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Photocatalytic water oxidation over BiVO₄ with interface energetics engineered by Co and Ni-metallated dicyanamides

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ABSTRACT

Photocatalytic water oxidation based on semiconductors usually suffers from poor charge transfer from the bulk to the interface, which is necessary for oxygen generation. Here, we construct a hybrid artificial photosynthesis system for photocatalytic water oxidation. The system consists of BiVO₄ as the light harvester, a transitional metal complex $M(dca)_2$ ($M = Co, Ni$, dca: dicyanamide) as the water oxidation catalyst, and $S_2O_8^{2-}$ as a sacrificial electron acceptor. The system exhibits enhanced oxygen evolution activity when $M(dca)_2$ is introduced. The BiVO₄/Co(dca)₂ and BiVO₄/Ni(dca)₂ systems exhibit excellent oxygen evolution rates of 508.1 and 297.7 $\mu\text{mol}/(\text{h}\cdot\text{g})$ compared to the pure BiVO₄ which shows a photocatalytic oxygen evolution rate of 252.2 $\mu\text{mol}/(\text{h}\cdot\text{g})$ during 6 h of photocatalytic reaction. Co(dca)₂ is found to be more effective than Ni(dca)₂ as a water oxidation catalyst. The enhanced photocatalytic performance is ascribed to the $M(dca)_2$ -engineered BiVO₄/electrolyte interface energetics, and to the $M(dca)_2$ -catalyzed surface water oxidation. These two factors lead to a decrease in the energy barrier for hole transfer from the bulk to the surface of BiVO₄, which promotes the water oxidation kinetics.

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1. Introduction

Developing techniques for producing renewable and clean fuels is necessary to deal with increasing energy and environmental issues [1,2]. Photocatalytic water splitting is one of the most attractive methods for utilizing solar energy for H₂ production [3,4]. However, the four-electron oxygen evolution reaction (OER) is generally considered to be the bottleneck for the water splitting reaction owing to its sluggish kinetics, multiple-electron transfer, and complicated O–O bond formation [5]. Numerous efforts have therefore been devoted to developing efficient water oxidation catalysts (WOCs) in the past few decades [6,7], since the pioneering work of Gersten et al. [8].

Metal oxide semiconductors have been widely studied for

photocatalytic water splitting, because of their suitable band structures and high stability [9]. BiVO₄ with a bandgap of 2.4 eV has received much attention. However, BiVO₄ suffers from excessive charge recombination, low charge transport efficiency, and slow water oxidation kinetics. Strategies such as morphology control, hybridizing with other materials, and doping have been attempted to improve the photocatalytic performance of BiVO₄ [10]. WOCs can also effectively reduce the recombination rate of photoinduced charge carries, which in turn improves the photocatalytic water oxidation. Noble metal-based WOCs such as Ru(bpy)₃²⁺ and IrO₂ have been widely employed for this purpose, and exhibit very high activities for water oxidation. However, their high cost and scarcity limit their scalable application. Catalysts consisting of more abundant elements

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such as Co, Ni, Fe, Mn, and Bi are more promising in this respect. In particular, transitional metal-based molecular complexes have attracted increasing attention in the past few years, because of their low cost, tailorable structures, and homogeneous properties. A promising approach is combining molecular WOCs with semiconductors to utilize the advantages of both molecular complexes and metal oxides for efficient photocatalytic oxygen evolution. Niu *et al.* [11] reported a system consisting of semiconductor quantum dots and an acetaminosalol cobalt(II) complex, which exhibited considerable activity and good stability during 72 h of photocatalytic reaction.

In the current study, we report a hybrid system consisting of $M(dca)_2$ (where M is a metal; dca is dicyanamide) as a WOC and $BiVO_4$ as the photosensitizer, for photocatalytic oxygen evolution in aqueous solution. Both $BiVO_4/Co(dca)_2$ and $BiVO_4/Ni(dca)_2$ exhibit better performance than pure $BiVO_4$, with turnover numbers (TONs) of 3.46 and 2.03 after 6 h of photocatalytic reaction, respectively. $BiVO_4/Co(dca)_2$ also possesses considerable photocatalytic activity after 30 h under visible light irradiation. Surface photovoltage (SPV) and electrochemical measurements show that efficient hole transfer from $BiVO_4$ to $M(dca)_2$ results in high charge separation efficiency, which in turn promotes the water oxidation reaction kinetics. It is demonstrated that the water nucleophilic attack (WNA) pathway could be responsible for the photocatalytic water oxidation. These findings provide insights for constructing earth-abundant element-based photocatalytic systems for efficient and stable oxygen evolution in aqueous solution.

2. Experimental

2.1. Materials

$Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $NaN(CN)_2$, $Bi(NO_3)_3 \cdot 5H_2O$, NH_4VO_3 , $Na_2S_2O_8$, Na_2SO_3 , urea, ethanol, and *N,N'*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Fluorine-doped tin oxide (FTO) coated glass was purchased from Nippon Sheet Glass Co., Ltd, Japan. All materials were of analytical grade and used without further processing. Millipore deionized water (resistivity: 18.25 $M\Omega \cdot cm$) was used throughout all experiments.

2.2. Syntheses of samples

2.2.1. Synthesis of $BiVO_4$

$BiVO_4$ was prepared by a simple homogeneous precipitation method according to the literature [5]. Typically, 19.4 g of $Bi(NO_3)_3 \cdot 5H_2O$ was added into 100 mL of water and stirred for 20 min to form a homogeneous solution. Simultaneously, 4.68 g of NH_4VO_3 was dissolved into 100 mL of water to form another solution. The two solutions were mixed, followed by the addition of 7.5 g of urea and then heating to 90 °C under stirring. After the crystallization of $BiVO_4$, the obtained slurry was stirred at 90 °C for 24 h to form the precipitate, which was then washed with water, collected by filtration, and dried at 45 °C.

2.2.2. Synthesis of $M(dca)_2$ ($M = Co, Ni$)

$M(dca)_2$ was synthesized according to a method reported previously [12]. In a typical synthesis, 5 mmol of $Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 20 mL of water; 10 mmol of $NaN(CN)_2$ was added into 20 mL of DMF. Then, the $NaN(CN)_2$ solution was slowly added into the $Co(NO_3)_2$ or $Ni(NO_3)_2$ aqueous solution. The resulting suspension was stirred at room temperature for 12 h. Finally, the resulting precipitate was collected by filtration, washed with ethanol, and dried at 60 °C in a vacuum oven.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of samples were collected using an X'Pert PRO MPD X-ray diffractometer (PANalytical, Netherlands) with ($u/2u$) Bragg-Brentano geometry (Ni filter; $Cu K\alpha$ radiation; $\lambda = 0.1541874$ nm). UV-Vis absorption spectra of $M(dca)_2$ solutions were collected using a Cary 7000 UV-Vis-near-IR spectrophotometer with a blank solution as the reference. Fourier-transform infrared (FT-IR) spectra were collected using a Nicolet Magna 670 FT-IR spectrometer. SPV spectra were collected using a PL-SPS1000 spectrometer (Beijing Perfectlight Technology Co., Ltd., P. R. China) with a monochromatic light source [13] and an irradiation range from 400 to 600 nm. The amount of molecular catalyst present during the photocatalytic O_2 evolution process was determined using inductively-coupled plasma mass spectrometry (ICP-MS, ICPE-9000*, Shimadzu, Japan). Typically, 0.5 mL aliquots of the photocatalytic system suspension were removed at intervals using syringe pumps, followed by high-speed centrifugation (15000 r/min for 10 min) to obtain supernatants for ICP-MS tests. X-ray photoelectron spectrometry (XPS) (AXIS Ultra DLD, Shimadzu/Kratos Analytical, Japan) was used to detect the surface chemical components and states of samples, with monochromatic $Al K\alpha$ radiation (150 W, 15 kV, 1486.6 eV) under high vacuum ($< 3.9 \times 10^{-10}$ kPa).

2.4. Photocatalytic tests

Photocatalytic oxygen production experiments were carried out in a 100 mL Pyrex glass cell under visible light. The light source was a 300 W Xe arc lamp (PLSSXE300, Beijing Trusttech Technology Co., Ltd, P. R. China) equipped with a 420 nm cut-off filter. In a typical photocatalysis experiment, 15 mg of $BiVO_4$ powder as a photosensitizer was well dispersed in an aqueous solution (70 mL) containing 5 mg of $M(dca)_2$ as a WOC and 0.8 g of $Na_2S_2O_8$ as a sacrificial electron acceptor. The reaction solution was purged with Ar for 30 min to remove air before irradiation. The evolved gas was detected by gas chromatography (GC, SP-2100, Beijing Beifen-Ruili Analytical Instrument Co., Ltd, P. R. China) equipped with a thermal conductivity detector (TCD) and TDX-01 column. Argon was used as the carrier gas. No oxygen production was detected in the control experiment in the absence of irradiation.

2.5. Adsorption measurement

The amount of $M(dca)_2$ adsorbed on $BiVO_4$ was calculated

using the following relationship [14]:

$$C_s = (C_0 - C_e) \times V_s / m \quad (1)$$

where C_s is the amount of $M(dca)_2$ adsorbed on $BiVO_4$ (mg/g), C_0 is the concentration of $M(dca)_2$ (mg/L) before adsorption, C_e is the equilibrium concentration of $M(dca)_2$ in the supernatant (mg/L), V_s is the solution volume (L), and m is the mass of $BiVO_4$ (g). The concentration of $M(dca)_2$ was determined using the Bouguer-Lambert-Beer law.

The adsorption data was fitted to the Freundlich model:

$$C_s = K_f C_e^{1/n} \quad (2)$$

or its logarithmic form:

$$\ln C_s = \ln K_f + (1/n) \ln C_e \quad (3)$$

where K_f is the Freundlich adsorption coefficient which indicates the adsorption capacity, and $1/n$ is the isotherm curvature which indicates the adsorptive intensity.

2.6. Preparation of $BiVO_4$ electrodes

The $BiVO_4$ electrode was used as the working electrode, which was prepared according to reported procedures with some modifications [12]. First, FTO-coated glass was successively washed by sonication in acetone, alcohol, and then deionized water for 15 min each. A 5 mg of $BiVO_4$ was dispersed in a mixture of 1.5 mL of water, 1.5 mL of ethanol, and 100 μ L of Nafion solution (5 wt%) by sonication for 30 min, to obtain a stable suspension. Then, 250 μ L of the resulting suspension was deposited on the FTO glass (2×2 cm), which was then dried at room temperature.

2.7. Electrochemical measurements

Electrochemical measurements were carried out using a potentiostat (273A, Princeton Applied Research Company, USA) and a three-electrode cell. All electrochemical measurements were carried out in the dark in a solution of 0.5 mol/L Na_2SO_4 (70 mL, pH = 6.8), which was purged with N_2 for 20 min prior to measurements. Linear sweep voltammetry (LSV) tests were carried out from 0.4 to 1.8 V vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) measurements were carried at 1.4 V vs. Ag/AgCl. Mott-Schottky (M-S) measurements were carried out in the dark at a frequency of 1000 Hz. Pt and a

Ag/AgCl (saturated KCl) electrode were employed as the counter and reference electrodes, respectively.

2.8. Photoelectrochemical measurements

Photoelectrochemical measurements were carried out using a potentiostat (273A, Princeton Applied Research Company, USA) with a three-electrode cell. All photoelectrochemical measurements were carried out in a solution of 0.5 mol/L Na_2SO_4 (70 mL, pH = 6.8), which was purged with N_2 for 20 min prior to measurements. The separation efficiency and injection efficiency were tested with the addition of 0.1 mol/L Na_2SO_3 as a hole scavenger under visible light irradiation. Pt and a Ag/AgCl (saturated KCl) electrode were employed as the counter and reference electrodes, respectively.

3. Results and discussion

3.1. Interaction between $M(dca)_2$ and $BiVO_4$

$BiVO_4$ was synthesized by a homogenous precipitation method according to literature [5]. The crystal structure was confirmed from the XRD pattern (Fig. S1). The main peaks at $2\theta = 18.5^\circ$ and 29.4° agreed well with standard data for the scheelite-monoclinic structure (JCPDS 14-0688). $M(dca)_2$ was prepared by a simple solution method [12], and the molecular structure of $M(dca)_2$ is shown in Fig. S2. The crystal and chemical structures and optical properties of $M(dca)_2$ were characterized by XRD and FT-IR spectroscopy (Figs S3–S6). All measured data agreed well with that from literature reports [12]. This confirmed the synthesis of $M(dca)_2$ ($M = Co, Ni$), which would serve as WOCs for photocatalytic oxygen evolution. As shown in Fig. S7, the $BiVO_4$ sample absorbed light from the UV to visible region ($\lambda < 530$ nm), while $M(dca)_2$ showed negligible absorption. This indicated that $BiVO_4$ acted as the photosensitizer in the photocatalytic system.

To investigate the adsorption behavior of $M(dca)_2$ on $BiVO_4$, a series of adsorption tests based on UV-vis measurements were carried out. As shown in Fig. 1(a), the adsorption of $M(dca)_2$ on $BiVO_4$ was fitted well with the Freundlich equation. The adsorption coefficients (K_f) for $Co(dca)_2$ and $Ni(dca)_2$ were

Fig. 1. (a) Fitting models of $Co(dca)_2$ (1) and $Ni(dca)_2$ (2) adsorbed on $BiVO_4$ in deionized water, and (b) SPV spectra of $BiVO_4$ (1), $BiVO_4/Co(dca)_2$ (2), and $BiVO_4/Ni(dca)_2$ (3).

3.14 and 0.014, respectively. These results indicated that Co(dca)_2 more efficiently adsorbed on BiVO_4 than Ni(dca)_2 . This indicated a stronger interaction between BiVO_4 and Co(dca)_2 , which should yield more efficient charge transfer and thus higher photocatalytic performance. The mode of adsorption of M(dca)_2 on BiVO_4 was determined from FT-IR spectra. As shown in Figs S8 and S9, the peak at $2360\text{--}2184\text{ cm}^{-1}$ corresponded to the $\text{C}\equiv\text{N}$ stretching vibration of dicyanamide ligands [15], while those at $1647\text{--}1640\text{ cm}^{-1}$ corresponded to the $\text{C}=\text{O}$ stretching vibration of DMF [16] anchored with M(dca)_2 during synthesis. All these FT-IR peaks did not shift after the hybridization of M(dca)_2 with BiVO_4 . This indicated that M(dca)_2 was adsorbed on BiVO_4 via physical interactions rather than via chemical bonds.

To investigate the possibility of charge transfer between BiVO_4 and M(dca)_2 , SPV spectra of BiVO_4 , $\text{BiVO}_4/\text{Co(dca)}_2$, and $\text{BiVO}_4/\text{Ni(dca)}_2$ were collected. As shown in Fig. 1(b), the addition of Co(dca)_2 or Ni(dca)_2 caused the amplitude of BiVO_4 to significantly increase. A higher amplitude generally indicates more efficient charge separation [17,18]. It was therefore reasonable that photogenerated charge separation in BiVO_4 should be enhanced when M(dca)_2 was introduced. $\text{BiVO}_4/\text{Co(dca)}_2$ showed better charge separation behavior than $\text{BiVO}_4/\text{Ni(dca)}_2$. This indicated that Co(dca)_2 was a better WOC than Ni(dca)_2 in the present hybrid systems.

3.2. Photocatalytic oxygen evolution

Photocatalytic tests for oxygen evolution in the $\text{BiVO}_4/\text{M(dca)}_2$ hybrid systems were carried out in a fully aqueous solution containing $\text{Na}_2\text{S}_2\text{O}_8$ as a sacrificial electron acceptor under visible light irradiation ($\lambda > 420\text{ nm}$). As shown in Fig. 2(a), both $\text{BiVO}_4/\text{Co(dca)}_2$ and $\text{BiVO}_4/\text{Ni(dca)}_2$ exhibited higher performance than pure BiVO_4 , which demonstrated the catalytic role of M(dca)_2 in the water oxidation process. In comparison to pure BiVO_4 which showed a photocatalytic oxygen evolution rate of $252.2\text{ }\mu\text{mol}/(\text{h}\cdot\text{g})$ during 6 h of reaction, the $\text{BiVO}_4/\text{Co(dca)}_2$ and $\text{BiVO}_4/\text{Ni(dca)}_2$ systems exhibited higher photocatalytic performances, with oxygen evolution rates of 508.1 and $297.7\text{ }\mu\text{mol}/(\text{h}\cdot\text{g})$ and TONs (vs. M(dca)_2) of 3.46 and 2.03, respectively. The $\text{BiVO}_4/\text{Co(dca)}_2$ system showed a pho-

tocatalytic oxygen evolution rate 1.7 times higher than that of the $\text{BiVO}_4/\text{Ni(dca)}_2$ system. This could be explained by the higher surface charge transfer of $\text{BiVO}_4/\text{Co(dca)}_2$ as evidenced by SPV analysis, and further evidenced in the following electrochemical measurements. The stability of $\text{BiVO}_4/\text{Co(dca)}_2$ was monitored throughout a 30 h photocatalytic experiment. Hybridizing Co(dca)_2 with BiVO_4 enhanced the oxygen evolution rate and resulted in good photocatalyst stability. Under visible light irradiation, $\text{BiVO}_4/\text{Co(dca)}_2$ showed a relatively stable oxygen evolution rate during the 30 h photocatalytic reaction, as shown in Fig. 2(b), producing $171.95\text{ }\mu\text{mol}$ of oxygen after the 30 h (TON = 13, vs. Co(dca)_2). The stability of $\text{BiVO}_4/\text{Co(dca)}_2$ was much higher than that of reported $\text{BiVO}_4/\text{molecular catalyst}$ photocatalytic systems, for which activities usually last $<10\text{ h}$ [17,19].

The stabilities of the molecular catalysts during the photocatalytic process were further investigated by ICP-MS. As shown in Fig. S10, the amount of Co(dca)_2 in the photocatalytic solution showed negligible decrease during the 30 h photocatalytic oxygen evolution test. This confirmed the high stability of Co(dca)_2 , with no evidence of the formation of insoluble Co species. After the photocatalytic test, the powder in the suspension was collected by filtration and analyzed by XPS. As shown in Fig. S11, the intensity of the Co 2p XPS peak was negligible for the powder residue of the $\text{BiVO}_4/\text{Co(dca)}_2$ system and was mainly due to trace Co(dca)_2 physically adsorbed on BiVO_4 . This adsorbed Co(dca)_2 suppressed the formation of cobalt oxides on the BiVO_4 surface during the photo-oxidation reaction. The N 1s peak of the powder residue after photocatalytic reaction was observed at $\sim 400\text{ eV}$, and showed no obvious shift compared with that of pristine Co(dca)_2 (Fig. S12). This result also supported the conclusion that there was minimal change in the structure of the molecular catalyst during the photocatalytic test, since the catalyst was the only N source. Similar results were observed for the $\text{BiVO}_4/\text{Ni(dca)}_2$ system as shown in Figs S13 and S14, which confirmed the good stability of Ni(dca)_2 as a WOC.

3.3. Interfacial properties of $\text{BiVO}_4/\text{M(dca)}_2$

To better understand the increased oxygen generation ac-

Fig. 2. (a) Photocatalytic O_2 evolution over 6 h for BiVO_4 (1), $\text{BiVO}_4/\text{Co(dca)}_2$ (2), and $\text{BiVO}_4/\text{Ni(dca)}_2$ (3) systems, and (b) photocatalytic oxygen evolution over 30 h for the $\text{BiVO}_4/\text{Co(dca)}_2$ (1) system and pure BiVO_4 (2).

tivity of BiVO_4 when M(dca)_2 was added, electrochemical tests were carried out to investigate the effects of M(dca)_2 on the charge transfer behavior at the BiVO_4 /electrolyte interface.

LSV curves of BiVO_4 , $\text{BiVO}_4/\text{Co(dca)}_2$, and $\text{BiVO}_4/\text{Ni(dca)}_2$ films were recorded in Na_2SO_4 (0.5 mol/L), as shown in Fig. 3(a). Both the $\text{BiVO}_4/\text{Co(dca)}_2$ and $\text{BiVO}_4/\text{Ni(dca)}_2$ systems showed much higher current densities than BiVO_4 . The onset potential of $\text{BiVO}_4/\text{Co(dca)}_2$ for the OER was 1.78 V, which was more negative than those of $\text{BiVO}_4/\text{Ni(dca)}_2$ (1.91 V) and BiVO_4 (2.06 V). The LSV results indicated that M(dca)_2 were superior WOCs to BiVO_4 , which agreed well with the photocatalytic results. M-S measurements were carried out to further investigate the interfacial energetics in terms of interfacial band bending. BiVO_4 is a typical n-type semiconductor, so its energy band bends upward at the BiVO_4 /electrolyte interface [20]. Thus, there is a driving force for hole transfer from the bulk to the surface for water oxidation [21]. As shown in Fig. 3(b), the flat band potential of BiVO_4 was negatively shifted by 78 and 49 mV when Co(dca)_2 and Ni(dca)_2 were added, respectively. This resulted in increased band bending and thus an enhanced driving force for hole transfer, as shown in Fig. 3(d), which benefited the water oxidation reaction. Stronger band bending

occurred at the Co(dca)_2 -engineered BiVO_4 /electrolyte interface vs. the Ni(dca)_2 -engineered interface, as demonstrated by the more cathodic shift of the flat band potential in the $\text{BiVO}_4/\text{Co(dca)}_2$ system. This implied that the Co(dca)_2 -engineered BiVO_4 /electrolyte interface energetics favored more efficient interfacial hole transfer. EIS tests were also carried out to investigate the interface charge transfer behaviors. The Nyquist plot of $\text{BiVO}_4/\text{M(dca)}_2$ showed a much smaller semicircle diameter than the plot of pure BiVO_4 , as shown in Fig. 3(c). This indicated the smaller interfacial resistivity for charge carrier transfer with the BiVO_4 /electrolyte interface energetics engineered by M(dca)_2 [22]. The inset in Fig. 3(c) shows the equivalent circuit for the obtained Nyquist plots. The charge transfer resistances (R_{ct}) of the three samples followed the order $\text{BiVO}_4/\text{Co(dca)}_2$ (507 Ω) < $\text{BiVO}_4/\text{Ni(dca)}_2$ (1747 Ω) < BiVO_4 (5130 Ω). This indicated that the most favorable OER kinetics were obtained for the $\text{BiVO}_4/\text{Co(dca)}_2$ system, in good agreement with the photocatalytic and LSV results. The M-S and EIS results showed that photogenerated hole transfer from BiVO_4 to the electrolyte was greatly promoted by the addition of M(dca)_2 , and that Co(dca)_2 promoted interfacial charge transfer and then catalyzed the OER more efficiently

Fig. 3. Electrochemical test results for BiVO_4 (1), $\text{BiVO}_4/\text{Co(dca)}_2$ (2), and $\text{BiVO}_4/\text{Ni(dca)}_2$ (3), (a) LSV curves; (b) Mott-Schottky plots; (c) Nyquist plots with the inset shows the equivalent circuit (R_s : solution resistance, R_{ct} : charge transfer resistance, Q : constant phase element); (d) Proposed band structure of the BiVO_4 /electrolyte interface with or without the addition of M(dca)_2 . E_{fb} : flat band potential, Φ : work function, E_{vac} : vacuum energy. Dotted lines represent the conduction band (CB) or valence band (VB) in the M-S measurement. Dashed-dotted lines represent the CB or VB counterbalanced in the M-S measurement.

than Ni(dca)_2 .

To evaluate the effects of M(dca)_2 on the surface charge recombination of BiVO_4 during the photocatalytic water oxidation reaction, the charge separation efficiency and charge injection efficiency were measured for films of BiVO_4 , $\text{BiVO}_4/\text{Co(dca)}_2$, and $\text{BiVO}_4/\text{Ni(dca)}_2$ as photoanodes. The photocurrent density (J_{PEC}) can be expressed as:

$$J_{\text{PEC}} = J_{\text{lim}} \times \eta_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{inj}} \quad (4)$$

where J_{lim} is the theoretical photocurrent limit under 1 sun irradiation, which is estimated from the bandgap of the semiconductor, η_{abs} is the light absorption efficiency, η_{sep} is the charge separation efficiency, and η_{inj} is the charge injection efficiency at the semiconductor/electrolyte interface. If all absorbed photons are converted to photocurrent (i.e. $\eta_{\text{sep}} = 100\%$, $\eta_{\text{inj}} = 100\%$), then the unity converted photocurrent density J_{abs} is expressed as:

$$J_{\text{abs}} = J_{\text{lim}} \times \eta_{\text{abs}} \quad (5)$$

The J_{lim} and J_{abs} for BiVO_4 were 7.5 and 6.02 mA/cm^2 , respectively, according to reported data from the literature [23]. When Na_2SO_3 was introduced as the hole scavenger, the charge injection could be considered to be very fast, and η_{inj} could be considered to be 100%. Thus, the resulting photocurrent J_{sep} can be expressed as:

$$J_{\text{sep}} = J_{\text{lim}} \times \eta_{\text{abs}} \times \eta_{\text{sep}} \quad (6)$$

Thus, we obtain expressions for η_{sep} and η_{inj} :

$$\eta_{\text{inj}} = J_{\text{PEC}}/J_{\text{sep}} \quad (7)$$

$$\eta_{\text{sep}} = J_{\text{sep}}/J_{\text{abs}} \quad (8)$$

The charge separation efficiencies (η_{sep}) of the three samples were similar, as shown in Fig. 4(a). This indicated that the addition of M(dca)_2 did not greatly improve the bulk charge separation in BiVO_4 . This result in turn confirmed that M(dca)_2 as a WOC mainly affected the charge transfer behavior at the BiVO_4 /electrolyte interface. As shown in Fig. 4(b), the hole injection efficiency (η_{inj}) of BiVO_4 was only $\sim 10\%$ at 1.8 V vs. RHE. This indicated excessive charge recombination at the surface of pure BiVO_4 . A very slight enhancement in η_{inj} was observed for $\text{BiVO}_4/\text{Ni(dca)}_2$, which was evidenced in the slight increase in photocatalytic activity of the $\text{BiVO}_4/\text{Ni(dca)}_2$ system vs. pure BiVO_4 . In comparison, the η_{inj} of $\text{BiVO}_4/\text{Co(dca)}_2$ was much

Scheme 1. Proposed reaction pathway for photocatalytic water oxidation by the $\text{BiVO}_4/\text{Co(dca)}_2$ system.

higher than that of $\text{BiVO}_4/\text{Ni(dca)}_2$, reaching $\sim 40\%$ at 1.8 V vs. RHE. These results demonstrated that hole transfer at the BiVO_4 surface could be efficiently enhanced by adding Co(dca)_2 , which led to the much higher photocatalytic activity of the $\text{BiVO}_4/\text{Co(dca)}_2$ system.

3.4. Photocatalytic mechanism and charge carrier transfer processes

The WNA and radical coupling (RC) mechanisms are generally considered to be responsible for water oxidation catalyzed by molecular catalysts [24,25]. To determine a possible reaction mechanism for $\text{BiVO}_4/\text{Co(dca)}_2$, we carried out a series of photocatalytic tests. As shown in Fig. S15, the initial oxygen generation rate of $\text{BiVO}_4/\text{Co(dca)}_2$ exhibited a linear relationship with the Co(dca)_2 concentration. This indicated a WNA mechanism, in which hydroperoxo species from a two-electron oxidation are attacked by water to generate oxygen.

Based on the above analysis, a possible reaction pathway for the $\text{BiVO}_4/\text{Co(dca)}_2$ system can be proposed, and is shown in Scheme 1. Electrons and holes are typically generated in BiVO_4 under visible light irradiation. Photogenerated electrons at the conduction band (CB) were consumed by the $\text{S}_2\text{O}_8^{2-}$ sacrificial agent. Holes at the valence band (VB) could be transferred to M(dca)_2 adsorbed on BiVO_4 , to catalyze oxygen evolution. According to the reported Pourbaix diagram for Co(dca)_2 [12], the $[\text{Co}^{\text{II}}-\text{OH}_2]^{2+}/[\text{Co}^{\text{III}}-\text{OH}]^{2+}$ and $[\text{Co}^{\text{III}}-\text{OH}]^{2+}/[\text{Co}^{\text{IV}}-\text{OH}]^{3+}$ couples

Fig. 4. (a) Charge separation efficiencies and (b) charge injection efficiencies for BiVO_4 (1), $\text{BiVO}_4/\text{Co(dca)}_2$ (2), and $\text{BiVO}_4/\text{Ni(dca)}_2$ (3).

are responsible for the water oxidation reaction of Co(dca)_2 , and the potentials of $\text{Co}^{\text{II}}\text{--Co}^{\text{III}}$ and $\text{Co}^{\text{III}}\text{--Co}^{\text{IV}}$ were 1.56 and 1.87 V (vs. RHE) at neutral pH, respectively. Based on the WNA mechanism discussed above [24], a possible reaction pathway for $\text{BiVO}_4/\text{Co(dca)}_2$ is proposed, as shown in the right part of Scheme 1. The Co(dca)_2 ligated a water molecule to form $[\text{Co}^{\text{II}}\text{--OH}_2]^{2+}$, which was deprotonated to form $[\text{Co}^{\text{III}}\text{--OH}]^{2+}$. The generated $[\text{Co}^{\text{III}}\text{--OH}]^{2+}$ could be converted to $[\text{Co}^{\text{IV}}\text{--OH}]^{3+}$ by photogenerated holes to catalyze oxygen generation. Thus, the photocatalytic redox cycle of oxygen evolution was established.

4. Conclusions

We constructed a hybrid system with BiVO_4 as the light harvester and a transitional metal complex M(dca)_2 ($\text{M} = \text{Co}$, Ni) as the water oxidation catalyst, for photocatalytic oxygen evolution under visible light irradiation in fully aqueous solution using persulfate as a sacrificial agent. Introducing Co(dca)_2 and Ni(dca)_2 enhanced the photocatalytic performance of BiVO_4 . The oxygen evolution rates were 508.1 and 297.7 $\mu\text{mol}/(\text{h}\cdot\text{g})$ for the $\text{BiVO}_4/\text{Co(dca)}_2$ and $\text{BiVO}_4/\text{Ni(dca)}_2$ systems, respectively. The excellent photocatalytic improvement, especially for the $\text{BiVO}_4/\text{Co(dca)}_2$ system, was ascribed to the Co(dca)_2 -engineered BiVO_4 /electrolyte interface energetics and Co(dca)_2 -catalyzed surface water oxidation. These two factors led to a decreased energy barrier for hole transfer from the bulk to the surface, which promoted the water oxidation reaction kinetics. These findings provide a means for hybridizing a semiconductor and molecular catalyst for active and stable photocatalytic water oxidation.

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Graphical Abstract

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Photocatalytic water oxidation over BiVO_4 with interface energetics engineered by Co and Ni-metallated dicyanamides

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$\text{BiVO}_4/\text{M(dca)}_2$ ($\text{M} = \text{Co}$, Ni) hybrid systems were constructed and exhibited better photocatalytic activity in water oxidation than pure BiVO_4 , mainly owing to their efficient photogenerated hole transfer from BiVO_4 to M(dca)_2 .

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二氰胺钴、镍调控钒酸铋界面载流子传输及光催化产氧研究

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摘要: 光催化水分解反应是解决当前世界范围严峻的能源与环境问题的一种有效途径。光催化分解水过程可以分为产氢和产氧两个半反应。产氧反应过程复杂, 动力学缓慢, 是光催化分解水的限速步骤, 因此需要探索性能优异的水氧化催化剂(WOCs)来提高产氧半反应的效率。钒酸铋近年来被广泛研究并应用于光催化产氧领域。钒酸铋拥有合适的带宽(2.4 eV)以及较好的稳定性, 但是其应用受到其严重的电子空穴复合率、较低的电荷传输能力以及较差的反应动力学的限制。以往研究表明, 通过构建复合光催化体系可以有效促进光生电荷的分离与传输, 提高材料的光催化性能。因此, 我们提出构建新型的 $\text{BiVO}_4/\text{M}(\text{dca})_2$ ($\text{M} = \text{Co}, \text{Ni}$)复合体系, 其中, BiVO_4 作为光敏化剂, $\text{M}(\text{dca})_2$ 作为水氧化催化剂。

红外测试和紫外可见测试的结果表明, $\text{M}(\text{dca})_2$ 通过物理吸附的方式附着在 BiVO_4 表面, 形成 $\text{BiVO}_4/\text{M}(\text{dca})_2$ 复合光催化剂体系。复合体系的产氧活性相较于纯 BiVO_4 有明显的提升。光催化产氧测试结果表明, $\text{BiVO}_4/\text{Co}(\text{dca})_2$ 和 $\text{BiVO}_4/\text{Ni}(\text{dca})_2$ 复合体系的产氧活性分别可达508.1和297.7 $\mu\text{mol}/(\text{h} \cdot \text{g})$, 而纯 BiVO_4 的产氧活性只有252.2 $\mu\text{mol}/(\text{h} \cdot \text{g})$ 。进一步的稳定性测试结果表明, $\text{BiVO}_4/\text{Co}(\text{dca})_2$ 复合体系在30 h的测试过程中能够保持稳定的活性。ICP-MS和XPS的表征结果证明了催化过程中分子催化剂良好的稳定性, 排除了反应过程中生成氧化物进而促进产氧活性的可能。对该复合体系的一系列电化学表征证明, $\text{M}(\text{dca})_2$ 有效改善了 BiVO_4 电解液界面的电荷传输性能, 从而促进了光催化产氧性能。其中, 莫特-肖特基测试表明, $\text{M}(\text{dca})_2$ 的加入增大了能带弯曲, 提高了空穴传递的驱动力, 阻抗谱的测试证明了复合体系具有较低的界面电阻, 有利于载流子的迁移。

通过对复合体系光生载流子分离和注入效率的表征, 可以证明, 在 $\text{BiVO}_4/\text{M}(\text{dca})_2$ 复合体系中, 光生空穴能够有效地从 BiVO_4 迁移到 $\text{M}(\text{dca})_2$, 进而参与光催化产氧反应并且光催化活性有明显的提升。其中, 由于 $\text{Co}(\text{dca})_2$ 能够更加有效地改善 BiVO_4 /电解质的水氧化反应动力学过程, 其活性显著优于 $\text{BiVO}_4/\text{Ni}(\text{dca})_2$ 体系和纯 BiVO_4 。此外, 基于实验结果和各项表征, 我们进一步提出了 $\text{BiVO}_4/\text{Co}(\text{dca})_2$ 光催化产氧反应的反应机理: 光照条件下, BiVO_4 中电子跃迁至导带, 进而被牺牲剂消耗, 而价带上的空穴则传递至分子催化剂进行化学反应, 其中, 分子催化的反应机理遵循水亲核攻击的模型。

关键词: 金属复合物; 钒酸铋; 水氧化; 光催化; 界面动力学

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