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# Au Nanoparticles Supported on BiVO<sub>4</sub>: Effective Inorganic Photocatalysts for H<sub>2</sub>O<sub>2</sub> Production from Water and O<sub>2</sub> under Visible Light

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**ABSTRACT:** Design of safe and sustainable process for the synthesis of hydrogen peroxide  $(H_2O_2)$  is a very important subject from the viewpoint of green chemistry. Photocatalytic  $H_2O_2$  production with earth-abundant water and molecular oxygen  $(O_2)$  as resources is an ideal process. A successful system has been proposed based on an organic semiconductor; however, it suffers from poor photostability. Here we report an inorganic photocatalyst for  $H_2O_2$  synthesis. Visible light irradiation ( $\lambda > 420$  nm) of semiconductor BiVO<sub>4</sub> loaded with Au nanoparticles (Au/BiVO<sub>4</sub>) in pure water with O<sub>2</sub> successfully produces  $H_2O_2$ . The bottom of the Bi-VO<sub>4</sub> conduction band (0.02 V vs. NHE, pH 0) is more positive than the one-electron reduction potential of O<sub>2</sub> (-0.13 V), while more negative than the two-electron reduction potential of O<sub>2</sub> (0.68 V). This thus suppresses one-electron reduction of O<sub>2</sub> and selectively promotes two-electron reduction of O<sub>2</sub>, resulting in efficient  $H_2O_2$  formation.

KEYWORDS: Photocatalysis · Hydrogen peroxide · Visible light · Bismuth vanadate · Gold nanoparticles

### INTRODUCTION

 $H_2O_2$  is a clean oxidant that emits only water as a byproduct and is widely used for pulp bleaching and disinfection.<sup>1</sup> It has also received much attention as a fuel cell energy carrier alternative to  $H_2$  because it is soluble in water and can be used in an one-compartment cell for electricity generation.<sup>2</sup>  $H_2O_2$  is currently manufactured by the anthraquinone method based on hydrogenation of anthraquinone with  $H_2$  on Pd-based catalyst followed by oxidation with  $O_2$ .<sup>3</sup> Alternative to this highenergy-consuming two-step process, one-step  $H_2O_2$  synthesis based on the reaction of  $H_2$  with  $O_2$  has also been studied with Pd-based catalysts.<sup>4,5</sup> This direct synthesis quantitatively produces  $H_2O_2$ , but needs special care due to the potential explosive nature of  $H_2/O_2$  mixed gases. A new method that produces  $H_2O_2$  without  $H_2$  is therefore desired.

Catalytic  $H_2O_2$  synthesis with earth-abundant water and  $O_2$  as resources is therefore ideal. Photocatalysis is one promising method for this purpose. The basic concept is as follows: the valence band holes (VB h<sup>+</sup>) formed by photoexcitation of the catalyst oxidize water and produce  $O_2$  and  $H^+$  (eq. 1). Twoelectron reduction of  $O_2$  by the conduction band electrons (CB e<sup>-</sup>) produces  $H_2O_2$  (eq. 2). As a result of this,  $H_2O_2$  can be produced from water and  $O_2$  (eq. 3).

$$2\mathrm{H}_{2}\mathrm{O} + 4\mathrm{h}^{+} \rightarrow \mathrm{O}_{2} + 4\mathrm{H}^{+} \tag{1}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

$$2H_2O + O_2 \rightarrow 2H_2O_2 \tag{3}$$

Some TiO<sub>2</sub>-based inorganic photocatalysts have been proposed,<sup>6-9</sup> but are inactive for H<sub>2</sub>O<sub>2</sub> production from water and O<sub>2</sub>. This is because they mainly promote one-electron reduction of O<sub>2</sub>, producing a superoxide (\*OOH) radical (eq. 4) rather than two-electron reduction of O<sub>2</sub> (eq. 2).<sup>9</sup> Another reason is that these TiO<sub>2</sub>-based catalysts have insufficient activity for water oxidation (eq. 1);<sup>10</sup> therefore, sacrificial electron donors such as alcohols are necessary. In addition, these catalysts require UV light (~400 nm) for photoexcitation; the formed H<sub>2</sub>O<sub>2</sub> is subsequently decomposed by absorbing UV light.<sup>11,12</sup> The design of photocatalysts that promote water oxidation and two-electron reduction of O<sub>2</sub> under visible light irradiation ( $\lambda$  >400 nm) is necessary.

$$O_2 + H^+ + e^- \rightarrow \bullet OOH \tag{4}$$

Earlier, we reported that an organic semiconductor based on graphitic carbon nitride (g- $C_3N_4$ ) promotes these reactions (eqs. 1 and 2) under visible light and successfully produces mM levels of  $H_2O_2$ .<sup>13</sup> This organic system, however, suffers from poor photostability, as often observed for related materials.<sup>14,15</sup> The design of robust inorganic system is therefore desired for sustainable  $H_2O_2$  synthesis.

One powerful approach for the design of inorganic photocatalyst for  $H_2O_2$  synthesis is the use of Au nanoparticles. Teranishi et al. prepared TiO<sub>2</sub> loaded with Au particles.<sup>16</sup> The

Au/TiO<sub>2</sub> catalyst, when irradiated by UV light in an EtOH solution, produces relatively larger amount of H<sub>2</sub>O<sub>2</sub> than the early reported inorganic systems.<sup>6–9</sup> As shown in Scheme 1a, the photoformed CB  $e^-$  of TiO<sub>2</sub> is trapped by the Au particles. These e<sup>-</sup> promote two-electron reduction of O<sub>2</sub> more selectively as compared to bare  $TiO_2$  or  $TiO_2$  loaded with other metals. This results in relatively efficient production of H<sub>2</sub>O<sub>2</sub>. The Au/TiO<sub>2</sub> catalyst is, however, inactive for H<sub>2</sub>O<sub>2</sub> formation in water. This is because TiO<sub>2</sub> is less active for water oxidation<sup>10</sup> and UV irradiation is required for its photoexcitation inevitably decomposes the formed  $H_2O_2$ .<sup>11,12</sup> In addition, as shown in Scheme 1a, the bottom of TiO<sub>2</sub> CB  $(-0.19 \text{ V vs. NHE, pH } 0)^{17}$ is more negative than the potentials for one-electron reduction of  $O_2$  (-0.13 V) and two-electron reduction of  $O_2$  (0.68 V).<sup>18</sup> This thus promotes both reduction reactions and decreases the selectivity for H<sub>2</sub>O<sub>2</sub> formation. The loading of Au particles onto the semiconductors that are active for water oxidation under visible light and have relatively positive CB would be effective for photocatalytic H<sub>2</sub>O<sub>2</sub> production.



Scheme 1. Energy diagrams for (a) Au/TiO<sub>2</sub> and (b) Au/BiVO<sub>4</sub>, and reduction potential of O2.

Here we report that the answer may lie in the use of semiconductor bismuth vanadate (BiVO<sub>4</sub>), active for water oxida-tion under visible light ( $\sim$ 550 nm).<sup>19</sup> We found that BiVO<sub>4</sub> loaded with Au particles (Au/BiVO<sub>4</sub>) successfully produces H<sub>2</sub>O<sub>2</sub> from water and O<sub>2</sub> under visible light; this is a first example of all-inorganic photocatalyst for H<sub>2</sub>O<sub>2</sub> synthesis. As shown in Scheme 1b, the bottom of  $BiVO_4 CB (0.02 V)^{20}$  is more positive than the one-electron reduction potential of O<sub>2</sub> (-0.13 V), while more negative than the two-electron reduction potential of O<sub>2</sub> (0.68 V).<sup>18</sup> Photoexcitation of Au/BiVO<sub>4</sub> therefore selectively promotes two-electron reduction of  $O_2$ , successfully producing H<sub>2</sub>O<sub>2</sub>.

#### **RESULTS AND DISCUSSION**

Catalyst preparation and characterization. BiVO<sub>4</sub> was prepared by stirring KV<sub>3</sub>O<sub>8</sub> and Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in water.<sup>19</sup> As shown in Figure 1, the obtained yellow powders (average size, 1.2  $\mu$ m; BET surface area, 1.5 m<sup>2</sup> g<sup>-1</sup>) absorb visible light at <550 nm. As shown in Figure S1 (Supporting Information), Xray diffraction (XRD) analysis of the powders shows distinctive diffractions for monoclinic BiVO<sub>4</sub>.<sup>21</sup> Au particles were loaded on BiVO<sub>4</sub> by the deposition-precipitation method:<sup>22</sup> The BiVO<sub>4</sub> powders were stirred in water (pH 7) containing HAuCl<sub>4</sub>·4H<sub>2</sub>O at 353 K and calcined at different temperatures, affording dark yellow powders of  $Au_x/BiVO_4$ , where x is the

amount of Au loaded [x (wt %) = Au/BiVO<sub>4</sub> × 100]. As shown in Figure 2, transmission electron microscopy (TEM) image of Au<sub>0.2</sub>/BiVO<sub>4</sub> prepared by calcination at 673 K shows Au particles with an average diameter 7.2 nm. The lattice spacings of the Au particles (0.24 nm) and BiVO<sub>4</sub> (0.31 nm and 0.26 nm) agree with those of standards Au(111) (JCPDS 01-1174, 0.235 nm), BiVO<sub>4</sub>(103) (JCPDS 01-074-4894, 0.312 nm), and Bi- $VO_4(200)$  (0.260 nm). As shown in Figure 1,  $Au_{0.2}/BiVO_4$ shows characteristic absorption at ca. 600 nm assigned to the surface plasmon resonance (SPR) of Au particles.



Figure 1. Absorption spectra of BiVO<sub>4</sub> and Au<sub>0.2</sub>/BiVO<sub>4</sub> prepared by calcination at 673 K. Plots show the action spectrum for  $H_2O_2$ formation on Au<sub>0.2</sub>/BiVO<sub>4</sub>. The apparent quantum yields were calculated with the equation  $[\Phi_{AOY} (\%) = ([H_2O_2 \text{ formed}] \times 2) / (M_2O_2 \text{ formed}] \times 2)$ (photon number entered into the reaction vessel)  $\times$  100]. The spectra for other catalysts are summarized in Figure S5 (Supporting Information).



Figure 2. (a) TEM image of  $Au_{0.2}/BiVO_4$  prepared by calcination at 673 K and (b) size distribution of the Au particles. (c, d) Highresolution images.

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58 59 60 **Photocatalytic reaction.** Photoreactions were performed by photoirradiation of pure water (30 mL) containing respective catalysts (50 mg) by a Xe lamp ( $\lambda > 420$  nm) with magnetic stirring under O<sub>2</sub> (1 atm) at 298 K. Table 1 summarizes the results obtained by 10 h reaction. Bare BiVO<sub>4</sub> (entry 1) scarcely produces H<sub>2</sub>O<sub>2</sub> (<5.0 µM, less than the detection limit). In contrast, Au loading onto BiVO<sub>4</sub> significantly enhances H<sub>2</sub>O<sub>2</sub> formation (40.2 µM, entry 2). Other metal particles loaded on BiVO<sub>4</sub> (entries 3–7) are ineffective (<12.4 µM). In addition, other semiconductors such as TiO<sub>2</sub>, <sup>16</sup> WO<sub>3</sub>, and AgNbO<sub>3</sub><sup>23</sup> loaded with Au particles (entries 8–10) are also inactive (<13.9 µM) even under UV irradiation. These data suggest that Au/BiVO<sub>4</sub> specifically produces H<sub>2</sub>O<sub>2</sub> very efficiently.

Table 1. Results of photocatalytic H<sub>2</sub>O<sub>2</sub> production.<sup>a</sup>

entry	catalyst	metal particle size [nm] <sup>b</sup>	light irradiation [nm]	$H_2O_2$ [ $\mu$ M] <sup>c</sup>
1	BiVO <sub>4</sub>		>420 <sup>g</sup>	<5.0
2	Au <sub>0.2</sub> /BiVO <sub>4</sub> <sup>d</sup>	$7.2 \pm 2.2$	>420 g	40.2
	1st reuse <sup>e</sup>		>420 g	39.2
	2nd reuse <sup>e</sup>	$7.4 \pm 1.8$	>420 g	40.0
3	Ag <sub>0.2</sub> /BiVO <sub>4</sub> <sup>f</sup>	$7.0 \pm 2.0$	>420 g	12.4
4	Pd <sub>0.2</sub> /BiVO <sub>4</sub> <sup>f</sup>		>420 g	<5.0
5	Pt <sub>0.2</sub> /BiVO <sub>4</sub> <sup>f</sup>		>420 <sup>g</sup>	<5.0
6	Co <sub>0.2</sub> /BiVO <sub>4</sub> <sup>f</sup>		>420 g	<5.0
7	Ni <sub>0.2</sub> /BiVO4 <sup>f</sup>		>420 g	<5.0
8	Au <sub>0.2</sub> /TiO <sub>2</sub> <sup>d</sup>		>300 <sup>h</sup>	<5.0
9	$Au_{0.2}/WO_3^{d}$		>420 g	13.9
10	Au <sub>0.2</sub> /AgNbO <sub>3</sub> <sup>d</sup>		>420 <sup>g</sup>	<5.0

<sup>*a*</sup> Reaction conditions: water (30 mL), catalyst (50 mg), O<sub>2</sub> (1 atm), temperature (298 K), time (10 h). <sup>*b*</sup> Determined by TEM observations (Figure S6, Supporting Information). <sup>*c*</sup> Determined by redox titration with KMnO<sub>4</sub> (detection limit, 5.0 μM). <sup>*d*</sup> Prepared by the deposition–precipitation followed by calcination at 673 K. <sup>*e*</sup> Catalysts were reused after simple washing with water followed by drying in vacuo. <sup>*f*</sup> Prepared with sodium formate as a reductant. <sup>*g*</sup> Light intensity at 420–500 nm is 26.9 W m<sup>-2</sup>. <sup>*h*</sup> Light intensity at 300–450 nm is 27.3 W m<sup>-2</sup>.

Figure 3 shows the time-dependent changes in the  $H_2O_2$ concentrations during reactions on  $Au_{0.2}/TiO_2$  and  $Au_{0.2}/BiVO_4$ .  $Au_{0.2}/TiO_2$  scarcely produces  $H_2O_2$  (<5.0 µM). In contrast, on  $Au_{0.2}/BiVO_4$ ,  $H_2O_2$  concentration increases with time. This suggests that photoexcited Au/BiVO<sub>4</sub> promotes water oxidation (eq. 1) and  $O_2$  reduction (eq. 2), producing  $H_2O_2$  (eq. 3). Figure 1 shows the action spectrum for  $H_2O_2$  formation on  $Au_{0.2}/BiVO_4$ . Change in the apparent quantum yields ( $\Phi_{AQY}$ ) agree well with the absorption spectrum of bare BiVO<sub>4</sub>. This indicates that band-gap excitation of BiVO<sub>4</sub> promotes the reactions, where the SPR absorption of the Au particles does not affect the reaction. As shown in Table 1 (entry 2), the catalyst recovered after the reaction exhibits almost the same activity as the fresh one, indicating that the catalyst is reusable without the loss of activity.



**Figure 3.** Time-dependent changes in the H<sub>2</sub>O<sub>2</sub> concentrations during photoreaction on Au<sub>0.2</sub>/TiO<sub>2</sub> ( $\lambda > 300$  nm) and Au<sub>0.2</sub>/BiVO<sub>4</sub> prepared by calcination at 673 K ( $\lambda > 420$  nm). Reaction conditions are identical to those in Table 1.

The photoexcited Au/BiVO<sub>4</sub> produces H<sub>2</sub>O<sub>2</sub> via water oxidation and two-electron reduction of  $O_2$  (eqs. 1–3). This is confirmed by the half reactions: the O<sub>2</sub> reduction with EtOH as an electron donor (Figure S2, Supporting Information) and the water oxidation with AgNO<sub>3</sub> as an electron acceptor (Figure S3, Supporting Information) successfully occur on the  $Au_{0.2}/BiVO_4$  catalyst. It is noted that  $O_2$  reduction with EtOH by 10 h photoreaction produces much larger amount of H<sub>2</sub>O<sub>2</sub> (257  $\mu$ M) than that formed in pure water (40  $\mu$ M, Figure 3). It is also noted that the initial rate of water oxidation with Ag-NO<sub>3</sub> on Au<sub>0.2</sub>/BiVO<sub>4</sub> (8.6  $\mu$ mol h<sup>-1</sup>) is larger than those on  $Au_{0.2}/TiO_2$ ,  $Au_{0.2}/WO_3$ , and  $Au_{0.2}/AgNbO_3$  (<3.5 µmol h<sup>-1</sup>); this is consistent with the activity tendency for H<sub>2</sub>O<sub>2</sub> production (Table 1, entries 2 and 8-10). These findings suggest that water oxidation (eq. 1) is the rate-determining step for  $H_2O_2$ production from water and O<sub>2</sub>; the Au/BiVO<sub>4</sub> catalyst with higher activity for water oxidation exhibits the best catalytic performance.<sup>2</sup>

As shown in Figure 3, during the reaction on Au<sub>0.2</sub>/BiVO<sub>4</sub>, the rate of H<sub>2</sub>O<sub>2</sub> formation decreases with photoirradiation time. This is due to the subsequent decomposition of the formed H<sub>2</sub>O<sub>2</sub> by photocatalytic reactions. Figure S4 (Supporting Information) shows the results for H<sub>2</sub>O<sub>2</sub> decomposition experiments on Au/BiVO<sub>4</sub>. In the dark condition, H<sub>2</sub>O<sub>2</sub> is scarcely decomposed. In contrast, visible light irradiation of the solution even with EtOH as an electron donor or with NaIO<sub>3</sub> as an electron acceptor under Ar atmosphere decreases the concentration of H<sub>2</sub>O<sub>2</sub>. This indicates that, as usually observed in related systems, H<sub>2</sub>O<sub>2</sub> is decomposed by the reduction with CB e<sup>-</sup> (eq. 5)<sup>16</sup> and by the oxidation with VB h<sup>+</sup> (eq. 6).<sup>25</sup>.

$$H_2O_2 + e^- \rightarrow {}^{\bullet}OH + OH^-$$
 (5)

$$\mathrm{H}_{2}\mathrm{O}_{2} + 2\mathrm{h}^{+} \rightarrow \mathrm{O}_{2} + 2\mathrm{H}^{+} \tag{6}$$

Selective two-electron reduction of O2. One-electron reduction of O<sub>2</sub> (eq. 4) is suppressed on the Au/BiVO<sub>4</sub> catalyst. As shown in Scheme 1b, the BiVO<sub>4</sub> CB  $(0.02 \text{ V})^{20}$  lies between the potentials for one-electron reduction of  $O_2$  (-0.13 V) and two-electron reduction of  $O_2$  (0.68 V),<sup>18</sup> although those of many other semiconductors such as TiO<sub>2</sub> lie on more negative positions (Scheme 1a).<sup>17</sup> This positive CB level of BiVO<sub>4</sub> therefore suppresses one-electron reduction of  $O_2$  (eq. 4). This is confirmed by electron spin resonance (ESR) analysis with 5.5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trapping reagent. An EtOH/water mixture (9/1 v/v, 5 mL) containing DMPO (0.1 mmol) was photoirradiated with Au<sub>0.2</sub>/BiVO<sub>4</sub> or Au<sub>0.2</sub>/TiO<sub>2</sub> catalyst (20 mg). Figure 4 shows the ESR spectra of the solutions recovered after 3 min photoirradiation. The Au<sub>0.2</sub>/BiVO<sub>4</sub> sample (red) shows almost no signal, but the Au<sub>0.2</sub>/TiO<sub>2</sub> sample (black) exhibits distinctive signals assigned to the DMPO-OOH spin adduct ( $\alpha_N = 13.5$  G;  $\alpha_H^{\beta} = 9.2$  G, g = 2.0066).<sup>26,27</sup> This clearly suggests that Au/BiVO<sub>4</sub> suppresses one-electron reduction of O<sub>2</sub>.

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**Figure 4.** ESR spectra measured at 298 K for the solutions obtained by (a)  $\lambda >$ 420 nm light irradiation of Au<sub>0.2</sub>/BiVO<sub>4</sub> or (b)  $\lambda >$ 300 nm light irradiation of Au<sub>0.2</sub>/TiO<sub>2</sub> in an EtOH/water/O<sub>2</sub> system with DMPO (0.1 mmol). The catalysts were prepared by the deposition–precipitation method followed by calcination at 673 K.

Photoexcited Au/BiVO<sub>4</sub> promotes selective two-electron reduction of O<sub>2</sub> on the Au particles. Electrochemical analysis with a rotating disk electrode confirms this. Figure 5a shows the linear-sweep voltammograms of the catalysts measured in a buffered water (pH 7) under O<sub>2</sub> (1 atm) at different rotating speeds.<sup>28,29</sup> At negative forward voltages, the e<sup>-</sup> transferred from the semiconductor CB to the Au particles promote O<sub>2</sub> reduction.<sup>30</sup> The Koutecky–Levich plots of the data obtained at the constant electrode potential (–0.3 V) are shown in Figure 5b. The slope of the plots obtained by linear regression was used to estimate the average number of electrons (*n*) involved in the overall O<sub>2</sub> reduction.<sup>31,32</sup> The plots were interpreted on the following equations, where *j* is the measured current density, *j*<sub>k</sub> is the kinetic current density, and  $\omega$  is the rotating speed (rpm), respectively:

$$j^{-1} = j_k^{-1} + B^{-1} \omega^{-1/2}$$
(7)

$$B = 0.2nFv^{-1/6}CD^{2/3}$$
(8)

*F* is the Faraday constant (96485 C mol<sup>-1</sup>), *v* is the kinetic viscosity of water (0.01 cm<sup>2</sup> s<sup>-1</sup>), *C* is the bulk concentration of O<sub>2</sub> in solution ( $1.3 \times 10^{-6}$  mol cm<sup>-3</sup>), and *D* is the diffusion coefficient of O<sub>2</sub> ( $2.7 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>), respectively.<sup>33</sup> The *n* for Au<sub>0.2</sub>/TiO<sub>2</sub> (black) is determined to be 1.6, suggesting that one-electron reduction of O<sub>2</sub> (*n* = 1) indeed occurs mainly on Au/TiO<sub>2</sub>, as supported by the ESR data (Figure 4). This indicates that, as shown in Scheme 1a, the negative CB level of TiO<sub>2</sub> promotes one-electron reduction of O<sub>2</sub>. In contrast, the *n* for Au<sub>0.2</sub>/BiVO<sub>4</sub> (red) is 2.5, indicating that the e<sup>-</sup> on the Au particles mainly promotes two-electron reduction of O<sub>2</sub> (*n* = 2). This suggests that, as shown in Scheme 1b, the relatively positive CB of BiVO<sub>4</sub> selectively promotes two-electron reduction of O<sub>2</sub> on the Au particles. This thus facilitates efficient production of H<sub>2</sub>O<sub>2</sub>.



**Figure 5.** (a) Linear-sweep voltammograms of  $Au_{0.2}/TiO_2$  and  $Au_{0.2}/BiVO_4$  prepared by calcination at 673 K, measured on a rotating disk electrode at different rotating speeds. (b) The Koutecky-Levich plots of the data obtained at the constant potential (-0.3 V).

Effect of Au particle size and amount of Au loaded. The size of Au particles strongly affects the catalytic activity. The  $Au_{0.2}/BiVO_4$  catalysts were prepared at different calcination temperatures to create Au particles with different sizes. As shown in Figure 6a (circle), the size of Au particles increases with a rise in temperature because the particle migration leads to their sintering;<sup>22</sup> the treatment at 623, 673, 773 and 873 K produces Au particles with 6.5, 7.2, 11.1 and 13.5 nm diameters, respectively.<sup>34</sup> These catalysts were used for photocatalyt-

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ic H<sub>2</sub>O<sub>2</sub> production. The bar data in Figure 6a show the H<sub>2</sub>O<sub>2</sub> concentration obtained by 10 h reaction. The catalyst prepared at 623 K shows lower activity than that of the catalyst prepared at 673 K. This is probably because, as observed in related systems,35-37 calcination at lower temperature leads to weaker adhesion of metal particles onto the semiconductor surface and suppresses electron transfer from photoexcited BiVO<sub>4</sub> to Au particles. In contrast, the calcination at higher temperature creates stronger interaction between BiVO<sub>4</sub> and Au particles, but the catalysts prepared at higher temperature (723, 773, and 823 K) show very low activity. This is because they contain larger Au particles, which have smaller surface areas and decrease the number of active sites for O2 reduction. Photocurrent response analysis confirms this. Figure 7 shows the photocurrent response of the catalysts loaded on a FTO glass electrode, obtained under visible light irradiation. Au<sub>0.2</sub>/BiVO<sub>4</sub> prepared at 673 K (red) generates current larger than that of bare BiVO<sub>4</sub> (black), suggesting that Au particles mediate the e<sup>-</sup> migration from BiVO<sub>4</sub> to FTO glass.<sup>38</sup> Au<sub>0.2</sub>/BiVO<sub>4</sub> prepared at 873 K (blue) that contains larger Au particles shows smaller current enhancement, indicating that the decreased number of surface Au atoms suppresses e migration from BiVO<sub>4</sub> to FTO glass. These findings suggest that smaller Au particles have larger number of reduction sites for  $O_2$  and efficiently produce  $H_2O_2$  (Figure 6a).



**Figure 6.** Effects of (a) calcination temperature of  $Au_{0.2}/BiVO_4$ and (b) amount of Au loaded (x) for  $Au_x/BiVO_4$  on the  $H_2O_2$  concentration formed by 10 h photoreaction. Reaction conditions are identical to those in Table 1. Circles denote the average diameters of Au particles on the catalysts. The calcination temperature for the catalysts (b) is 673 K. Typical TEM images of catalysts and size distributions of their Au particles are summarized in Figure S6 (Supporting Information).

The amount of Au loaded also affects the catalytic activity. Au<sub>x</sub>/BiVO<sub>4</sub> catalysts with different Au loadings (x = 0.2, 0.5, 0.5) 1.0, and 2.0 wt %) were prepared by calcination at 673 K. As shown by the circles in Figure 6b, the sizes of Au particles increase with an increase in the Au loadings;<sup>22</sup> the average diameters for x = 0.2, 1.0 and 2.0 catalysts are 7.2, 11.9 and 12.5 nm, respectively. As shown by the bar data in Figure 6b, the activities of these catalysts decrease with the Au loadings, although the loading of larger amount of Au increases the net surface areas of Au particles. This is due to the suppression of e<sup>-</sup> injection from the photoexcited BiVO<sub>4</sub> to Au particles. The metal/semiconductor heterojunction creates a Schottky barrier  $(\phi_{\rm B})$  that strongly affects the efficiency for e<sup>-</sup> injection. The increase in the amount of metal loaded onto the semiconductor leads to an increase in the height of  $\phi_{\rm B}$ , because of the decrease in the Fermi level of the semiconductor.<sup>39</sup> The decreased catalytic activity for larger Au loading catalysts is therefore because the increased  $\phi_{\rm B}$  suppresses the e<sup>-</sup> injection from the photoexcited BiVO<sub>4</sub> to Au particles. As shown in Figure 7, Au<sub>2.0</sub>/BiVO<sub>4</sub> (green) generates current much smaller than that of Au<sub>0.2</sub>/BiVO<sub>4</sub> (red), suggesting that the e<sup>-</sup> injection is indeed suppressed. The above findings indicate that loading of smaller numbers of small Au particles (ca. 7 nm) exhibits best catalytic performance for the H<sub>2</sub>O<sub>2</sub> production.



**Figure 7.** Photocurrent response of bare BiVO<sub>4</sub>, Au<sub>0.2</sub>/BiVO<sub>4</sub>, Au<sub>2.0</sub>/BiVO<sub>4</sub> prepared by calcination at 673 K, and Au<sub>0.2</sub>/BiVO<sub>4</sub> prepared by calcination at 873 K, obtained under visible light irradiation ( $\lambda > 420$  nm) at a bias of 0.5 V. The average sizes of Au particles on the respective catalysts ( $d_{Au}$ ) are denoted in the figure.

#### CONCLUSION

We found that Au/BiVO<sub>4</sub> promotes photocatalytic H<sub>2</sub>O<sub>2</sub> production from water and O<sub>2</sub> under visible light irradiation, via the promotion of water oxidation and selective twoelectron reduction of O<sub>2</sub>. At present, the catalytic activity is insufficient; the  $\Phi_{AQY}$  at 420 nm is 0.24%, which is one-tenth of that of the organic semiconductor photocatalysts (2.6%).<sup>13</sup> Activity improvement is therefore necessary for practical applications. Nevertheless, the inorganic system presented here based on water oxidation and selective two-electron reduction of  $O_2$  may contribute to the design of green, stable and sustainable  $H_2O_2$  synthesis based on photocatalysis.

## **EXPERIMENTAL SECTION**

**Materials.** All of the reagents used were purchased from Wako, Tokyo Kasei, and Sigma-Aldrich and used without further purification. Water was purified by the Milli Q system.  $TiO_2$  (JRC-TIO-4) was kindly supplied from the Catalyst Society of Japan (Japan Reference Catalyst). WO<sub>3</sub> was purchased from Kojundo Chemical Laboratory Co..

**Catalyst preparation.** BiVO<sub>4</sub> was prepared as follows:<sup>19</sup> a mixture of  $K_2CO_3$  (115 mg) and  $V_2O_5$  (455 mg) was calcined in air at 730 K for 10 h, producing  $KV_3O_8$ . The obtained  $KV_3O_8$  was added to water (50 mL) with Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (2.3 g) and stirred at 298 K for 72 h. The solids were recovered by centrifugation, washed with water, and dried in vacuo.

AgNbO<sub>3</sub> was prepared according to literature procedure:<sup>23</sup> a mixture of Ag<sub>2</sub>O (232 mg) and Nb<sub>2</sub>O<sub>5</sub> (266 mg) was calcined in air at 1173 K for 12 h.

Au<sub>x</sub>/BiVO<sub>4</sub> [*x* (wt %) = 0.2, 0.5, 1.0, and 2.0] were prepared as follows:<sup>22</sup> HAuCl<sub>4</sub>·4H<sub>2</sub>O (2.1, 5.2, 10.5, or 20.9 mg) was added to water (50 mL). The pH of the solution was adjusted to 7 by an addition of 1 M NaOH. BiVO<sub>4</sub> (0.5 g) was added to the solution and stirred vigorously at 353 K for 3 h. The solids were recovered by centrifugation, washed with water, and calcined at the disignated temperature (673, 723, 773, or 873 K) for 2 h under air flow. Au<sub>0.2</sub>/TiO<sub>2</sub>, Au<sub>0.2</sub>/WO<sub>3</sub>, and Au<sub>0.2</sub>/AgNbO<sub>3</sub> were prepared in a similar manner.

 $M_{0.2}$ /BiVO<sub>4</sub> [M = Ag, Pd, Pt, Co, and Ni] were prepared as follows:<sup>40</sup> BiVO<sub>4</sub> (0.5 g) was added to water (20 mL) containing AgNO<sub>3</sub> (1.6 mg), Pd(NO<sub>3</sub>)<sub>2</sub> (2.2 mg), H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (2.7 mg), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (5.0 mg), or CoCl<sub>2</sub>·6H<sub>2</sub>O (4.0 mg), and evaporated under stirring at 393 K for 12 h. The resultant was dried at 673 K for 2 h. The powders were added to a sodium formate solution (0.1 M, 20 mL) and stirred at 313 K for 2 h under Ar (1 atm). The particles were recovered by centrifugation, washed with water, and dried in vacuo.

Photoreaction. Catalyst (50 mg) was added to water (30 mL) within a borosilicate glass bottle ( $\varphi$  35 mm; capacity, 50 mL), and the bottle was sealed with a rubber septum cap. The catalyst was dispersed well by ultrasonication for 5 min, and O<sub>2</sub> was bubbled through the solution for 15 min. The bottle was immersed in a temperature-controlled water bath (298 K) and photoirradiated at  $\lambda$  >420 nm using a 2 kW Xe lamp (USHIO Inc.) with magnetic stirring.<sup>41</sup> Photocatalytic O<sub>2</sub> reduction with EtOH as sacrificial electron donor was performed with catalyst (50 mg) in an EtOH/water (9/1 v/v) mixture (30 mL) under O<sub>2</sub> atmosphere.<sup>42</sup> Photocatalytic water oxidation was performed with catalyst (50 mg) in water (30 mL) containing AgNO<sub>3</sub> (0.05 M) under Ar atmosphere.<sup>13</sup> Decomposition experiment of H<sub>2</sub>O<sub>2</sub> was performed with catalyst (50 mg) in solution (30 mL) containing H<sub>2</sub>O<sub>2</sub> (10 mM) under Ar atmosphere, where water, EtOH/water (9/1 v/v), and aqueous NaIO<sub>3</sub> solution (0.05 M) were used as a solvent. Spectral irradiance for the Xe lamp was measured with a spectroradiometer USR-40 (USHIO Inc.). After the reaction, the gas-phase products were analyzed by GC-TCD (Shimadzu; GC-14B). The catalyst was recovered by centrifugation, and H<sub>2</sub>O<sub>2</sub> concentration in solution was determined by the redox titration with  $KMnO_4$ .

Action spectrum analysis. Photoreactions were carried out in water (30 mL) with Au<sub>0.2</sub>/BiVO<sub>4</sub> (50 mg) within a borosilicate glass bottle ( $\varphi$  35 mm; capacity, 50 mL). After ultrasonication and O<sub>2</sub> bubbling, the bottle was photoirradiated using a Xe lamp for 10 h, where the incident light was monochromated by the band-pass glass filters (Asahi Techno Glass Co.).<sup>43</sup> The full-width at half-maximum (fwhm) of the lights was 11–16 nm.

**ESR analysis.** The spectra were recorded at the X-band using a Bruker EMX-10/12 spectrometer with a 100 kHz magnetic field modulation at a microwave power level of 10.5 mW, where microwave power saturation of the signals does not occur.<sup>44</sup> The magnetic field was calibrated with a 1,1'-diphenyl-2-picrylhydrazyl (DPPH) as a standard. The measurements were carried out as follows: catalyst (20 mg) was suspended in an EtOH/water mixture (9/1 v/v, 5 mL) containing DMPO (0.1 mmol) within a Pyrex glass tube ( $\varphi$  12 mm; capacity, 20 mL), and the tube was sealed with a rubber septum cap. After ultrasonication (3 min) and O<sub>2</sub> bubbling (5 min), the solution was photoirradiated with magnetic stirring for 3 min. After the irradiation, the catalyst was recovered by centrifugation, and the resulting solution was subjected to analysis.

**Electrochemical analysis.** Rotating disk electrode analysis was performed on a computer-controlled CHI600D advanced electrochemical system with a three-electrode cell. An Ag/AgCl electrode and a Pt wire electrode were used as the reference and counter electrode, respectively. The working electrode was prepared according to literature procedure:<sup>45</sup> catalysts (50 mg) were dispersed in EtOH (2 mL) with Nafion (50 mg) as an ionomer by ultrasonication. The suspension (20  $\mu$ L) was put onto a Pt disk electrode and dried at room temperature. The linear-sweep voltammograms were obtained in O<sub>2</sub>-saturated 0.1 M phosphate buffer solution (pH 7) with a scan rate 10 mV s<sup>-1</sup> at different rotating speeds (400–1600 rpm). After each scan, O<sub>2</sub> was bubbled through the electrolyte for 5 min to saturate O<sub>2</sub>.

Photocurrent response was measured in a conventional three-electrode cell using an electrochemical analyzer (SI 1280B, TOYO Corp.). The working electrode was prepared using a fluoride tin oxide (FTO) glass. Catalysts (50 mg) were dispersed in EtOH (1 mL) with *p*-ethylene glycol (60 mg), and the suspension was ultrasonicated for 1 h. The resultant slurry (10 µL) was put onto a FTO glass. After drying in air, the glass was annealed at 623 K for 30 min under air flow for strong adhesion of the catalyst.<sup>46</sup> An water containing 0.5 M Na<sub>2</sub>SO<sub>4</sub> was used as the electrolyte. N<sub>2</sub> gas was bubbled through the solution 10 min. The working electrode was immersed in the solution with a Pt sheet and a Ag/AgCl electrode as the counter and reference electrodes, respectively. The working electrode was photoirradiated ( $\lambda > 420$  nm) from the back side (FTO glass/semiconductor interface) at a potential of 0.5 V. The exposed area under photoirradiation was 0.25 cm<sup>2</sup>.

**Other analysis.** XRD patterns were measured on a Philips X'Pert-MPD spectrometer. Diffuse-reflectance (DR) UV-vis spectra were measured on an UV-vis spectrophotometer (JASCO Corp.; V-550) equipped with Integrated Sphere Ap-

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58 59 60 paratus ISV-469, using  $BaSO_4$  as a reference. The spectra for catalysts are summarized in Figure S5 (Supporting Information). TEM observations were performed using an FEI Tecnai G2 20ST analytical electron microscope operated at 200 kV.<sup>47</sup> Typical TEM images of catalysts and size distributions of their metal particles are summarized in Figure S6 (Supporting Information).

## ASSOCIATED CONTENT

XRD patterns of catalysts (Figure S1), time-profiles for  $H_2O_2$  formation in an EtOH/water/O<sub>2</sub> system (Figure S2), time-profiles for water oxidation with AgNO<sub>3</sub> (Figure S3), results of  $H_2O_2$  decomposition on Au/BiVO<sub>4</sub> (Figure S4), DR UV-vis spectra of catalysts (Figure S5), and TEM images of catalysts and size distribution of metal particles (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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