

Photodegradation of BiNbO₄ Powder during Photocatalytic Reactions

Scott S. Dunkle and Kenneth S. Suslick*

Department of Chemistry, University of Illinois at Urbana–Champaign, 600 S. Mathews Avenue, Urbana, Illinois 61801

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BiNbO₄ powders prepared by solid state reaction were tested for photocatalytic activity in methanol solutions under UV irradiation. When the material is tested without the presence of a Pt cocatalyst, photocatalytic activity for H₂ evolution is superior to that of TiO₂. It was also found that BiNbO₄ photodegrades into metallic Bi and reduced Nb oxides after use; materials were characterized by SEM, XRD, and XPS. Adding Pt to the surface of the photocatalyst increases photocatalytic activity and importantly, helps to prevent photodegradation of the oxide material. With 1 wt % Pt loading, photodegradation is essentially absent.

Introduction

Considering that in 1 h more energy strikes the earth than all of the energy consumed by the world in a whole year,¹ solar energy seems to be a viable option to our society's increasing energy demand. Without doubt, however, there are major efforts yet required to produce robust materials and devices that are able to harness the sun's radiation and convert it into a useable form of energy in an efficient manner.^{1–3} Developing photocatalysts for the efficient splitting of water into H₂ and O₂ is a particularly attractive goal and has received considerable attention since the work by Fujishima and Honda showing the photooxidation of water using TiO₂.^{4,5} Metal oxides continue to be popular materials for photocatalysts because of their inherent stability and relatively low cost of synthesis.⁵

We report here a study of BiNbO₄ as a photocatalyst, its problems due to photodegradation, and a facile solution to that limitation. BiNbO₄ exists in two polymorphs, a low temperature orthorhombic (α) phase^{6,7} and a high temperature triclinic (β) phase.⁸ An irreversible (in powders)⁹ phase transition occurs from the α phase to the β phase at ~ 1020 °C.^{6,7,10–12} The greatest interest in BiNbO₄ is as a promising dielectric material,^{13,14} and only a limited amount of research has been directed toward its photocatalytic capabilities.^{15–18} Both phases have a layered structure that consist of vertex-sharing NbO₆ octahedra,^{10,12} but the low temperature orthorhombic (α) phase shows the greater photocatalytic activity.¹⁵ Previous studies by Arakawa and co-workers have shown BiNbO₄ to be an active photocatalyst for H₂ evolution from aqueous methanol and pure water solutions under ultraviolet (UV) irradiation.^{16–18} In this work, we confirm the photocatalytic activity of BiNbO₄, but we also find that substantial photodecomposition of the catalyst occurs during use, which has not been reported in previous studies. Importantly, we have discovered that Pt nanoparticle cocatalysts can essentially suppress the photodecomposition of BiNbO₄ photocatalysts.

Experimental Section

Materials and Synthesis. Bi₂O₃ (99.9+% purity) and Nb₂O₅ (99.99% purity) were each obtained from Sigma-Aldrich. TiO₂ (P-25) used in control experiments was obtained from Degussa. All materials were used as received. BiNbO₄ was synthesized using standard solid state reaction techniques: Bi₂O₃ and Nb₂O₅ precursors were weighed out in an appropriate stoichiometric ratio and ground together by mortar and pestle until the mixture was uniform. The mixture was then placed in an alumina combustion boat and heated in air at 900 °C in an electric tube furnace. After 4 h of heating, the sample was removed from the furnace and vigorously ground again by mortar and pestle for 2 min. The sample was then placed back in the furnace for an additional 16 h, after which the sample was removed and ground once more as previously described. The powder was then returned to the furnace and allowed to react an additional 4 h. The furnace was then shut off and the sample was allowed to cool with the furnace and removed after the furnace reached room temperature. The resulting white powder was ground by mortar and pestle once more after cooling.

Materials Characterization. All powder X-ray diffraction (XRD) measurements were conducted with a Rigaku D-MAX diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å) and operated at 45 kV and 20 mA with a scan rate of 1 deg/min and a step size of 0.02°. For higher resolution scans, a scan rate of 0.24 deg/min was employed. Scanning electron micrographs (SEM) were taken using a JEOL 7000F operating at 15 kV. Diffuse reflectance UV–vis measurements were taken using a Hitachi 3300 double monochromator UV–vis spectrophotometer. Surface characterization was performed by X-ray photoelectron spectroscopy (XPS) with a Kratos Axis ULTRA employing a Mg anode.

Photocatalytic Testing. Photocatalytic reactions were carried out using a standard inner-radiation reaction vessel with a water-jacketed quartz immersion well connected to a closed gas handling system. Hydrogen evolution was detected by an online gas chromatograph (GC) equipped with a thermal conductivity detector (Agilent 6890 GC, G1532–60720 TCD). All reactions were run in 500 mL of a 10 vol % methanol solution and were

* To whom correspondence should be addressed. E-mail: ksuslick@illinois.edu.

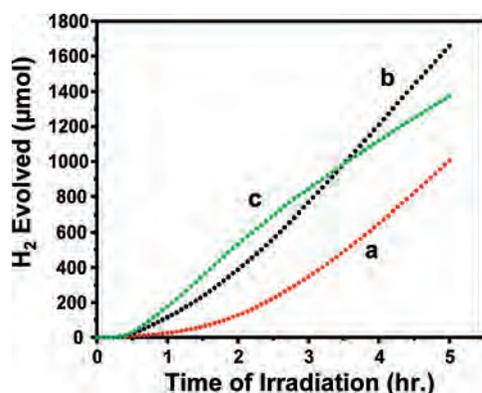


Figure 1. Amount of H₂ evolved over time for BiNbO₄ (a) without a cocatalyst, (b) with 0.2 wt % Pt nanoparticles, and (c) with 1.0 wt % Pt.

irradiated with a 450 W medium-pressure Hg lamp with a Vycor sleeve as filter ($\lambda > 210$ nm). 500 mg of catalyst was used in each reaction and was kept suspended with magnetic stirring. Pt nanoparticle deposition was performed in situ by adding the desired amount of H₂PtCl₆ (Sigma-Aldrich) to the photocatalytic testing solution and irradiating with light.

Results and Discussion

Photocatalytic Activity. BiNbO₄ powder prepared by the method above results in a material with a band gap of ~ 2.8 eV (estimated from the absorption edge obtained by diffuse reflectance measurements) in which the valence band is comprised from the Bi 6s orbital and the conduction band from the Nb 4d.¹⁶ With a band gap of this size, the material absorbs almost no visible light, indicating that the photocatalyst will only be active for photocatalysis under UV irradiation. A previous study reports BiNbO₄ to be active for water splitting in pure water although H₂ evolution rates were extremely low.^{16,18} The fact the material is capable of completing overall water cleavage implies that the valence and conduction bands of BiNbO₄ straddle the redox potentials of water. In this study, the photocatalytic activity of BiNbO₄ powder was examined by monitoring H₂ evolution from aqueous methanol solutions (Figure 1). Without Pt nanoparticles as a cocatalyst, BiNbO₄ is indeed shown to evolve H₂ at a rate of 200 $\mu\text{mol/h}$. Given the irreversible photoreduction of pure BiNbO₄ in the absence of a cocatalyst (cf. below), it is uncertain whether H₂ evolution from bare BiNbO₄ is actually catalytic or is a result of BiNbO₄ decomposition. When 0.2 wt % Pt nanoparticles are loaded onto the oxide surface as a cocatalyst, the activity jumps to 330 $\mu\text{mol/h}$, which is likely due to the noble metal acting as an electron reservoir thus decreasing the rate of electron–hole recombination and promoting photocatalytic activity. Increasing the Pt loading to 1.0 wt % has a slight negative effect on the activity of the material, lowering the H₂ evolution rate to 270 $\mu\text{mol/h}$. The drop in activity may be due to the high levels of Pt covering a significant portion of the catalyst surface, shielding the material from the light, and therefore decreasing the number of photons absorbed by the BiNbO₄.

The activity of BiNbO₄ photocatalysts was compared to the activity from TiO₂ (Degussa P-25) at varying Pt loadings using the same photochemical apparatus in all cases. Without a cocatalyst, BiNbO₄ outperforms the TiO₂ powder, which shows a H₂ evolution rate of only 30 $\mu\text{mol/h}$. When Pt is loaded onto the TiO₂ surface, however, the photocatalytic activity of the material jumps dramatically, reaching rates of 1.88 mmol/h with 0.2 wt % Pt and 12.63 mmol/h with 1.0 wt % Pt. This trend is

TABLE 1: Average H₂ Evolution Rates from BiNbO₄ and TiO₂ (Degussa P-25) Photocatalysts in Methanol Solution and UV Irradiation

catalyst	Pt loading (wt %) ^a	avg. H ₂ evolution rate (mmol/h) ^b
BiNbO ₄	0	0.20
BiNbO ₄	0.2	0.33
BiNbO ₄	1.0	0.27
TiO ₂	0	0.03
TiO ₂	0.2	1.88
TiO ₂	1.0	12.63

^a Deposited in situ using photolysis of H₂PtCl₆. ^b 500 mg catalyst in 500 mL aqueous 10 vol % methanol solution and irradiation with a 450 W medium pressure Hg lamp with Vycor filter ($\lambda > 210$ nm).

consistent with previous studies in which BiNbO₄ has been shown to be more active than TiO₂ without a cocatalyst, but less active with one.^{16,18} A summary of the photocatalytic activities of each of the materials can be found in Table 1.

Scanning Electron Microscopy of BiNbO₄ Photocatalysts.

Once BiNbO₄ powders had been used in a photocatalytic reaction, it was noticed that the color of the powder had turned from white to dark gray. SEM was performed in order to see if the particle morphology had changed during photolysis. Micrographs of the initial BiNbO₄ powder show particle sizes on the order of several micrometers comprised of aggregates of smaller, 1–3 μm , rounded particles (Figure 2A). After use of the photocatalyst in the absence of Pt cocatalyst, a significant particle morphology change occurs (Figure 2B). Images indicate that the particles have broken into 1–3 μm sized pieces along the large grain boundaries seen in Figure 2A. In addition, the particles no longer look rounded and significant delamination is evident (Figure 2E). When a 0.2 wt % Pt cocatalyst is employed, it seems that some of the original particle morphology is maintained, however most still show signs of delamination (Figure 2C and F). Finally, when 1.0 wt % Pt is loaded onto the photocatalyst surface, almost all of the original particle morphology is preserved (Figure 2D). From the micrographs it appears that increasing amounts of Pt cocatalyst help prevent BiNbO₄ powders from delaminating during photocatalytic reactions in addition to promoting photocatalytic activity.

It is also worth noting that a thin film was created on the surface of the catalyst during reaction in the absence of Pt cocatalysts. When the electron beam from the SEM was focused on the BiNbO₄ powder, that thin film began to melt and bead up. Because melting does not usually occur in a metal oxide powder (which are generally quite refractory) under SEM conditions, this implies that the thin film is comprised of a low melting metal. As discussed below, this thin film is indeed Bi metal, which has an extremely low melting point (272 °C).

Powder X-ray Diffraction. Given the dramatic change in particle morphology as seen by SEM, powder XRD studies were performed to determine if there is a change in the crystal structure of the BiNbO₄ after use as a photocatalyst (Figure 3A). A scan of the catalyst before use indicates that the as-made product is phase pure, highly crystalline, and of the orthorhombic type. After the material has been used in a photocatalytic reaction with no cocatalyst present, the crystal structure is almost completely destroyed and rendered nearly amorphous. A few peaks are present, but indicate a low degree of crystallinity; with a slower scan rate, the improved signal-to-noise ratio permitted several species to be identified (Figure 3B). XRD indicates that elemental Bi is formed from the BiNbO₄ during photocatalytic reaction. In addition, several reduced Nb oxide species were present including NbO₂, Nb₃O₄, and Nb₄O₅. When

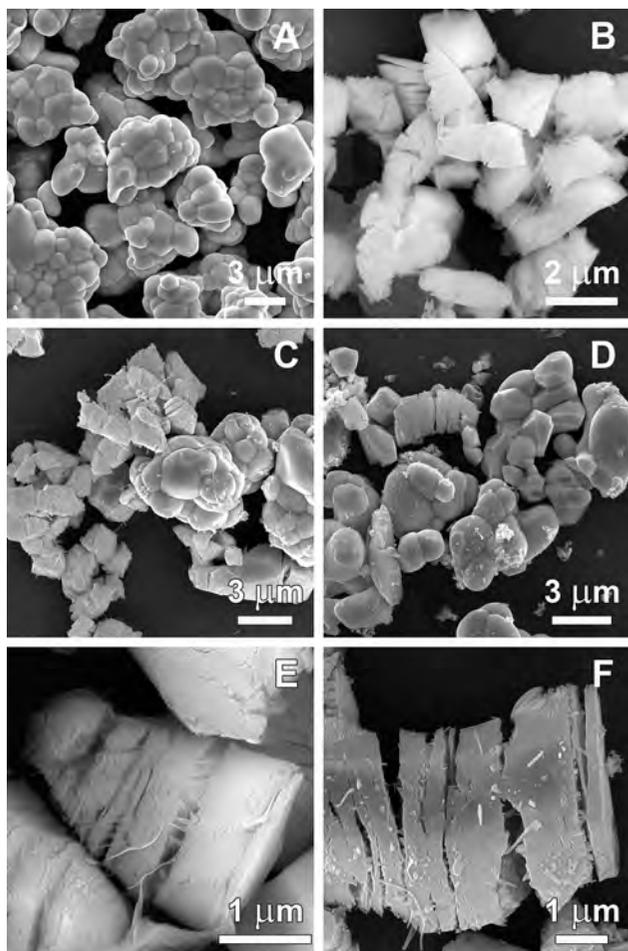


Figure 2. SEM micrographs of BiNbO₄ photocatalysts (A) before use, (B) after use without a cocatalyst, (C) with 0.2 wt % Pt, and (D) with 1.0 wt % Pt. Higher magnification images of delaminated particles found in samples after use (E) without a cocatalyst and (F) with 0.2 wt % Pt.

only 0.2 wt % Pt is loaded onto the BiNbO₄ surface, the XRD scan of the material after use is quite different. Instead of complete degradation, most of the crystal structure was maintained; only sharp peaks corresponding to orthorhombic BiNbO₄ were found. Similar results were seen from the sample with 1.0 wt % Pt loading with even less degradation observed. XRD has confirmed that the presence of Pt on BiNbO₄ surfaces helps to preserve the material's structure and composition during photocatalytic reactions.

X-ray Photoelectron Spectroscopy. To confirm that the photodegradation of BiNbO₄ produces elemental Bi and reduced Nb oxide species, XPS was used. Because an oxide layer will form on the surface of the elemental Bi particles during sample handling, the XPS spectrum was taken as a control of Bi powder (Sigma-Aldrich) handled in air, so that the Bi 4f peaks associated with the commercial product could be compared directly with the peaks obtained from BiNbO₄ photocatalysts after use. For the Bi powder, peaks corresponding to the 4f_{5/2} and 4f_{7/2} were located at binding energies of 164.7 and 159.4 eV respectively (Supporting Information). As can be seen in Figure 4A, the as-prepared BiNbO₄ powder shows 4f binding energies for Bi at 164.9 and 159.6 eV. Spectra from used BiNbO₄ catalysts without Pt loading show a 0.2 eV shift to lower binding energy, corresponding to a reduction of the Bi in the catalyst. Furthermore, the binding energies for the used catalyst exactly match the peaks obtained from the Bi powder sample, confirming the

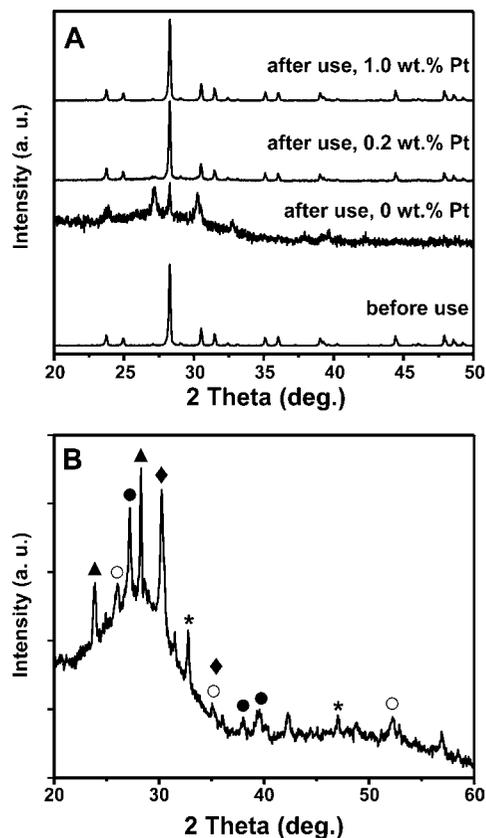


Figure 3. XRD scans of BiNbO₄ (A) before and after use as a photocatalyst with varying loadings of Pt cocatalyst (at 1 deg/min scan rate; baselines have been offset for clarity); (B) a high resolution scan (0.24 deg/min) after use as a photocatalyst in the absence of Pt cocatalyst, in which BiNbO₄ (▲), Bi (●), NbO₂ (○), Nb₃O₄ (◆), and Nb₄O₅ (*) species were identified.

presence of elemental Bi on the surface, in agreement with the XRD results. In contrast, the Bi 4f peaks for photocatalysts that have 1.0 wt % Pt loading were unchanged with respect to the unphotolyzed BiNbO₄, confirming that the Pt nanoparticle cocatalyst helps prevent photodegradation.

XPS spectra for Nb 3d show a similar trend to the Bi 4f results (Figure 4B). Nb 3d peaks are shifted to lower binding energy compared to the unused material when either no cocatalyst is present or a 0.2 wt % Pt loading is employed. This is consistent with the XRD data showing the formation of reduced Nb oxide species. When 1.0 wt % Pt is present, the peaks are no longer at lower binding energies and actually show slight oxidation, again consistent with our findings from XRD that the photocatalyst is largely preserved from photodegradation by Pt loading.

Photodegradation of BiNbO₄ Photocatalysts. When a semiconductor photocatalyst is irradiated with light of equal or greater energy than the material's band gap, an electron-hole pair is created. Ideally, in a water splitting photocatalyst the pair of charge carriers is transported to the catalyst surface and participate in the oxidation and reduction of water. With BiNbO₄ photocatalysts, considering the data presented, it appears many of the electrons are reducing Bi(III) and Nb(V) to metallic Bi and causing Nb to form reduced oxides as well as performing the desired reactions. As a control, BiNbO₄ powder was irradiated in air (i.e., in the absence of methanol) with the same UV light used during photocatalytic reactions and no photodecomposition occurred, suggesting that the electron-hole pairs generated simply recombine in the absence of methanol.

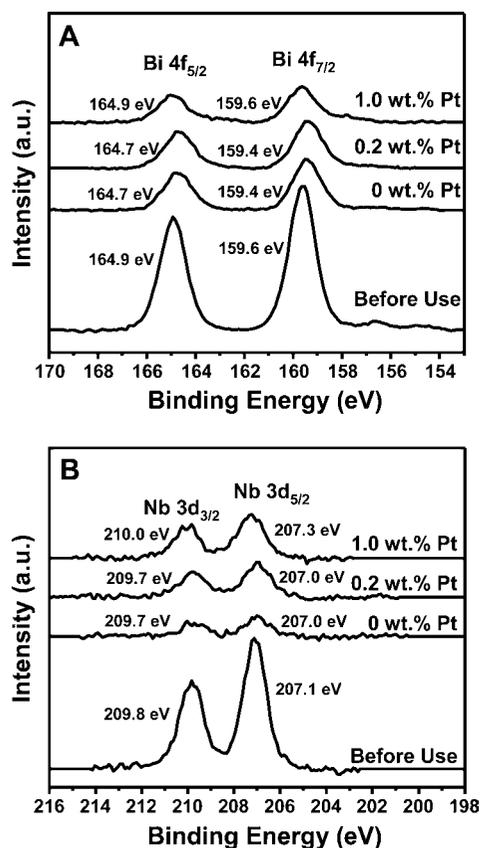


Figure 4. Background corrected XPS spectra (A) of Bi 4f and (B) of Nb 3d for BiNbO₄ photocatalysts before and after use with varying loadings of Pt cocatalyst. Intensities are all on the same scale with baselines offset for clarity.

Methanol acts as a hole scavenger,^{19–21} discouraging electron–hole recombination, and allowing the electrons to reduce the metal ions in the oxide catalyst. Considering the high-energy UV light used in the experiments, photogenerated electrons formed deep in the valence band (i.e., from oxygen orbitals) could potentially be responsible for the reduction of the Bi and Nb.

The delamination observed in SEM micrographs also suggests that metallic Bi is being formed on the photocatalyst surface. As mentioned previously, BiNbO₄ is a layered material that contains sheets of edge sharing NbO₆ octahedra with Bi atoms layers in between. We suggest that as Bi(III) is reduced and moves to the surface, the material splits along its atomic layers, forming the structures seen in Figure 2.

The increase in the rate of H₂ evolution over time for bare and 0.2 wt % Pt-loaded catalysts as seen in Figure 1 is of interest and its source is uncertain. It is possible that the metallic Bi that develops on the surface of the catalyst acts as a cocatalyst and aids in electron transport, therefore increasing the amount of H₂ produced. A similar phenomenon has been observed in ZnS materials where catalytic activity was attributed to the metallization of the catalyst by photoreduced Zn.²² Alternatively, photocatalytic activity could be due to an increase in surface area from the delamination and fracture of BiNbO₄ particles during reaction. The fact that the material with 1.0 wt % Pt does not show an increase in activity over time suggests that the enhancement is coupled with the photodegradation of the catalyst.

The Role of the Pt Cocatalyst. The deposition of a noble metal onto the surface of photocatalysts has been a popular way to enhance the photocatalytic activity of materials for water splitting. The role of the metal is to produce an electric field

gradient, causing effective electron–hole separation and electron transfer. The metal cocatalyst essentially acts as an electron reservoir off of which water reduction can occur. This leaves the holes in the semiconductor photocatalyst where they are free to complete the oxidation portion of the reaction. This phenomenon occurs with the BiNbO₄ catalysts presented in this work, as evidenced by the increase in photocatalytic activity with 0.2 wt % Pt loading. The Pt nanoparticle cocatalyst, however, is also playing a secondary role to preserve the integrity of the photocatalyst. When no Pt is present, photogenerated electrons are free to reduce the metal centers of the BiNbO₄. With Pt loading, instead of reacting with the oxide catalyst, the electrons move to the Pt sites (as well established in other systems⁵), leaving the catalyst itself largely unreduced. Even a small amount of Pt loading helps protect the catalyst's crystallinity by drawing electrons away from the oxide portion of the material. When Pt loading is higher (e.g., 1.0 wt % Pt), the effects of the noble metal are even more dramatic, and particle morphology is largely maintained, as observed in the SEM images (Figure 2).

Conclusion

BiNbO₄ powders synthesized by solid state reaction have been tested for potential use as photocatalysts for water splitting in aqueous methanol solutions under UV irradiation. BiNbO₄ powders show superior activity to TiO₂. UV irradiation of the BiNbO₄, however, in the presence of methanol causes reduction of the metal centers, leading to the formation of metallic bismuth and reduced Nb oxide species. The reduction leads to the destruction of the orthorhombic crystal structure of the material and causes BiNbO₄ to delaminate along its atomic layers. The effects of reduction can be mitigated by loading nanoparticles of Pt as a cocatalyst on the BiNbO₄ powder. Adding even a small amount of Pt helps retain the crystallinity of the catalyst dramatically, as well as promote enhanced photocatalytic activity. This is due to the noble metal loading acting as an electron reservoir, preventing many of the electrons from reacting directly with the oxide itself.

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Supporting Information Available: Additional materials characterization such as diffuse reflectance spectroscopy of BiNbO₄, XPS of commercial Bi powder, and an SEM image of surface melting on a used catalyst is included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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