photocatalytic activity of $KNbO_3$ and $NaNbO_3$ crystals *via* polarization

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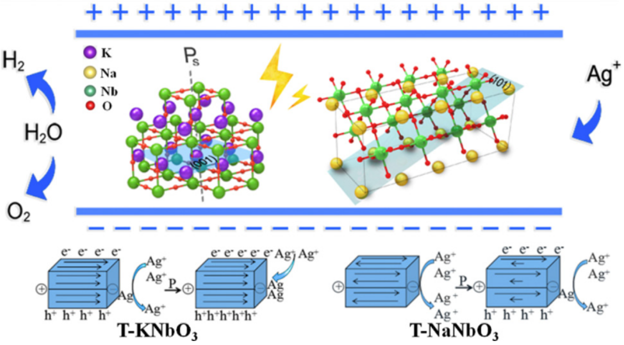
HIGHLIGHTS

- T-$KNbO_3$ and O-$NaNbO_3$ crystal powder samples have been polarized by using an external electric field.
- The crystal lattices for T-$KNbO_3$ and O-$NaNbO_3$ crystals have been changed after the polarization.
- The photocatalytic activity of T-$KNbO_3$ and O-$NaNbO_3$ samples on each exposed facet has been enhanced to a certain extent after the polarization.
- The influence of the polarization on photocatalytic activity is greater than that of surface energy

GRAPHICAL ABSTRACT



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ABSTRACT

A representative ferroelectric tetragonal potassium niobate (TKN) and antiferroelectric orthorhombic sodium niobate (ONN) crystalline powder samples were polarized by using an external electric field. The changes in lattice distortion and crystal symmetry of these samples polarized were revealed. The photocatalytic activities of the samples before and after the polarization were evaluated by photocatalytic decomposition of water and photocatalytic reduction of Ag^+. The results imply that the polarization of such kind of perovskite-type niobate samples using the external electric field is one of effective ways to improve the photocatalytic performance, whether ferroelectric TKN or antiferroelectric ONN. The exploration of mechanism suggests that the polarization can change the ferroelectricity of niobate powder crystals. Furthermore, the photocatalytic activity on different exposed facets of these niobate crystals was also evaluated by detecting Ag content on the surfaces of sample *via* photocatalytic reduction of Ag^+. It is found that {001} facet is the highest active facet of TKN, and {101} facet of ONN crystals has the highest photocatalytic activity among the exposed facets. The photocatalytic activity on each exposed facet can be increased to a certain extent by polarization, and the influence of polarization on photocatalytic activity is greater than that of surface energy.

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1. Introduction

The discovery of water photolysis on a TiO_2 electrode by Fujishima and Honda in 1972 [1] is recognized as the milestone significant event, that is, the investigation of photonic energy conversion stimulated by photocatalytic methods. Photocatalysis has emerged as one of the most promising technologies because it is an easy way to utilize the energy of both natural sunlight and artificial indoor illumination [2–5]. The common inorganic photocatalysts are semiconductor materials [6]. The role of irradiated semiconductor as photocatalyst is to initiate or accelerate specific reduction and oxidation reactions. Light absorption and the consequent photoexcitation of electron-hole pairs happens when the energy of the incident photons matches or exceeds the band gap. In the semiconductors, the conduction-band electrons have a chemical potential of $+0.5$ to -1.5 V *versus* the normal hydrogen electrode, so they can act as reductant. The valence-band holes exhibit a high oxidative potential of $+1.0$ to $+3.5$ V *versus* the normal hydrogen electrode [7–9]. The photocatalytic materials have attracted extensive and increasing attention owing to their applications in the areas of environmental cleansing, photochemical water splitting, and solar fuel production [10]. Its photocatalytic activity strongly depends on the band gap, the surface lattice structure of crystal, the separation of electron-hole pair photogenerated, and crystallinity *etc.* [11–13].

Ferroelectrics are considered as wide band gap semiconductors because they can produce photo generated carriers under super band gap illumination [14]. The ferroelectric with a spontaneous polarization can be reversed by using an external electric field [15]. In addition, ferroelectric materials also possess a surface polarization, which has been measured between 0.1 and 78 $\mu C \cdot cm^{-2}$ below the Curie temperature [16]. The influence of the polarization on ferroelectric materials has been discovered to produce functions that may be propitious to photocatalytic processes, which promotes the photocatalytic performances of the material [17–20]. The study on ferroelectric catalysts and solar cell materials with perovskite structure currently receive intensive attention because their properties are of fundamental scientific importance [21–24]. The study on the ferroelectric photocatalysts is interesting since the spontaneous polarization of ferroelectric solids is likely to affect the kinetics of charge transfer at the catalyst-adsorbate interface and the free energy of polar-adsorbed species as well [25]. Many methods on improving the photocatalytic activity have been proposed in [26,27]. The polarization can produce an internal electric field in the crystals, resulting in the separation of positive and negative charge centers, especially in ferroelectric crystal possessing spontaneous polarization potential, which can help enhance the photocatalyst activity. However, there is no report on the improvement of the photocatalytic property for perovskite type photocatalyst by controlling the ferroelectricity of the powder crystal *via* polarization. The reported polarization method is only used in the research on ceramic samples such as lead-free piezoelectric ceramics [28], and the research on the polarization of ceramic samples only shows that polarization can produce a stretching of unit cells but without explaining the mechanism of polarization.

Perovskite semiconductor photocatalysts are promising since their conduction band edge are often more negative than the H^+/H_2 energy level. Thus they can split water without any external bias potential and are relatively stable under light illumination [29,30]. Potassium niobate ($KNbO_3$), a classical perovskite oxide with excellent photocatalysis and ferroelectric properties at room temperature and non-toxicity, has been used in photocatalytic processes [31–34]. While perovskite type sodium niobate ($NaNbO_3$) has an antiferroelectric structure at room temperature. The antiferroelectric material is substantially nonpolar, but can restore to a ferroelectric polar state by applying an external electric field [35,36]. Such remarkable property is especially significant for developing high photocatalyst activity.

In this study, the representative ferroelectric tetragonal potassium niobate (T-$KNbO_3$, TKN) and the representative antiferroelectric orthorhombic sodium niobate (O-$NaNbO_3$, ONN) powder crystals were prepared by a hydrothermal process. The obtained perovskite niobate powder crystals were polarized by applying an external electric field in order to explore the effect of polarization on photocatalytic activity. The cell parameters and the photocatalytic reactivity of the samples obtained before and after polarization were investigated. Furthermore, the photocatalytic activities of these perovskite type niobate crystals on different exposed facets are evaluated by photocatalytic reduced reaction in $AgNO_3$ aqueous solution. The photocatalytic activity of the exposed facets for the niobate crystals is discussed as well. The strategy about the enhancement of the photocatalytic activity for powder crystals by changing its ferroelectricity by the polarization treatment is first proposed in this study. The changes in cell parameter and ferroelectric property of crystals *via* polarization are helpful to design a new material. In particular, such strategy on the enhancement of photocatalytic activity *via* polarization can help develop novel photocatalyst with high photocatalytic activity.

2. Experimental section

2.1. Synthesis of perovskite niobates

The TKN crystal sample was hydrothermally synthesized at 200 °C while using potassium hydroxide and niobium oxide as the raw materials. The ONN crystal sample was also hydrothermally synthesized at 200 °C while using sodium hydroxide and niobium oxide as the raw materials. Required details of the synthesis protocol are shown in the Supporting Information.

2.2. Physical analysis

The crystal phases of the sample were investigated by using a powder X-ray diffractometer (XRD, Rigaku D/max-2200PC) with Cu K_a ($\lambda = 0.15418$ nm radiation). The size and morphology of the particles were observed by a field-emission scanning electron microscope (FEI, FE-SEM, Quanta FEG 250G). Transmission electron microscope (TEM) (Tecnai G2F20STWIN) and selected-area electron diffraction (SAED) observations were performed on a system at 200 kV, and the sample was supported on a Cu microgrid. Chemical composition analysis was performed with *in situ* energy dispersive X-ray spectroscopy (EDX) using an instrument equipped in the FE-SEM system. TEM, SAED, and EDX were also used to confirm the chemical composition of the sample. Moreover, Raman spectroscopy was used as a complementary technique to investigate the phase transitions as well as crystal structure of the powder samples. The Raman spectra were collected by a Renishaw InVia Raman microscope, from a laser operating at 532 nm, 50 times objectives. The laser power at the sample was estimated to be 1% and nominal laser spot size was 10 μm. The UV–visible absorption spectra of the samples were measured on a SHIMADZU UV-2450 spectrophotometer. The XPS examinations of the obtained samples allowed to estimate their average composition. X-ray photoelectron spectroscopy (XPS, Perkin Elmer) analysis was carried out by using a PHI-5700 multifunctional X-ray photoelectron spectroscopy system, using Al-Kα radiation as the excitation source.

2.3. Polarization of potassium niobate and sodium niobate powder

About 2 g powder sample was pressed into a disc with the size of 10 mm both in diameter and thickness. Then the disc was sealed in a quartz tube with the size of 10 mm in inside diameter and 30 mm in outside diameter. Polarization of disc was performed by using a pair of copper electrodes at room temperature in atmosphere and applying external voltage with a fixed value from 0.25 kV to 2.00 kV for 1 h. Two ends of the disc were connected with copper wires for 12 h to remove the residual charges caused by the polarization. In order to distinguish the samples before and after polarization, the polarized sample is