DOI: 10.1002/ange.201408352

Multi-Electron Oxygen Reduction by a Hybrid Visible-Light-Photocatalyst Consisting of Metal-Oxide Semiconductor and Self-Assembled Biomimetic Complex**

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Abstract: *Adsorption experiments and density functional theory (DFT) simulations indicated that Cu(acac)$_2$ is chemisorbed on the monoclinic sheelite (ms)-BiVO$_4$ surface to form an O$_2$-bridged binuclear complex (OBBC/BiVO$_4$) like hemocyanin. Multi-electron reduction of O$_2$ is induced by the visible-light irradiation of the OBBC/BiVO$_4$ in the same manner as a blue Cu enzyme. The drastic enhancement of the O$_2$ reduction renders ms-BiVO$_4$ to work as a good visible-light photocatalyst without any sacrificial reagents. As a model reaction, we show that this biomimetic hybrid photocatalyst exhibits a high level of activity for the aerobic oxidation of amines to aldehydes in aqueous solution and imines in THF solution at 25°C giving selectivities above 99% under visible-light irradiation.*

In industry, approximately 30% of fine chemicals are produced by oxidation processes.[1] The development of "green" oxidative synthetic routes utilizing the sunlight and O_2 in the air as the energy source and oxidizing agent, respectively, is crucial for reducing CO_2 emissions and saving energy. O_2 reduction is the key process in photocatalytic reactions as well as in fuel cells and biological energy conversion. Among a variety of visible-light photocatalysts developed so far,[2] metal oxide semiconductors represented by $BiVO_4$[3] are very attractive because of the moderate oxidation ability and the good physicochemical stability. Since the solar spectrum peaks at around 500 nm, the metal oxide should possess an absorption edge longer than 500 nm or a band gap (E_g) smaller than 2.5 eV for an efficient use of the sunlight. However, there is a trade-off between the visible-light absorptivity and the driving force for O_2 reduction, i.e., the decrease in the band gap necessarily lowers the conduction band (CB) minimum or the reducing ability of the excited electrons, because the valence band (VB) maximum, mainly consisting of O2p orbitals, is almost constant (+2.94 V vs. standard hydrogen electrode, SHE).[4] Thus, the CB minimum for the metal oxide semiconductors with $E_g <$ 2.5 eV is located below +0.44 V vs. SHE, which means that the photocatalysts cannot use O_2 with the standard redox potential of oxygen ($E^0(O_2/O_2^-)$) of −0.284 V[5] as a one-electron acceptor. In fact, sacrificial electron acceptors such as Ag^+ ions ($E^0(Ag^+/Ag) = +0.799$ V)[5] are necessary for $BiVO_4$ to operate as a photocatalyst. Thermodynamically, the increase in the number of electrons participating in the O_2 reduction facilitates its progress ($E^0(O_2/H_2O_2) = +0.695$ V and $E^0(O_2/H_2O) = +1.229$ V).[5] If metal oxide semiconductors with $E_g < 2.5$ eV can be endowed with electrocatalytic activity for the multi-electron O_2 reduction, the method would be accessible for efficient and selective oxidative chemical transformation processes. A fascinating approach is the hybridization of metal oxide semiconductors exhibiting a strong absorption in the wide spectral range and molecular metal complexes with highly efficient and selective electrocatalytic activity.[6,7] Although this type of hybrid photocatalysts has recently attracted much interest for H_2 generation,[8] CO_2 reduction,[9,10] and environmental purification,[11] there is no report on oxidative organic synthesis.

Here we show that $BiVO_4$ with an O_2-bridged (acetylacetonato)copper(II) binuclear complexes on the surface gives rise to the multi-electron O_2 reduction leading to a high level of visible-light activity for the oxidation of amines to aldehydes and imines. Both of them are important versatile intermediates for fine chemicals and pharmaceuticals.[12] Several conventional synthetic methods use stoichiometric amounts of harmful or explosive reagents accompanied by the emission of the corresponding amount of pollutants.[13,14] The development of "green" efficient and selective catalytic processes to produce aldehydes and imines is highly desired.

$BiVO_4$ can take the crystal forms of monoclinic sheelite (*ms*-) and tetragonal zircon structures with E_g's of 2.4 and 2.9 eV, respectively.[15] *ms*-$BiVO_4$ particles with a specific surface area of 0.54 $m^2\,g^{-1}$ were synthesized by a liquid-phase method.[16] Bis(acetylacetonato)copper(II) (Cu(acac)$_2$) and bis(hexafluoroacetylacetonato)copper(II) (Cu(hfacac)$_2$) were used as the copper complexes, and (ethylenediaminetetraacetato)copper(II) ($[Cu(edta)]^{2-}$) for comparison. The adsorption property of Cu(acac)$_2$ on *ms*-$BiVO_4$ was studied. Figure 1a shows the Cu adsorption isotherm on *ms*-$BiVO_4$ from the solution of Cu(acac)$_2$ at 298 K and the Langmuir

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[**] This work was supported by a Grant-in-Aid for Scientific Research (C) No. 24550239 and MEXT-Supported Program for the Strategic Research Foundation at Private Universities.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408352.

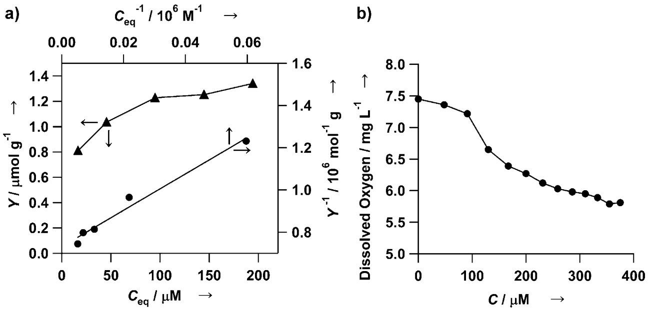


Figure 1. a) Cu adsorption isotherm on *ms*-BiVO$_4$ from the Cu(acac)$_2$ solution at 298 K and the Langmuir plot. b) Change in the amount of dissolved O$_2$ in an aqueous suspension of BiVO$_4$ with the addition of Cu(acac)$_2$ in a closed system.

plot. The adsorption follows the Langmuir-type behavior suggesting that Cu(acac)$_2$ is chemisorbed on the *ms*-BiVO$_4$ surface. From the Langmuir plot, the saturated adsorption amount (Γ_s) and the equilibrium constant (K) were calculated to be 1.52 molecule nm^{-2} and 8.50×10^4 M^{-1}, respectively. The K value yields the standard Gibbs energy of adsorption ($\Delta_{ad}G^0$) of -28.12 kJ mol^{-1}. Curiously, the cross-sectional area of Cu(acac)$_2$ in the saturated adsorption state ($\Gamma_s^{-1}=0.66$ nm^2 molecule^{-1}) is significantly smaller than the value for the free molecule estimated by the density functional theory (DFT) calculations (0.97 nm^2 molecule^{-1}). The concentration of dissolved O$_2$ in an aqueous suspension of *ms*-BiVO$_4$ was measured by a dissolved O$_2$ meter in a closed system. Figure 1 b shows the change in the concentration of dissolved O$_2$ with the stepwise addition of Cu(acac)$_2$, where C expresses the nominal Cu(acac)$_2$ concentration at each step. The O$_2$ concentration decreases with an increase in the concentration of Cu(acac)$_2$ added. Evidently, Cu(acac)$_2$ is chemisorbed on the BiVO$_4$ surface, and its adsorption is accompanied by the uptake of O$_2$ from the solution.

The adsorption state of Cu(acac)$_2$ on the *ms*-BiVO$_4$ surface was studied by X-ray photoelectron spectroscopy (XPS). Cu2p-XPS spectra were measured for Cu(acac)$_2$-adsorbed *ms*-BiVO$_4$ with varying amount of Cu(acac)$_2$ (Figure S1). A signal appears with the Cu(acac)$_2$ adsorption at the binding energy (E_B) of 931.8 eV due to the emission from Cu2p3/2, and the shake-up features unique to Cu^{II} are absent.[17] Figure 2 a shows the optimized structure of Cu(acac)$_2$ by DFT calculations. The atomic charge was estimated to be 1.417 for the Cu atom. The actual oxidation number of the Cu ion in the complex is significantly reduced from the formal oxidation number of +2 as a result of coordination by the acetylacetonato ligands. In the biosystem, the active center of hemocyanin is known to involve an O$_2$-bridged Cu^I binuclear complex (OBBC).[18] The assumption for the formation of an OBBC on the *ms*-BiVO$_4$ surface (OBBC/*ms*-BiVO$_4$) rationalizes the abnormally large adsorption amount of Cu(acac)$_2$ with the uptake of O$_2$ from the solution. Figure 2 b is the DFT-optimized structure showing an O$_2$-bridging structure with the bond of O$_2$ shortened from 1.208 Å for the free molecule to 1.204 Å due to the complexation. The enthalpy of the OBBC formation ($\Delta_{ad}H^0$) was calculated to be -44.2 kJ mol^{-1} from the energy change with the uptake of O$_2$ into the (Cu-complex)dimer (E(Cu-complex)dimer-O$_2$–E((Cu-complex)dimer)). These results indicate that an OBBC can be spontaneously formed on the *ms*-BiVO$_4$ surface against the entropy loss $((\Delta_{ad}H^{0}-\Delta_{ad}G^0)/T=-54.0\ \mathrm{J\,mol^{-1}\,K^{-1}})$.

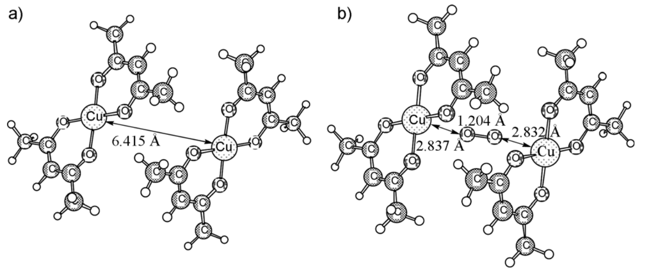


Figure 2. Optimized structures of Cu(acac)$_2$ (a) and Cu(acac)$_2$-O$_2$-Cu(acac)$_2$ dimer complex (b) with neutral triple and quintet states, respectively, by the hybrid-type DFT calculations.

The effect of the surface Cu complex on the O$_2$ reduction property of *ms*-BiVO$_4$ was studied by electrochemical measurements for *ms*-BiVO$_4$ film-coated fluorine-doped tin oxide electrodes (*ms*-BiVO$_4$/FTO) in the dark. Figure 3 shows current (J)–potential (E) curves for *ms*-BiVO$_4$/FTO in deaerated (a) and aerated (b) 0.1 M NaClO$_4$ solutions containing various amounts of Cu(acac)$_2$. In the absence of O$_2$, only a small current flows at $E<+0.2$ V regardless of the addition of Cu(acac)$_2$. In the presence of O$_2$, the addition of Cu(acac)$_2$ causes a drastic increase in the current scaling with an increase in the Cu(acac)$_2$ concentration. Interestingly, there are two current shoulders around +0.12 V (p$_1$) and -0.2 V (p$_2$). The potentials for p$_1$ and p$_2$ are more positive than the E^0(O$_2$/O$_2^-$) value. The p$_1$ and p$_2$ can be attributed to the four- and two-electron reductions of O$_2$, respectively. Clearly, the surface modification by Cu(acac)$_2$ endows *ms*-BiVO$_4$ with the ability for multi-electron O$_2$ reduction, and thus, we can expect that OBBC/*ms*-BiVO$_4$ works as a visible-light photocatalyst in the presence of O$_2$.

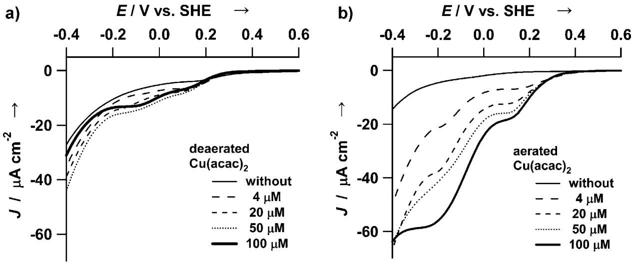


Figure 3. Dark current (J)–potential (E/V vs. SHE) curves for the *ms*-BiVO$_4$/FTO electrodes in deaerated (a) and aerated (b) 0.1 M NaClO$_4$ solutions containing various amounts of Cu(acac)$_2$.

As a model reaction, the OBBC/*ms*-BiVO$_4$-photocatalyzed oxidation of benzylamine was chosen. *ms*-BiVO$_4$ particles (0.2 g) were added to 200 mL of aqueous (2% acetonitrile) or THF (2% acetonitrile) solutions of Cu(acac)$_2$ or Cu(hfacac)$_2$. The small amount of acetonitrile was added for the complexes to be dissolved completely. After the

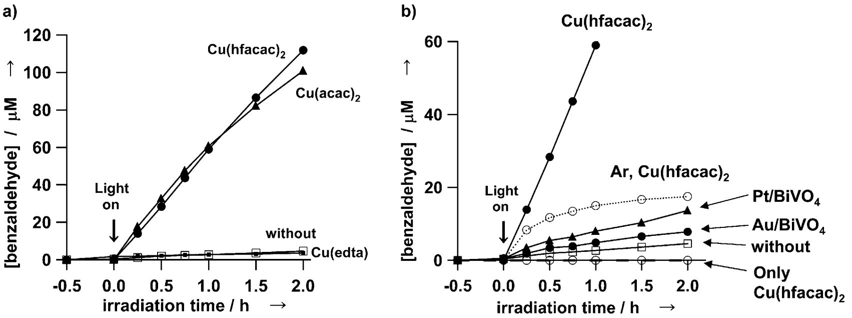
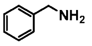
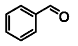
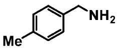
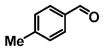
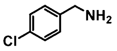
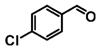
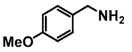
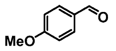


Figure 4. a) Time course for the oxidation of benzylamine with and without copper(II) complexes. b) Time course for the control experiments of the oxidation of benzylamine. Reaction conditions: *ms*-$BiVO_4$ 0.2 g, benzylamine (500 µM) solution (200 mL, H_2O:acetonitrile = 98:2 v/v) with and without copper(II) complex (4.0 µM), visible-light ($\lambda > 430$ nm, 6 mW cm^{-2}) irradiation at 25 °C under aerated or deaerated conditions.

suspension had been stirred for 1 h under aerobic conditions in the dark, it was irradiated by visible light ($\lambda > 430$ nm, $I_{420\text{–}485\,\mathrm{nm}} = 6$ mW cm^{-2}). Figure 4a shows the time course for the reactions with and without addition of copper complexes. No reaction occurred in the dark as well as under irradiation in the absence of copper complexes or in the presence of Cu(edta). Visible-light irradiation of *ms*-$BiVO_4$ in the presence of $Cu(acac)_2$ or $Cu(hfacac)_2$ induces the efficient oxidation of benzylamine to benzaldehyde. Chemical analysis by inductively coupled plasma spectroscopy of the particles recovered after the reaction confirmed that no Cu was deposited as metal and oxides on the surface. The turnover number (TON) for benzaldehyde generation after 2 h is 25. A serious problem that is common for molecular complex/semiconductor photocatalysts is the degradation of the complex. In the present system, the amount of generated benzaldehyde increases in proportion to the irradiation time. The OBBC is self-repaired by the self-assembling nature even if it partially degrades during the reaction. As shown in Figure 4b, O_2 is necessary for the reaction to be sustained. Previously, loading Pt nanoparticles on WO_3 was reported to boost its visible-light activity for the decomposition of acetic acid and acetaldehyde.[19] The enhanced activity was attributed to the multi-electron O_2 reduction affected by the Pt nanoparticles. The photocatalytic activity of $Cu(hfacac)_2$/*ms*-$BiVO_4$ is far greater than that of Pt/*ms*-$BiVO_4$ and Au/*ms*-$BiVO_4$. Evidently, the very high level of photocatalytic activity stems from the cooperative effect of $Cu(acac)_2$ or $Cu(hfacac)_2$ and *ms*-$BiVO_4$, where the copper complex acts not as a sacrificial agent but as an excellent electrocatalyst for the O_2 reduction. Table 1 summarizes the results on the OBBC/*ms*-BVO_4-photocatalyzed oxidation of benzylamine derivatives. In every case, the corresponding aldehydes are generated in high selectivity (> 99 %). Further, the reactions were carried out by changing the solvent from H_2O to THF. In this case, the corresponding imines are selectively formed (> 99 %; Table 2).

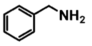
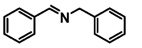
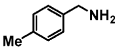
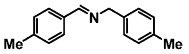
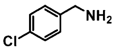
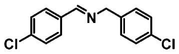
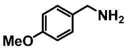
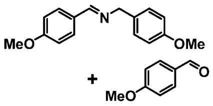
On the basis of these results, we present the a basic reaction mechanism for the oxidation of benzylamine derivatives to the corresponding aldehydes and imines. In the dark, $Cu(acac)_2$ or $Cu(hfacac)_2$ molecules are self-assembled on the *ms*-$BiVO_4$ surface with the uptake of O_2 to form an OBBC. The square-planar $Cu(acac)_2$ complex can further have basic solvent molecules like THF as axial ligands,[20] whose coordination bond is rather weak due to the Jahn–Teller effect. Thus, the axial ligand may be partially replaced by O_2 to form the OBBC. In Cu(edta), edta strongly coordinates to Cu^{2+} as a hexadentate ligand to form a stable complex, which would be inactive for the ligand exchange with O_2. $Cu(acac)_2$ and $Cu(hfacac)_2$ do not absorp at $\lambda > 350$ nm and therefore do not participate in the photoprocess. Visible-light irradiation of OBBC/*ms*-$BiVO_4$ excites the electrons from the VB to the CB of *ms*-$BiVO_4$. The VB holes oxidize benzylamines to yield the corresponding imines and H^+. In the presence of H_2O, the resulting imines undergo hydrolysis to afford aldehydes. In the absence of H_2O as shown in Table 2, the imines react with another amine to give the substituted imines. The VB maximum of $BiVO_4$ is raised up to + 2.53 V from + 2.94 V for the usual O2p band by the mixing of O2p and Bi6s orbitals.[21] The high selectivity of the reactions can be partly attributed to the mild oxidation ability of the VB holes. On the other hand, the direct copper complex–$BiVO_4$ bonding and the concentration of O_2 near the surface enable

Table 1: OBBC/*ms*-$BiVO_4$-photocatalyzed oxidation of benzylamines.[a]

Substrate	Product	Yield [µM]	Selectivity [%]
		112	> 99
		83	> 99
		68	> 99
		108	> 99

[a] Reaction conditions: *ms*-$BiVO_4$ 0.2 g, amine (500 µM) solution (200 mL, H_2O:acetonitrile = 98:2 v/v) with $Cu(hfacac)_2$ (4.0 µM), visible-light ($\lambda > 430$ nm, 6 mW cm^{-2}) irradiation for 2 h at 25 °C under aerated conditions.

Table 2: OBBC/*ms*-$BiVO_4$-photocatalyzed oxidation of benzylamines.[a]

Substrate	Product	Yield [µM]	Selectivity [%]
		166	> 99
		228	> 99
		188	> 99
		154 + 20	> 99

[a] Reaction conditions: *ms*-$BiVO_4$ 0.2 g, amine (500 µM) solution (200 mL, THF : acetonitrile = 98:2 v/v) with $Cu(hfacac)_2$ (4.0 µM), visible-light ($\lambda > 430$ nm, 6 mW cm^{-2}) irradiation for 2 h at 25 °C under aerated conditions.

the rapid electron transfer from the CB of $BiVO_4$ to O_2 in the OBBC through the copper ions.[7,22] Consequently, the multi-electron reduction of O_2 efficiently proceeds through the pair of Cu ions in the OBBC, being accompanied by the coupling with H^+. H_2O_2 was not detected from the solutions after the reaction. The CB electrons have a potential (+0.13 V at pH 0) that is high enough for the four-electron reduction of O_2 but insufficient for its two-electron reduction (Figure 3b). The H^+-transfer-coupled electron transfer may proceed in a concerted fashion with the O–O bond cleavage to produce H_2O.[23] This reminds us of laccase with a trinuclear Cu site that catalyzes the four-electron reduction of O_2.[18] The regeneration of the OBBC by the ligand exchange between the H_2O and O_2 completes the catalytic cycle.

We have shown that a *ms*-$BiVO_4$ light harvester self-integrated with an O_2-bridged binuclear copper complex on the surface is an efficient electrocatalyst for the multi-electron reduction of O_2 under visible-light irradiation. This biomimetic hybrid photocatalyst exhibits high levels of visible-light activity for the selective aerobic oxidation of benzylamines to the corresponding aldehydes and imines without a sacrificial reagent. We anticipate that the exploitation of each component of the hybrid photocatalyst will pave the way to new "green" routes for the synthesis of valuable organic compounds.

Experimental Section

Catalyst preparation and characterization: According to the literature reported by Kohtani et al., *ms*-$BiVO_4$ was prepared from $Bi(NO_3)_2$ and NH_4VO_3.[16] X-ray photoelectron spectroscopic (XPS) measurements were performed on a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromated Al Kα X-ray source operated at 15 kV and 10 mA using C1s as the energy reference (284.6 eV).

Electrochemical measurements: A paste of the *ms*-$BiVO_4$ precursor was prepared from $Bi(NO_3)_3$ (1 mmol), NH_4VO_3 (1 mmol), poly(ethylene glycol) 20000 Da (4 g), Triton X-100 (1 drop), and conc. HNO_3 (2 mL). The paste was coated on fluorine-doped SnO_2 (FTO)-film-coated glass substrates (sheet resistance = 10 Ω/square), and the samples were heated in air at 673 K for 4 h to form mp-*ms*-$BiVO_4$/FTO electrodes. The electrochemical cells comprising of the mp-*ms*-$BiVO_4$/FTO | $Cu(acac)_2$ + 0.1 M $NaClO_4$ (aqueous electrolyte solution) | glassy carbon were fabricated. The active area of the cell was $3.0 \times 2.5\ cm^2$. The current density ($\mu A\,cm^{-2}$) was measured at the dark rest potential by using a galvanostat/potentiostat (HZ-5000, Hokuto Denko).

Oxidation of benzylamine derivatives: A suspension of *ms*-$BiVO_4$ (200 mg) in a solution (H_2O:acetonitrile = 98:2 v/v or tetrahydrofuran:acetonitrile = 98:2) of benzylamine (500 μM, 200 mL) with Cu-complex (4 μM) was stirred at 298 K for 30 min in the dark. Irradiation was started using a 300 W Xe lamp (HX-500, Wacom) with a cut-off filter Y-45 (AGC TECHNO GLASS) in a double jacket type reaction cell (81 mm in diameter and 77 mm in length). The light intensity integrated from 420 to 485 nm ($I_{420-485}$) through a Y-45 optical filter was adjusted to 6.0 $mW\,cm^{-2}$. The yield and selectivity were determined by high-performance liquid chromatography (LC-6 AD, SPD-6 A, C-R8 A (Shimadzu)) [measurement conditions: column = Shim-pack CLC-ODS (4.6 mm × 150 mm) (Shimadzu); eluent = acetonitrile; flow rate = 1.0 $mL\,min^{-1}$; $\lambda = 280$ nm].

Received: August 19, 2014

Keywords: biomimetic complex · oxidation · photocatalysis · oxygen reduction · visible light

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