

Fabrication of Highly Crystalline SnNb₂O₆ Shell with a Visible-Light Response on a NaNbO₃ Nanowire Core

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Supporting Information

ABSTRACT: A visible-light-absorbing SnNb₂O₆ shell with high crystallinity was successfully fabricated on a NaNbO₃ nanowire through a molten salt treatment of the NaNbO₃ nanowire of the starting material with SnCl₂, whereas the fabrication was not successful on the TT phase of a niobia nanowire. The difference will come from the formation processes of SnNb₂O₆ crystals (ion-exchange reaction vs thermally induced crystallization reaction). The core/shell nanowire obtained from NaNbO₃ showed photocatalytic activity comparable to that of H₂ evolution in the presence of an electron donor under visible-light irradiation ($\lambda > 420$ nm), compared with the corresponding bulky counterpart.

Extensive efforts have been made to devise a strategy leading to structural changes in functional semiconductor materials from 3D networks to lower dimensional forms such as nanoparticle, nanowire, and nanoplate. It is important to apply these nanomaterials as potential building blocks in a variety of fields.^{1–4} SnNb₂O₆ possesses a fooridite structure in which two corner-sharing NbO₆ sheets linked together at their edges and a distorted SnO₈ sheet due to the existence of a lone-pair electron are alternating.⁵ This material absorbs visible light because Sn^{II} with a 5s² electronic configuration contributes to the formation of a hybrid orbital with O 2p as a valence band. So far, SnNb₂O₆ has been reported to function as a H₂- and O₂-evolving photocatalyst in the presence of sacrificial reagents and appropriate cocatalysts under visible-light irradiation.^{6,7} The photocatalytic performance was enhanced by structural transformation from bulk to nanoplate, which was prepared by a molten SnCl₂ treatment of layered perovskite Sr₂Nb₂O₇ as a starting material.⁸ Further structural changes of this material are of interest. However, a nanowire or nanoparticle structure of SnNb₂O₆ has yet to be reported. The molten salt treatment has been found to be effective in converting the surface of a NaNbO₃ nanowire (NaNbO₃-NW), which was obtained by the thermal reaction of a mixture of (NH₄)₃[NbO(C₂O₄)₃]·H₂O, triethylamine, and NaOH to visible-light-absorbing AgNbO₃.⁹ In this context, fabrication of a SnNb₂O₆ shell on the NaNbO₃ nanowire core has merited attention.

In the present study, the molten SnCl₂ treatment of a NaNbO₃ nanowire¹⁰ was examined, in addition to using the TT phase of a

Nb₂O₅ nanowire (TT-Nb₂O₅-NW)¹¹ as a reference. These treated nanowires were employed as photocatalysts for H₂ and O₂ evolution reactions in the presence of sacrificial reagents under visible-light irradiation ($\lambda > 420$ nm).

Figure 1 shows XRD patterns of powders obtained after the molten SnCl₂ treatment of TT-Nb₂O₅-NW and NaNbO₃-NW.

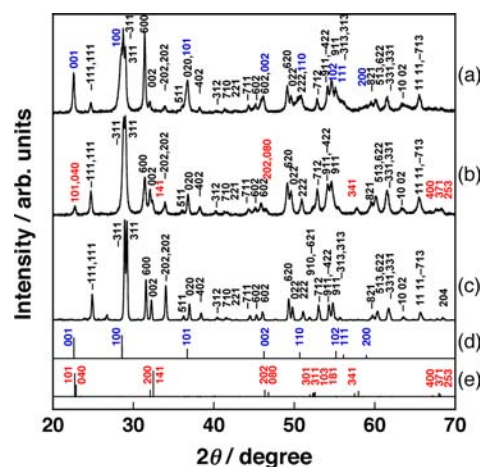


Figure 1. XRD patterns of (a) SnNb₂O₆/TT-Nb₂O₅-NW, (b) SnNb₂O₆/NaNbO₃-NW, (c) SnNb₂O₆-B, (d) TT-Nb₂O₅ (PDF 28-0317), and (e) NaNbO₃ (PDF 33-1270). Miller indices due to TT-Nb₂O₅ and NaNbO₃ are highlighted in blue and red, respectively, for clarity.

The XRD patterns indicated that obtained powders were a mixture of monoclinic SnNb₂O₆ [lattice constants are $a = 17.063(3)$ Å, $b = 4.8838(7)$ Å, and $c = 5.5775(11)$ Å] with pseudo-hexagonal TT-Nb₂O₅ [lattice constants are $c = 3.951(13)$ Å and $a = 3.6158(9)$ Å] or monoclinic SnNb₂O₆ [lattice constants are $a = 17.065(3)$ Å, $b = 4.8755(10)$ Å, and $c = 5.5781(12)$ Å] with orthorhombic NaNbO₃ [lattice constants are $a = 5.5588(3)$ Å, $b = 15.608(3)$ Å, and $c = 5.4853(3)$ Å]. NaNbO₃-NW was converted to SnNb₂O₆ more efficiently than TT-Nb₂O₅-NW. (600)/(002) of SnNb₂O₆/TT-Nb₂O₅-NW was stronger than that of SnNb₂O₆-B. The crystal structure of

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SnNb_2O_6 with inputting crystal plane (Figure S1) suggests that (600) has possibly causes the preferred orientation if anisotropic grain growth occurs along with bc plane. Half-widths of (-111) reflections of SnNb_2O_6 were determined in order to roughly estimate their crystallinities. The half-widths were in the order $\text{SnNb}_2\text{O}_6\text{-B}$ (0.20°) < $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ (0.26°) = $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$ (0.27°). To confirm which of the peak broadenings of $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ and $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$ compared with that of $\text{SnNb}_2\text{O}_6\text{-B}$ was due to poor crystallinity or small crystallite size, microscopic analyses by SEM and high-resolution TEM (HR-TEM) were carried out. SEM images (Figure S2) indicated that $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ obtained from $\text{TT-Nb}_2\text{O}_5\text{-NW}^{11}$ possessed a structure in which grains with ca. 100 nm size were connected with each other, forming a continuous network. Short nanowires and particles coexisted near the surface of the network. $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ s prepared by using 5% excess SnCl_2 under heat treatment at 623 K for 30 h and a 2-fold excess of SnCl_2 under heat treatment at 673 K for 12 h possessed nanoparticles and ca. 100-nm-thick plate morphologies, respectively. Thus, the continuous network seen in $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ was created by severely limited conditions. On the other hand, nanowire morphology of NaNbO_3 ¹⁰ was maintained for $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$ at this SEM resolution. TEM of $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$ showed evidence of a core/shell structure that appeared as areas of contrast density (Figure S2). Clear lattice fringes on the core and the widths of the fringes were estimated as 0.82 ± 0.01 nm, the value of which agreed well with (200) due to SnNb_2O_6 (Figure 2a and 2b). STEM-EDX

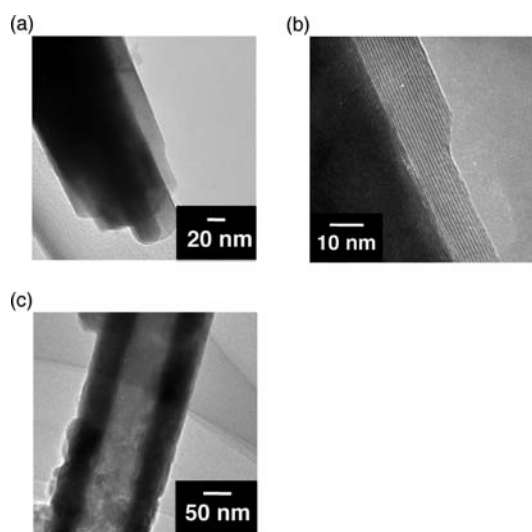


Figure 2. HR-TEM images of (a) $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$, (b) the magnified view of part a, and (c) $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$.

elemental mapping images further supported this result (Figure S3). It is difficult to distinguish the thin shell from the core because of the small sample volume of the shell. However, Nb and Na components were clearly overlapped with the blurred Sn component, suggesting a $\text{NaNbO}_3/\text{SnNb}_2\text{O}_6$ core/shell structure. Consistent with the TEM results, XPS indicated that SnNb_2O_6 existed at the surface of the nanowire because the atomic ratio of Sn/Nb was almost the same between $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$ and $\text{SnNb}_2\text{O}_6\text{-B}$ (Table S1 in the SI). The composition of a single nanowire was further analyzed by TEM-EDX. NaNbO_3 existed at a rate of 30.9% in $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$

(Table S1 in the SI). Because the thickness of the SnNb_2O_6 layer was ca. 20 nm, the broadening of the (-111) diffraction peak compared with that of $\text{SnNb}_2\text{O}_6\text{-B}$ will be due to the small crystallite size. Using the Scherrer equation, the crystallite size of SnNb_2O_6 in $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$ was determined as 17.7 ± 0.6 nm. This was consistent with the TEM result (Figure 2b). $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ also had a core/shell structure judging from the contrast (Figure 2c). However, lattice fringes were not observed in this case, suggesting less crystallinity of the SnNb_2O_6 shell than that of $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$. TEM-EDX results suggested that only 8.1% of SnNb_2O_6 existed in the $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ sample. An excess amount of Nb was detected for $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ by XPS compared with $\text{SnNb}_2\text{O}_6\text{-B}$. The results would originate from one of the following possibilities: (1) this sample was a mixture of $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ with unreacted $\text{TT-Nb}_2\text{O}_5\text{-NW}$; (2) the unreacted $\text{TT-Nb}_2\text{O}_5$ region was partially exposed on the $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ surface. These results precluded a clear estimation of the reason for XRD peak broadening. The SnNb_2O_6 crystallite size in $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ was 41.1 ± 2.7 nm using the Scherrer equation and thereby larger than that in $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$. The differences in the formation and crystallization of the SnNb_2O_6 shells $\text{NaNbO}_3\text{-NW}$ and $\text{TT-Nb}_2\text{O}_5\text{-NW}$ used herein will be due to the reaction processes. When $\text{TT-Nb}_2\text{O}_5\text{-NW}$ is used, thermally induced crystallization of SnNb_2O_6 like a solid-state reaction on the nanowires takes place. On the other hand, NaNbO_3 can function as a reaction substrate for an ion-exchange reaction of Na^+ with Sn^{2+} . The latter process will be favorable to maintaining the nanowire structure. BET surface areas of $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ and $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$ were 17 and $14 \text{ m}^2 \text{ g}^{-1}$, respectively. These values were more than 10 times larger than the SnNb_2O_6 bulk ($0.9 \text{ m}^2 \text{ g}^{-1}$) but lower than the pristine nanowires (63 and $38 \text{ m}^2 \text{ g}^{-1}$ for $\text{TT-Nb}_2\text{O}_5\text{-NW}$ and $\text{NaNbO}_3\text{-NW}$, respectively). As established by the microscopic and spectroscopic results, highly crystalline SnNb_2O_6 was homogeneously fabricated on $\text{NaNbO}_3\text{-NW}$. Such an increase in the crystallinity generally lowers the surface area. In contrast, the molten SnCl_2 treatment lowered the structural homogeneity of $\text{TT-Nb}_2\text{O}_5\text{-NW}$, affording a mixture of grains as a major species with short nanowires and particles. This would be the major reason for the low surface area of $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$.

DRS spectra of $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ and $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$ are shown in Figure S2 in the SI, in addition to nontreated $\text{TT-Nb}_2\text{O}_5\text{-NW}$, $\text{NaNbO}_3\text{-NW}$, and $\text{SnNb}_2\text{O}_6\text{-B}$ as the references. Onset wavelengths in absorptions were red-shifted significantly by the treatment of $\text{TT-Nb}_2\text{O}_5\text{-NW}$ and $\text{NaNbO}_3\text{-NW}$ with molten SnCl_2 . The spectral shapes indicated that $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$ contained a small amount of the SnNb_2O_6 component, in good agreement with the XRD and TEM-EDX results. $\text{SnNb}_2\text{O}_6/\text{NaNbO}_3\text{-NW}$ contained a larger amount of SnNb_2O_6 than $\text{SnNb}_2\text{O}_6/\text{TT-Nb}_2\text{O}_5\text{-NW}$. The red shift in the absorptions was attributable to the contribution of the $\text{Sn } 5s^2$ orbital to the formation of a hybrid orbital with $\text{O } 2p$ as the valence band at a more negative potential than the $\text{O } 2p$ orbital. The band gap estimated by absorption edges was 2.3 eV, identical with that of $\text{SnNb}_2\text{O}_6\text{-B}$.

Photocatalytic reactions for H_2 and O_2 evolution (Table 1) were carried out in the presence of methanol or AgNO_3 , each of which acts as an electron donor or an acceptor, under visible-light irradiation ($\lambda > 420$ nm). Both nanowires showed almost no photoresponse regarding an O_2 evolution reaction, although highly crystalline SnNb_2O_6 was formed on the NaNbO_3

Table 1. H₂ and O₂ Evolution Reactions over SnNb₂O₆-Based Photocatalysts in the Presence of Methanol and AgNO₃ under Visible-Light Irradiation^a

photocatalyst	BG/eV ^b	Pt cocatalyst/wt %	rate of gas evolution/ μmol h ⁻¹	
			H ₂ ^c	O ₂ ^{d,e}
SnNb ₂ O ₆ /TT-Nb ₂ O ₅ -NW	2.3	0	0	0
SnNb ₂ O ₆ /TT-Nb ₂ O ₅ -NW	2.3	0.3	0.7	
SnNb ₂ O ₆ /TT-Nb ₂ O ₅ -NW	2.3	1.0	1.0	
TT-Nb ₂ O ₅ -NW	3.3	1.0	0	
TT-Nb ₂ O ₅ -NW	3.3	0		0
SnNb ₂ O ₆ /NaNbO ₃ -NW	2.3	0		t
SnNb ₂ O ₆ /NaNbO ₃ -NW	2.3	0.3	5.5	
SnNb ₂ O ₆ /NaNbO ₃ -NW	2.3	0.5	5.6	
SnNb ₂ O ₆ /NaNbO ₃ -NW	2.3	1.0	10	
SnNb ₂ O ₆ /NaNbO ₃ -NW	2.3	1.5	5.4	
NaNbO ₃ -NW	3.4	1.0	1.1	
NaNbO ₃ -NW	3.4	0	0	0
SnNb ₂ O ₆ -B	2.3	0	0	0.9
SnNb ₂ O ₆ -B	2.3	0.3	14	
SnNb ₂ O ₆ -B	2.3	0.5	12	–
SnNb ₂ O ₆ -B	2.3	1.0	0	–

^aCatalyst, 0.1 g; reactant solution, 150 mL; light source, 300 W xenon-arc lamp ($\lambda > 420$ nm); cell, top-irradiation Pyrex cell. ^bBG represents the band gap. ^c10 vol % of an aqueous methanol solution. ^d0.02 mol L⁻¹ of an aqueous silver nitrate solution. ^eInitial rate of O₂ evolution.

nanowire surface. However, this is in agreement with the previous reports using SnNb₂O₆-B.^{6,7} SnNb₂O₆/TT-Nb₂O₅-NW showed low activity for the H₂ evolution reaction. In contrast, a SnNb₂O₆/NaNbO₃ composite nanowire showed activity comparable with that of the bulk when an optimized amount of platinum cocatalyst was loaded onto the photocatalysts. Here, the conduction band potentials of TT-Nb₂O₅-NW with a 3.3 eV band gap and of NaNbO₃-NW with a 3.4 eV band gap¹⁰ will lie at -0.3 and -0.4 eV vs NHE, respectively, because the valence bands of these nanowires consist of O 2p orbitals, of which the potential is ca. 3 eV vs NHE. Taking band gaps of SrNb₂O₆ (3.85 eV)¹² and SnNb₂O₆ (2.3 eV) into account, the conduction and valence band levels of SnNb₂O₆ will lie at around -0.85 and 1.55 eV, respectively. Hence, photogenerated electron transfer from the SnNb₂O₆ shell to the TT-Nb₂O₅- or NaNbO₃-NW core is exothermic.⁸ However, because the edge and sidewall of the TT-Nb₂O₅- or NaNbO₃-NW core will be covered with SnNb₂O₆, the conduction band electron in the TT-Nb₂O₅ or NaNbO₃ core is considered to make no contribution to the water reduction reaction. Thus far, efforts devoted to enhance the photocatalytic performance of the bulk under visible light by semiconductor nanowires have been hampered.^{13,14} Herein, this was overcome by transcription of the SnNb₂O₆ crystal onto NaNbO₃-NW while maintaining high crystallinity, through ion exchange of Na⁺ with Sn²⁺ ions. This work will offer a new strategy to developing a visible-light-responsive semiconductor nanowire possessing a superior photocatalytic performance.

In conclusion, a molten salt treatment of simple and complex niobate (TT-Nb₂O₅ and NaNbO₃) nanowires was examined in order to fabricate visible-light-responsive SnNb₂O₆ layers on the niobate nanowires. Structural characterizations using XRD, HR-TEM, and XPS indicated that the SnNb₂O₆ shell on the NaNbO₃ nanowire core possessed high crystallinity, in contrast to that on TT-Nb₂O₅-NW. The nanowire-dependent crystallization of SnNb₂O₆ originated from different reaction processes: thermally

induced crystallization versus ion exchange. SnNb₂O₆/NaNbO₃-NW showed an activity for the H₂ evolution reaction comparable with that of the corresponding bulk in the presence of an electron donor under visible-light irradiation.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section, crystal structure of Sn₂Nb₂O₆ with inputting (600), SEM images, STEM-EDX mapping results, summary of elemental analyses, and DRS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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