

An Undoped, Single-Phase Oxide Photocatalyst Working under Visible Light

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Photocatalysts convert solar energy into clean hydrogen energy by splitting water, and decompose harmful organic and inorganic pollutants. The remarkable progress of the past decade in photocatalysis has been limited to ultraviolet (UV) light instead of the more useful visible-light region. The development of visible-light photocatalysts, therefore, has become one of the most important topics in photocatalysis research today. Traditional visible-light photocatalysts are either unstable¹ (CdS, CdSe, etc.) or have low activity² (Fe₂O₃, WO₃, etc). Recently, some UV-active oxides turned into visible-light photocatalysts by substitutional doping of metals as in Ni_xIn_{1-x}TaO₄³ and (V-, Fe-, or Mn-)TiO₂,⁴ or of C, N, and S, as in TiO_{2-x}N_x,⁵ TiO_{2-x}C_x,⁶ TaON,⁷ and Sm₂Ti₂O₅S₂.⁸ But their activities are usually low, and there is concern for the stability of substituted anions under reaction conditions. Here we describe an undoped, single-phase oxide photocatalyst, PbBi₂Nb₂O₉, an Aurivillius-phase perovskite, which is an efficient photocatalyst for isopropyl alcohol degradation to CO₂, generation of photocurrent, and decomposition of water into O₂ or H₂, all under visible light ($\lambda \geq 420$ nm). It is much more active than the recently disclosed TiO_{2-x}N_x⁵ and, in particular, exhibits an unusually high quantum yield (QY, the number of photons utilized for a desired chemical reaction divided by the number of photons absorbed by the catalyst) of 29% in oxygen production from water containing AgNO₃. Further, the material was found to be stable in water under irradiation conditions.

Perovskite-type oxide materials based on transition metals with d(0) electron configuration such as Nb(V),⁹ Ta(V),¹⁰ and Ti(IV)¹¹ are efficient photocatalysts for overall water splitting with high quantum yields. However, the large band gaps of these materials (ca. 3.8–4 eV) are not suitable for visible light-induced photocatalysis. Although PbBi₂Nb₂O₉ also belongs to the layered perovskites, it absorbs visible light ($\lambda \geq 420$ nm) and shows high photocatalytic activities. Aurivillius compounds with a general formula (Bi₂O₂)²⁺(A_{m-1}B_mO_{3m+1})²⁻ consist of *m* perovskite units sandwiched between bismuth oxide layers, where A and B are the two types of cations that enter the perovskite unit.¹² The material was synthesized by the solid-state reactions of PbO, Bi₂O₃, Nb₂O₅ at 1473 K (see Supporting Information.) The crystal structure of prepared material was confirmed from the X-ray diffraction (XRD) analysis using Cu K α radiation. As shown in Figure 1, highly crystalline PbBi₂Nb₂O₉ was identified with a space group of A₂₁am, *a* = *b* = 5.496 Å, *c* = 25.55 Å. Its structure model is also shown together with the high-resolution TEM image that clearly exhibits fringes corresponding to repeating perovskite slabs. TiO_{2-x}N_x, known for its good photocatalytic activity in decomposition of methylene blue and acetaldehyde under visible light was also prepared as a reference.⁵

The UV–visible diffuse reflectance spectra for these compounds are shown in Figure 2. From these spectra, we estimated the band gap energy of these materials as summarized in Table 1. The PbBi₂Nb₂O₉ sample showed a sharp edge, while TiO_{2-x}N_x

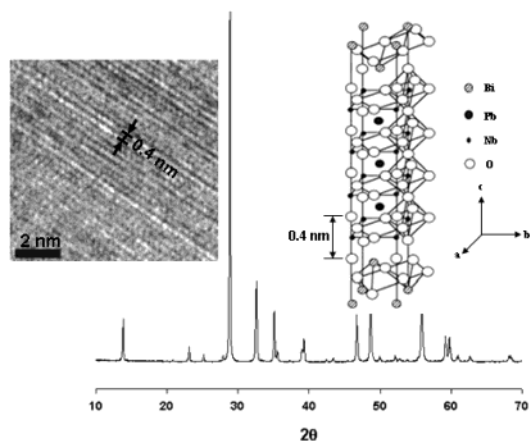


Figure 1. X-ray diffraction pattern and the high-resolution TEM image of PbBi₂Nb₂O₉ sintered at 1473 K for 24 h and its structure model.

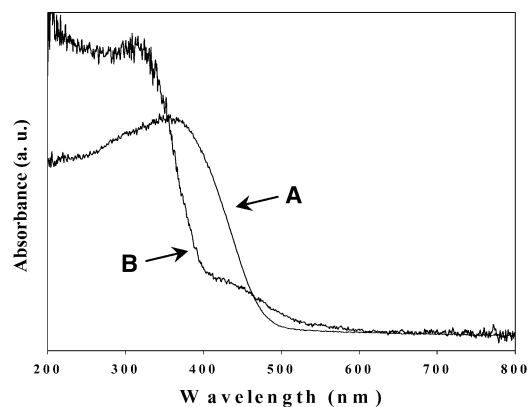


Figure 2. UV–vis diffuse reflectance of (A) PbBi₂Nb₂O₉ and (B) TiO_{2-x}N_x.

Table 1. Photocatalytic Activities for H₂ Evolution from an Aqueous Methanol Solution and O₂ Evolution from Aqueous AgNO₃^a

catalyst	band gap energy		H ₂ evolution		O ₂ evolution	
	E _g (eV)	λ(nm) ^b	μmol/h	QY ^c	μmol/h	QY ^c
PbBi ₂ Nb ₂ O ₉	2.88	431	7.6	0.95	520	29
TiO _{2-x} N _x	2.73	451	Trace	0	221	14

^a Catalyst loaded with 1 wt % Pt, 1.0 g; light source, 450-W W-Arc lamp (Oriel) with UV cutoff filter ($\lambda \geq 420$ nm). Reaction was performed in aqueous methanol solution (methanol 30 mL + distilled water 170 mL) or in an aqueous AgNO₃ solution (0.05 mol/L, 200 mL). ^b The wavelength at the absorption edge, λ , was determined as the intercept on the wavelength axis for a tangent line drawn on absorption spectra. ^c The quantum yield QY = 2 × number of H₂ or 4 × number of O₂ generated per number of photon absorbed by photocatalyst. See Supporting Information.

showed two absorption edges; the main edge due to the oxide at 390 nm and a shoulder due to the nitride at 451 nm. The color of both materials was yellow, indicating that these materials indeed

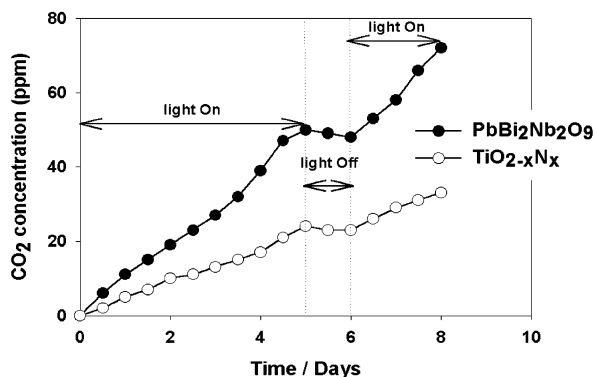


Figure 3. Time courses of CO₂ evolution from IPA decomposition over PbBi₂Nb₂O₉ and TiO_{2-x}N_x under visible light irradiation ($\lambda \geq 420$ nm). Photocatalyst, 0.3 g; IPA concentration, 200 ppm in air.

absorbed the visible light. These band gap energies are also greater than theoretical energy required for water splitting (> 1.23 eV).

To evaluate the photocatalytic activities of these materials under visible light ($\lambda \geq 420$ nm), oxidative decomposition of gaseous isopropyl alcohol (IPA) was tested first. Figure 3 shows gaseous CO₂ concentrations, generated as a result of the photodegradation of IPA over PbBi₂Nb₂O₉ and TiO_{2-x}N_x, as a function of irradiation time. The concentration of CO₂ increased steadily with irradiation time at a decomposition rate of ca. 9.3×10^{-3} mol/h only under irradiation of light. The CO₂ production stopped when light was turned off and was resumed at the same rate when light was turned on again. The photocatalytic activity of TiO_{2-x}N_x for IPA decomposition was about a half of that for PbBi₂Nb₂O₉.

Active photocatalysts should generate photocurrents upon absorption of light,¹³ and we found that PbBi₂Nb₂O₉ indeed generated photocurrent under visible light irradiation (see Supporting Information). Undoped TiO₂ did not generate any current, while TiO_{2-x}N_x generated about half the current measured for PbBi₂Nb₂O₉.

Finally, photocatalytic reduction of H₂O into H₂ and oxidation of H₂O into O₂ were performed as test reactions. Methanol and silver ions were used as scavengers of holes and photoelectrons, respectively. In Table 1, H₂ evolution from aqueous methanol solutions and O₂ evolution from aqueous AgNO₃ solution over these photocatalysts are summarized. H₂ evolution was observed only over PbBi₂Nb₂O₉ when Pt was loaded on its surface. H₂ was evolved steadily with no indication of catalyst deactivation during 20 h, and no reaction took place without irradiation. The estimated quantum yield of Pt/PbBi₂Nb₂O₉ for H₂ evolution was ca. 0.95%. The quantum yield for O₂ evolution on PbBi₂Nb₂O₉ was estimated to be ca. 29%. TiO_{2-x}N_x showed a trace amount of H₂ evolution, but the quantum yield for O₂ evolution was as high as ca. 12%. The quantum yield of PbBi₂Nb₂O₉ for both H₂ and O₂ evolution, to our best knowledge, is one of the highest reported for semiconductor photocatalysts under visible light, and the high quantum yield for O₂ formation is particularly impressive. Only TaON showed comparable quantum yields with ca. 0.2% for H₂ production and ca. 34% for O₂ production under similar conditions.⁷

PbBi₂Nb₂O₉, a novel photocatalyst, has been discovered that shows high photocatalytic activities for degradation of organic pollutants, generation of photocurrent, and decomposition of water to form either O₂ or H₂, all under visible light irradiation ($\lambda \geq 420$

nm). According to the band structure calculation using the Wien 97 program¹⁴ (see Supporting Information), the conduction and valence bands of this compound consist mostly of empty Nb4d and occupied O2p orbitals, respectively, but the latter is hybridized with Bi6s and Pb6s. This hybridization would push up the position of the valence band, giving the smaller band gap compared to compounds that do not contain Pb and Bi in their structures.¹⁵ It is notable that this reduction in the band gap energy of PbBi₂Nb₂O₉ is accomplished without any dopant such as nitrogen as in TiO_{2-x}N_x. Although dopants such as N, Fe, and Cr could induce the visible light absorption, they also serve as sites for electron-hole recombination that leads to low quantum yields. In any case, this work is the first example of an undoped, single-phase oxide photocatalyst that shows such high reactivities. Its activities are much higher than those for most of the previously reported materials, especially in oxygen generation from water containing AgNO₃ (QY = 29%). In this regard, it is an important discovery that the visible light could be absorbed and induce both photocatalytic reduction and oxidation without any dopant for PbBi₂Nb₂O₉. Since it is a single-phase oxide, there is much less concern for stability under light irradiation. Indeed, its crystal structure did not change and postreaction analysis of the reaction solution showed no indication of dissolved catalyst components even after more than 100 h of water decomposition reaction under visible light (see Supporting Information).

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Supporting Information Available: Experimental procedures, photocurrent generation, calculated total and partial density of states of PbBi₂Nb₂O₉, XRD patterns before and after water decomposition over PbBi₂Nb₂O₉, X-ray crystallographic file for PbBi₂Nb₂O₉ in CIF format. These materials are available free of charge via the Internet <http://pubs.acs.org>.

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