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Layered lithium niobium (III) oxide—LiNbO₂ as a visible-light-driven photocatalyst for H₂ evolution

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Abstract
The search for visible-light photocatalysts is of great significance in clean energy and environmental applications to best utilize solar radiation. Some layered semiconductor photocatalysts have been found to exhibit promising performance levels. Their superior activity has been linked to the layering within the crystal structure, which may facilitate separation of carriers and, hence the reduction and oxidation reactions. Previous investigations on layered materials focused on oxides containing early transition metal cations with d⁰ electronic configurations utilizing ultraviolet radiation. Attempts to synthesize layered materials with visible light response have been less successful and the photoactivity of such materials is not very high. Here, we have investigated a layered semiconductor compound, LiNbO₂ with nominal d² electronic configuration (Nb³⁺). As a result of a sub-valence band originating from filled d orbitals, LiNbO₂ exhibits visible light absorption extending to 650 nm and demonstrates interesting photocatalytic activity for hydrogen production.

Solar energy is the most promising energy feedstock across the world due to its inexhaustible nature and environmental friendliness [1]. The distribution of solar incidence worldwide ensures easy accessibility of energy resource and wide applicability of solar technologies [2]. Among various solar technologies available, converting solar power directly into chemical fuels is one of most promising means of solar energy utilizations, as it can be readily adopted into our current energy infrastructure built upon fossil fuels [3, 4]. A typical example is solar hydrogen production from water [5, 6]. Under appropriate irradiation conditions, preferably visible light, hydrogen is produced on the surface of a photocatalyst without any other energy input. Such a simple energy conversion process is very tempting, yet only a few materials were found be to photocatalytically active for hydrogen production without sacrificial elements, let alone an appreciable conversion efficiency under visible light radiation [7–10]. A number of layered compounds have been found to exhibit interesting photocatalytic activity [9, 11–25]. Their activity seems to be associated with the peculiar layered crystal structures that promote separation of charges and reactions [11, 13, 26, 27]. Previous investigations of layered compounds were largely limited to those active only under UV radiation [11, 13, 27–32]. Here, we investigated a layered compound LiNbO₂ with nominal d² electronic configuration that shows very high hydrogen production rate under visible light radiation.

The layered compound LiNbO₂ has been studied previously due to the occurrence of superconductivity at ∼5 K if around 30% of the Li cations are removed [33, 34]. Its layered structure comprises of alternating NbO₆ trigonal prism sheets and layers of Li⁺ cations (figure S1 is available in the supplementary material: stacks.iop.org/JENERGY/1/015001/mmedia). Conductivity measurement and theoretical calculations suggest an
insulator-to-metal transition driven by decreasing Li content; zero or low deficiency of Li yields a semiconductor with band gap energy around 2 eV [34–37]. This bandgap indicates that semiconducting LiNbO2 might be a promising photocatalyst despite the low oxidation state of Nb suggesting redox instability in contact with water. Recent results on cubic Sr1−xNbO3 demonstrate that reduced niobium oxides do not necessarily react with water at ambient conditions and hence can deliver stable photocatalytic activity in aqueous systems [7, 38], hence we have investigated layered LiNbO2 as a possible photocatalyst.

Results and discussions

LiNbO2 was synthesized by reacting Li3NbO4 and Nb2O5 precursors with Nb metal in a flowing Ar atmosphere [39]. The refined x-ray diffraction (XRD) patterns of the final sample obtained are displayed in figure 1S. All of the peaks can be indexed and refined in the hexagonal symmetry (space group P63/mmc) in accord with previous reports [33]. The final R factors ($R_{wp} = 8.57\%$ and $R_p = 6.69\%$) and the value of reduced $\chi^2$ (2.015) suggest a reasonable fit of the structure model to the observed XRD patterns, confirmed by the absence of any unassigned peaks and, hence, no secondary phase in the sample. The refined unit cell parameters ($a$ and $c$) and cell volume are (2.9100(3) Å and 10.4708(6) Å) and 76.78 (1) Å$^3$, respectively. Thermogravimetric analysis under flowing oxygen atmosphere suggests a weight gain of 12.08% up to 1000 °C, which agrees well with the theoretical value 12.13% on the assumption that all Nb cations in LiNbO2 are oxidized to Nb$^{5+}$ during the TGA in air. The molar ratio of Li to Nb is determined to be 0.95(7) based on inductively coupled plasma (ICP) measurements, which is very close to the stoichiometric value in ideal LiNbO2.

In accord with previous reports and the reddish appearance of the powders, UV-visible absorption spectrum of the synthesized LiNbO2, figure 1, reveals an intense absorption in the visible region with absorption extending as far as 650 nm. Kubelka–Munk transformation versus the energy of the light suggests an onset of light absorption starts from 1.94 eV (see inserted image in figure 1), which agrees well with a band gap ~2 eV and the reported semiconducting nature of the sample [37].

We evaluated the photocatalytic activity of LiNbO2 for water splitting by monitoring H2 production from oxalic acid aqueous solution under visible light irradiation. Oxalic acid is known as a common pollutant from industrial treatment processes such as textile industry and metallurgy, the low potential of its redox couple $\text{H}_2\text{C}_2\text{O}_4$ (aq)/$\text{CO}_2$ (g) = −0.49 V suggests that it can be used as a good hole scavenger [40]. Measurements were firstly carried out in the dark conditions with the purpose of evaluating any reaction that does not proceed photocatalytically. No H2 was detected during the measured 5 h in the absence of radiation. Figure 2 displays the typical time courses of H2 production under visible light radiation. Although only a trace of hydrogen was generated in the initial 2 h, the pristine LiNbO2 (0.2 g) shows a hydrogen evolution rate of ca. 12 μmol h$^{-1}$ in the subsequent experiment. The inducement period of the first two hours might be due to the passivated surface as samples were synthesized by annealing at ultra-high temperature (1250 °C) for 20 h. To acquire a sample with a large fresh surface, the as-prepared LiNbO2 powders were then ball milled to break down the large particles (figure S2). The ball milled sample shows an apparent improvement on the hydrogen evolution rate
provides additional reaction sites. Microscopic analysis indicates the formation of Pt nanoparticles. The role of Pt in this experiment is as a co-catalyst that not only collects photo-generated charges but also band gap energy compared to the experimental value. Photocatalytic performance can be further improved by introducing Pt and an average H2 production rate is achieved by loading 1 wt% Pt, approaching an apparent quantum efficiency ca. 0.277%. The role of Pt in this experiment is as a co-catalyst that not only collects photo-generated charges but also provides additional reaction sites. Microscopic analysis indicates the formation of Pt nanoparticles (~10 nm) on the surface of LiNbO2 with core-shelled micro-structures (figure S3). The action spectrum of photocatalytic hydrogen production showed a strong dependence upon the wavelength of photons with maximum performance around 600 nm (figure S4), confirming a real photocatalytic process. The corresponding apparent quantum efficiency reaches 1.8% at 550 nm. The linear sweep voltammogram based on LiNbO2 thin film electrode clearly shows a light driven current response under chopped light (figure S5). Photocurrent was observed up to 650 nm and the plots of photocurrent versus wavelength roughly follow UV–vis absorption spectrum (figure S6). Other hole scavengers like methanol and sodium sulphite were also employed and steady hydrogen evolution was observed with apparent quantum efficiency ca. 0.38% under full range irradiation and without change in activity in repeated experiments (figure S7, table S1); the turnover number is calculated to be 7.18 according to the amount of hydrogen produced and number of atoms in the material [5]. Besides, the powders before and after photocatalytic experiment showed an identical XRD pattern (figure S8), SEM image (figure S9) and x-ray photoelectron spectroscopy (XPS) signals (figure S10). More interestingly, XPS spectra suggest the existence of Nb2+ and Nb4+ species, which implies LiNbO2 is probably a charge transfer insulator and Nb only has an effective charge of 3+. Based on the above results, we confirm that LiNbO2 is a real photocatalyst and is capable of splitting water in the presence of sacrificial elements. It should also be noted that the surface area of LiNbO2 particles after ball-milling is still quite low and particles are fairly large (see figure S2) therefore the capability of photocatalytic hydrogen evolution may be improved by further decreasing the particle size. Mechanical processing will not only help to decrease the particle size but also may provide additional trapping sites that are favorable for reactions and charge separation.

To better understand the photocatalytic activity and its relation to the layered structure, we carried out some theoretical calculations on the electronic structure of LiNbO2. The calculated band structure is displayed in figure 3. According to the calculations, conduction band and valence band are well separated from the Femi level with a direct band gap 1.6 eV, therefore, LiNbO2 is indeed a semiconductor. The smaller calculated band gap compared to the experimental value (1.94 eV) is due to the drawbacks of GGA method that often underestimates band gap energy [41]. Nevertheless, the calculations do give useful qualitative information. Layered materials are well known for their anisotropies in physical or chemical properties, such as electronic conductivity of graphite. The question then arises whether the photogenerated charge carriers (electron hole pairs) behave in an anisotropic manner in the case of layered LiNbO2. This can be examined by analyzing its band structure in different crystallographic directions (figure 3). Take for example, along E–k curve, traversing from point a to point b covers a large energy dispersion ~2 eV of conduction band in the [100] direction. Recalling that the

![Figure 2](https://via.placeholder.com/150)

**Figure 2.** Time-dependent photocatalytic hydrogen evolution from pristine LiNbO2, ball-milled LiNbO2 and ball-milled LiNbO2 with 1 wt% Pt. Measurements were performed upon 0.2 g powders in 200 ml oxalic acid aqueous solution (0.025 M). Light source: 250 W iron doped metal halide UV–vis lamp with a UV cut-off filter (λ > 420 nm).
mobility of electrons/holes is inversely proportional to their effective mass $m^*$ and the effective mass is inversely proportional to the second derivative of $E$ versus $k$ curve (wide band leads to high mobility):

$$m^* = \frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)^{-1}} \quad (1)$$

therefore, the electrons in the CB will have a high mobility in the [100] direction [42, 43]. In other words, a large curvature of $E$–$k$ curve indicates ‘light’ electrons/holes that are easy to move. Similar observations are also found in other directions such as [−120] (from point $b$ to point $c$), therefore, electrons are highly mobile parallel to the NbO$_6$ trigonal prism sheets. However, dispersion in the [001] direction (from point $c$ to point $d$) is almost negligible, suggesting electron migration across different layers are virtually forbidden. Similar situations are also found in the valence band thereby charge carriers in LiNbO$_2$ will be more or less restricted in separated layers. These restrictions to the charge carriers are of great significance to the photocatalytic activity, as electron hole recombination between different layers can be considerably mitigated.

Partial density of states (PDOS) from constituent elements in LiNbO$_2$ were also calculated (figure S11). The absence of Li PDOS near Fermi level suggests negligible contributions of Li to both CB and VB. The CB and VB are found to be predominantly composed by Nb atoms (4d orbitals), with some contributions from O atoms (mainly 2p orbitals). In this respect and above analysis, electrons and holes are primarily confined in the individual NbO$_6$ trigonal prism sheets with high intrasheet mobility. The role of interlayer Li$^+$ ions can therefore be understood as steric barriers preventing charge interactions between different sheets. This specific structure is
highly beneficial for fast charge transfers as each \( \text{NbO}_6 \) trigonal prism sheet can act as an independent photocatalyst.

Knowledge of the energy band positions is also crucial in understanding the photocatalytic reactions. The conduction band edge can be roughly inferred from the Mott–Schottky (MS) plot according to impedance measurement (figure S12). The flat-band potential determined from MS plot \( 
\sim -0.534\, \text{V versus NHE} \) will lie very close to the conduction band edge. Thereby the valence band edge can be simply estimated using the band gap energy \( (1.94\, \text{eV}) \), which approximately lies at \( +1.4\, \text{V versus NHE} \). The final proposed energy band positions are displayed in figure 4. The energy gap between CB and VB straddles the redox potentials of water, which meets the thermodynamic requirement for water splitting. Nevertheless, the CB edge is suitably more negative \( (\sim -0.534\, \text{V versus NHE}) \) than the reduction potential of water, so the electrons in the conduction band will have high reducing power for hydrogen evolution and a strong driving force for the separation from holes due to the large potential drop across depletion layer when equilibrating with water. The VB edge, on the other hand, lies very close to the oxidation potential of water, suggesting \( \text{LiNbO}_2 \) might not be suitable for \( \text{O}_2 \) production. This is confirmed in the photocatalytic \( \text{O}_2 \) evolution experiment (table S2), where only a small amount of \( \text{O}_2 \) was produced even under full range radiation \( (\text{UV} + \text{Vis}) \) and a low turnover number around 0.07.

Conclusions

In summary, we have synthesized a layered compound \( \text{LiNbO}_2 \), which demonstrates a high photocatalytic activity in \( \text{H}_2 \) production. Its good photocatalytic performance might be related to the anisotropic dispersion of its electronic structure such that charge recombination can be inhibited. The very negative CB edge position endows photogenerated electrons with high reducing power and facile charge separation that favors \( \text{H}_2 \) production. Such a layered structure as well as the special \( d^2 \) electronic configurations of transition metal enlightens our search for new photoactive materials in the future.

Methods

Sample synthesis

\( \text{LiNbO}_2 \) was synthesized by calcining homogenized \( \text{Li}_2\text{NbO}_4, \text{Nb and Nb}_2\text{O}_5 \) mixtures in a flowing \( \text{Ar} \) atmosphere at 1250 °C for 20 h \[33, 39\]. Details for synthesis can be found in supplementary information.

Characterization

Crystal structure and phase purity were examined by XRD analysis of powders on a STOE STADI/P powder diffractometer. Incident radiation was generated using a \( \text{CuK_\alpha 1} \) source \( (\lambda = 1.54056\, \text{Å}) \). The step size for data collection was 0.02° with a collection time 1000 s at each step. Vaseline was used to mount the powders onto the holder. X-POW software and General Structure Analysis System program under EXPGUI interface was used to perform least square refinement and Rietveld refinement. A Micromeritics instrument ASAP 2020 was used to examine the \( \text{N}_2 \) adsorption and desorption properties and specific surface areas were calculated via the Brunauer–Emmett–Teller (BET) model. The microstructure of the powders was inspected using a scanning electron microscope (JEOL 5600 SEM) equipped with a Mica energy dispersive x-ray spectroscopy analysis system. Diffuse reflectance spectra were collected on a UV–vis spectrophotometer (JASCO-V550) and the absorbance was transformed by the Kubelka–Munk method. Thermogravimetric analysis was carried out on a Rheometric Scientific TG 1000M+ and TA instruments with heating and cooling rate of 10 °C min\(^{-1}\) to 1000 °C under flowing oxygen. An Agilent 7500a ICP mass spectroscopy with laser ablation was used for surface element analysis. MS analysis was carried out through impedance measurements using a Schlumberger Solartron 1255 frequency response analyzer couple with a 1287 Electrochemical Interface. Sintered \( \text{LiNbO}_2 \) pellet, Pt wire, Ag/AgCl electrode and 1 M KCl aqueous solution were used as working, counter, reference electrode and electrolyte respectively. The configuration of the set up was as described in prior literature \[44\]. The impedance analysis was performed at frequency range from 100 kHz–0.1 Hz at 50 mV rms under potential bias from \( -1.6 \) to \( +0.5\, \text{V} \) (versus Ag/AgCl). The capacitance was then extracted from the impedance spectra and was used to derive the MS plot. The XPS measurements were performed on Thermo Escalab 250 with a monochromatic Al K\( _\alpha \) x-ray source. All binding energies were referenced to the C 1 s peak \( (284.6\, \text{eV}) \) arising from adventitious carbon.

Photoreactivity measurements

Measurement of photocatalytic hydrogen evolution was performed in a home-made Teflon reactor with window sealed by a quartz glass. In a typical experiment, photocatalyst was dispersed in aqueous solution (oxalic acid, Methanol or sodium sulftite). The suspension was then sealed within the home-made photoreactor. The
reactor was purged with pure Ar gas as a protective gas. Gas composition within the reactor was monitored by a gas chromatograph (Agilent 3000 Micro Gas Chromatograph). A 250 W iron doped metal halide UV–vis lamp with or without a UV cut-off filter (λ ≥ 420 nm) was used as the light source. The photon flux of the lamp is calibrated using a quantum meter (Apogee MQ-200). The average photon flux is 1305 ± 27 μmol m⁻² s⁻¹ under visible light radiation and 1510 ± 31 μmol m⁻² s⁻¹ under full range radiation. The photocatalytic oxygen evolution was performed in a similar set up, except using 0.1 g LiNbO₂ powder and 200 ml AgNO₃ aqueous solution (0.005 M) as a sacrificial element.

The LiNbO₂ thin film electrode was prepared according to the following procedure: 40 mg powders and 10 mg iodine were dispersed in 50 ml acetonitrile solution ultrasonically. Two pieces of fluorine-doped tin oxide (FTO) glasses were then placed in parallel into the suspension with a separate distance 10 mm. 30 V bias was applied for 30 min between these two FTO glass under potentiostatic control. The as-prepared electrode was then dried in the oven for 1 h before photocurrent measurements. The photocurrent measurements were performed in 0.2 M Na₂SO₄ aqueous solution using LiNbO₂ thin film electrode, platinum sheet and Ag/AgCl electrode as working, counter and reference electrode respectively.

Theoretical calculations

Theoretical calculations were carried out by using the density functional theory implemented in the Vienna ab initio simulation package [45]. Perdew, Burke and Ernzerhof exchange-correlation functional within the generalized gradient approximation [46] and the projector augmented-wave pseudopotential [47] were adopted. Spin-polarization was also taken into account in this calculation. A hexagonal super cell with a = 2.91 Å and c = 10.47 Å was used for simulations. All geometry structures were fully relaxed until the forces on each atom are less than 0.01 eV Å⁻¹. Static calculations were done with a 19 × 19 × 5 Monkhorst–Pack k-point grid [48].

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Author contributions

XX performed the synthesis and collected data with GL and SN carried out the theoretical calculations. All the authors contributed to the writing of the manuscript.

Additional information

The authors declare no competing financial interests.

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