Sillén–Aurivillius-related Oxochloride $\text{Bi}_2\text{NbWO}_{14}\text{Cl}$ as a Stable O$_2$-evolving Photocatalyst in Z-scheme Water Splitting under Visible Light

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Following the recent discovery of a Sillén–Aurivillius perovskite $\text{Bi}_2\text{NbO}_3\text{Cl}$ with a stable photocatalytic activity for water oxidation under visible light, we studied a structurally related intergrowth compound $\text{Bi}_2\text{NbWO}_{14}\text{Cl}$. It also works as a stable O$_2$-evolving photocatalyst in a Z-scheme water splitting system, but has a slightly wider band gap than that in $\text{Bi}_2\text{NbO}_3\text{Cl}$. These results suggest the importance of the Sillén–Aurivillius framework, offering possible band gap tuning by varying structural motifs and their sequence in the Sillén–Aurivillius-related systems.

**Keywords:** Photocatalyst | Oxochloride | Z-scheme water splitting

Visible-light-induced water splitting using semiconductor photocatalysts has attracted significant attention due to the potential of this method for production of hydrogen as a clean energy carrier. Over the past decades, various mixed-anion compounds such as oxynitrides, oxysulfides, and oxylahides have been extensively studied as promising candidates. The valence band maximum (VBM) of these mixed-anion semiconductors is generally more negative than that of oxide counterparts due to the p orbitals of non-oxide anions (e.g., N$^{3-}$, S$^{2-}$, Br$^-$, or I$^-$) being located at a higher energy, which results in the band gap to be narrowed and affords visible light absorption. Such mixed-anion compounds, however, often suffer from self-oxidative deactivation by photogenerated holes, thereby imposing surface modifications such as loading some cocatalysts to circumvent the oxidative deactivation.

We have recently demonstrated that a layered oxochloride $\text{Bi}_2\text{NbO}_3\text{Cl}$ can stably and efficiently oxidize water to O$_2$ under visible light, without any surface modifications. $\text{Bi}_2\text{NbO}_3\text{Cl}$ belongs to an $n=1$ member of the Sillén–Aurivillius perovskite family $[(\text{Bi}_2\text{O}_2)\text{X}]\text{A}_{n-1}\text{M}_n\text{O}_{3n+1}$ (X = Cl, M = Nb, $n = 1$), composed of perovskite $[\text{A}_{n-1}\text{M}_n\text{O}_{3n+1}]^{2-}$ layers sandwiched by $[(\text{Bi}_2\text{O}_2)\text{X}]^{1+}$ blocks (Figure 1a). First principles calculations revealed that the VBM of $\text{Bi}_2\text{NbO}_3\text{Cl}$ consists mainly of O-2p orbitals (instead of Cl-3p), with its VBM level much more negative than available by conventional oxides or oxochlorides (e.g., BiOCl). It was presumed that the photogenerated holes populated on the O-2p band near VBM rather stably exist and only bring about O$_2$ evolution, instead of oxidative decomposition.

Given the novel catalytic property found in $\text{Bi}_2\text{NbO}_3\text{Cl}$, it will be interesting to study structurally related compounds. Aurivillius demonstrated in 1984 that $\text{Bi}_2\text{NbWO}_{14}\text{Cl}$ adopts an orthorhombic structure with $a = 5.4801$ Å, $b = 5.4398$ Å, $c = 45.236$ Å. Although structural refinement was absent, it was proposed from the obtained lattice parameters that $\text{Bi}_2\text{NbWO}_{14}\text{Cl}$ is an intergrowth structure between a Sillén–Aurivillius unit $[(\text{Bi}_2\text{O}_2)\text{Cl}]\text{Nb}_2\text{W}_2\text{O}_{16}$ and an Aurivillius unit $\text{Bi}_2\text{O}_2\text{(Nb,W)}\text{O}_4$ (Figure 1b). In other words, it has perovskite $[\text{Nb}_2\text{W}_2\text{O}_{16}]^{2-}$ layers, sandwiched alternatively by $[(\text{Bi}_2\text{O}_2)\text{Cl}]^{1+}$ and $[\text{Bi}_2\text{O}_2]^{2-}$ blocks. $\text{Bi}_2\text{NbWO}_{14}\text{Cl}$ hence provides an opportunity to see the role of $[(\text{Bi}_2\text{O}_2)\text{Cl}]$ block in the unique band structure of $\text{Bi}_2\text{NbO}_3\text{Cl}$ and resultant photocatalytic activity. In this study, we investigate the structural and photocatalytic properties of $\text{Bi}_2\text{NbWO}_{14}\text{Cl}$.

The $\text{Bi}_2\text{NbWO}_{14}\text{Cl}$ sample was prepared via a solid-state reaction. $2.5$ mmol of $\text{Bi}_2\text{O}_3$ (Wako, 99.99%), $1$ mmol of $\text{BiOCl}$ (Wako), $0.5$ mmol of $\text{Nb}_2\text{O}_5$ (Wako, 99.9%), and $1$ mmol of $\text{WO}_3$ (Kojundo Chemicals, 99.99%) were weighted, mixed, pelletized, and heated in an evacuated silica tube at 1073 K for 20h. The synchrotron X-ray powder diffraction (SXRD) pattern for $\text{Bi}_2\text{NbWO}_{14}\text{Cl}$ was collected at the BL02B2 in SPring-8, Japan ($\lambda = 0.41866$ Å) and analyzed by the Rietveld method using JANA2006. As seen in the SEM images (Figure S1), the $\text{Bi}_2\text{NbWO}_{14}\text{Cl}$ sample consists of relatively large particles (1–2 μm in diameter) with poorly defined morphology. For comparison, $\text{Bi}_2\text{WO}_5$ was synthesized via a solid-state reaction, where $\text{Bi}_2\text{O}_3$ and $\text{WO}_3$ in a stoichiometric quantity were mixed and heated in air at 1073 K for 20h. The XRD pattern of $\text{Bi}_2\text{WO}_5$ obtained (Figure S2) is in good agreement with the database (PDF 00-039-0256). Photocatalytic reactions were carried out using a Pyrex glass reactor connected to a closed gas-circulation system. For the photocatalytic oxidation of water (O$_2$ evolution), $0.1$ g of a photocatalyst powder was suspended in $250$ mL of an aqueous solution (aq) containing $\text{AgNO}_3$ (5 mM) or $\text{FeCl}_3$ (5 mM, pH 2.4 adjusted with HCl). For the two-step water-splitting reaction with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox...
couple, SrTiO<sub>3</sub> doped with a Rh species (SrTiO<sub>3</sub>:Rh)<sup>14</sup> was employed as the H<sub>2</sub>-evolving photocatalyst after loading the Ru cocatalyst (0.7 wt%). Both the Ru-loaded SrTiO<sub>3</sub>:Rh (0.15 g) and Bi<sub>6</sub>NbWO<sub>14</sub>Cl (0.1 g) were suspended in FeCl<sub>3</sub>(aq) (2 mM, 250 mL, pH 2.4 adjusted with HCl) by using a set of magnetic stirrer and bar. Prior to the reactions, the suspension was thoroughly degassed and then exposed to visible light (λ > 400 nm) emitted from a Xe lamp (300 W) fitted with a cutoff filter. The evolved gasses were analyzed using on-line gas chromatography (TCD, molecular sieve 5A, Ar carrier).

Figure 2 shows the SXRD pattern of the sample prepared. Le Bail analysis performed within the 2–30° range (Figure S3) showed that all peaks could be indexed using the orthorhombic cell with a = 5.47826(5) Å, b = 5.44114(5) Å, c = 45.2874(4) Å, except for one small peak at 7.57°, possibly indicating the presence of a small amount of Bi<sub>2</sub>WO<sub>6</sub>. The obtained lattice parameters are in good agreement with those in the previous study.<sup>11</sup> Rietveld analysis was performed using a previously proposed highest symmetry model (Fmmn space group) describing a non-distorted structure (Figure 1b).<sup>11</sup> The Nb<sup>5+</sup> and W<sup>6+</sup> ions were assumed disordered. Although the fit to this model indicates that the structure of Bi<sub>6</sub>NbWO<sub>14</sub>Cl is overall described by the ideal structure (Figure 2 and Table S1), we observed a deviation in intensities for several reflections such as 106 at 5.4°, 029 and 213 at 9.95°, 126 at 10.28°, and 306 at 13.6° (Figure S4), and this resulted in the agreement indices of R<sub>wp</sub> = 15.31% and GOF = 6.53. We attempted other structural models with lower symmetry (e.g., Pca<sub>2</sub> space group) such that the structure reproduces the distortions observed in the Aurivillius phase Bi<sub>2</sub>WO<sub>6</sub> and acquired a considerable improvement (R<sub>wp</sub> = 7.99%) when only the heavy elements positions were varied. Unfortunately, the numerous oxygen positions did not allow adequately converge with our X-ray data. Extensive structural analyses are necessary to clarify possible octahedral distortions occurring in this material.

Figure 3 shows the UV–vis diffuse reflectance spectrum of Bi<sub>6</sub>NbWO<sub>14</sub>Cl, along with those of Bi<sub>2</sub>WO<sub>6</sub>, BiOCl, and Bi<sub>6</sub>NbO<sub>4</sub>Cl for comparison. It was revealed that Bi<sub>6</sub>NbWO<sub>14</sub>Cl exhibited visible light absorption up to ca. 480 nm, which is considerably longer than those of Bi<sub>2</sub>WO<sub>6</sub> (ca. 430 nm) and BiOCl (ca. 340 nm). The flat-band potentials were determined from the Mott–Schottky plots in an aqueous Na<sub>2</sub>SO<sub>4</sub> solution (pH 2.0) under dark condition, where the measurements were conducted several times for each sample. The Bi<sub>6</sub>NbWO<sub>14</sub>Cl sample showed n-type nature with ca. −0.42 V (vs. Ag/AgCl) of flat-band potential (see the representative plots in Figure S6). Then, the conduction band minimum (CBM) and VBM of these materials were estimated by assuming that the flat-band potentials are located just below the CBM; the obtained values are summarized in Table 1.

It is notable that the VBM of Bi<sub>6</sub>NbWO<sub>14</sub>Cl (ca. +2.3 V vs. SHE at pH 2) is located at a more negative level as compared with Bi<sub>2</sub>WO<sub>6</sub> and BiOCl (respectively, ca. +2.7 and +3.0 V vs. SHE at pH 2). Such unique, highly negative VBM has been observed in Bi<sub>6</sub>NbO<sub>4</sub>Cl with the VBM located at around +2.1 V (vs. SHE at pH 2), which is attributed, by density functional theory (DFT) calculations, to highly dispersive O-2p orbitals, rather than Cl-3p orbitals.<sup>9</sup> Although DFT calculations on the ideal structural model of Bi<sub>6</sub>NbWO<sub>14</sub>Cl (Fmmn) did not converge possibly due to the inaccurate structure, the present experimental result, along with the structural similarity with Bi<sub>6</sub>NbO<sub>4</sub>Cl, strongly suggests that the valence band of Bi<sub>6</sub>NbWO<sub>14</sub>Cl is also composed of highly dispersive O-2p orbitals, and this will account for the elevated VBM level. The larger band gap of Bi<sub>6</sub>NbWO<sub>14</sub>Cl relative to Bi<sub>6</sub>NbO<sub>4</sub>Cl may be related to the half density of the [Bi<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub>] block.

Bi<sub>6</sub>NbWO<sub>14</sub>Cl showed activity for H<sub>2</sub> evolution from an aqueous methanol solution (Figure S7). At present, the rate is quite low, but the steady H<sub>2</sub> evolution observed validates the

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**Table 1.** Estimated band potentials for Bi<sub>6</sub>NbWO<sub>14</sub>Cl, Bi<sub>2</sub>WO<sub>6</sub>, BiOCl, and Bi<sub>6</sub>NbO<sub>4</sub>Cl.

<table>
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<th>Compound</th>
<th>CBM&lt;sup&gt;a&lt;/sup&gt;/eV</th>
<th>VBM&lt;sup&gt;a&lt;/sup&gt;/V</th>
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<td>2.39</td>
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<td></td>
<td>2.11</td>
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<sup>a</sup>Ref: 9; H. Fujito et al., J. Am. Chem. Soc. 2016, 138, 2082.

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above-estimated CBM, which is slightly higher than the water reduction potential. Figure 4 shows the time courses of O2 evolution from water on Bi6NbWO14Cl under visible light irradiation. One can see that Bi6NbWO14Cl exhibited photocatalytic activity for O2 evolution even in the presence of reversible electron acceptor (Fe3+) as well as sacrificial one (Ag+), while no O2 evolution occurred in the presence of IO3- or Mn3+ polyoxometalate ([SiW11O39Mn10(H2O)]5-) as an electron acceptor.15 The rate of O2 evolution from AgNO3(aq) is comparable to that of the previous Bi6NbO3Cl, in marked contrast to Bi2WO6 and BiOCl that showed negligibly low activity (Figure S8). The rate of O2 evolution on Bi6NbWO14Cl in FeCl3(aq) is much lower than that in AgNO3(aq), which is probably due to the occurrence of backward reaction, i.e., reoxidation of Fe2+ to Fe3+ by photogenerated holes. As seen in the inset of Figure 4, the onset of apparent quantum yield (AQY) in AgNO3(aq) was ca. 480 nm, which well agrees with the photoabsorption spectrum of Bi6NbWO14Cl. This verifies that the reaction took place photocatalytically through the band gap excitation of Bi6NbWO14Cl. The AQY at 420 nm was ca. 1.4% and 0.4% in AgNO3(aq) and FeCl3(aq), respectively. The value for FeCl3(aq) is comparable to that of the Bi6NbO3Cl system (ca. 0.4% at 420 nm) under the similar reaction condition.9 It is notable that there is no significant change in particle size (Figure S1) and in the XRD pattern (Figure S9) of the sample after the reaction in FeCl3(aq). This indicates the robustness of Bi6NbWO14Cl against visible light photoradiation and provides a further support that the VBM consists of the O-2p orbitals.

As shown in Figure 5, a simultaneous evolution of H2 and O2 under visible light (λ > 400 nm) was observed for the Bi6NbWO14Cl photocatalyst, coupled with a H2-evolving photocatalyst of Ru-loaded SrTiO3:Rh,14 through the Z-scheme mechanism involving a redox cycle of Fe3+/Fe2+.16 H2 and O2 were produced steadily in a stoichiometric ratio of H2/O2 = 2. The rates of gas evolution without any redox were much smaller than those in the presence of the Fe3+/Fe2+ redox (open circles in Figure 5). The reaction for 40 h resulted in the generation of ca. 101 μmol of O2 gas in total, which sufficiently exceeds the molar amount of Bi6NbWO14Cl (55.9 μmol) used for the reaction, indicating that this reaction proceeded photocatalytically.

In conclusion, we studied a Sillén–Aurivillius related oxychloride Bi6NbWO14Cl. The VBM of this compound is located at a much more negative level than those of Bi6WO3 and BiOCl, resulting in the smaller band gap of ca. 2.5 eV, though it is slightly larger than ca. 2.4 eV in Bi6NbO3Cl. Bi6NbWO14Cl showed photocatalytic activity for water oxidation under visible light and was also employed in Z-scheme water splitting when combined with the Fe3+/Fe2+ redox. The elevated VBM as well as the stability against photogenerated holes strongly suggests that the O-2p orbitals in the valence band of this material are highly dispersive as in the case of Bi6NbO3Cl.9 The present results imply that manipulating structural motifs and their sequence in Sillén–Aurivillius-related oxychlorides offers great possibilities toward acquiring a suitable band structure as visible-light-responsive photocatalysts.

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References


