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Article

Blocking backward reaction on hydrogen evolution cocatalyst in a photosystem II hybrid Z-scheme water splitting system

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ABSTRACT

Photocatalytic Z-scheme water splitting is considered as a promising approach to produce solar hydrogen. However, the forward hydrogen production reaction is often impeded by backward reactions. In the present study, in a photosystem II-integrated hybrid Z-scheme water splitting system, the backward hydrogen oxidation reaction was significantly suppressed by loading a PtCrO_x cocatalyst on a ZrO₂/TaON photocatalyst. Due to the weak chemisorption and activation of molecular hydrogen on PtCrO_x, where Pt is stabilized in the oxidized forms, Pt^{II} and Pt^{IV}, hydrogen oxidation is inhibited. However, it is remarkably well-catalyzed by the metallic Pt cocatalyst, thereby rapidly consuming the produced hydrogen. This work describes an approach to inhibit the backward reaction in the photosystem II-integrated hybrid Z-scheme water splitting system using Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ redox couple as an electron shuttle.

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1. Introduction

Z-scheme electron transfer mode in natural photosynthesis is well-known for combining two photosynthetic systems and separating the oxidation and reduction reactions spatially to avoid undesirable charge recombination [1–5]. Learning from nature's Z-scheme, the artificial Z-scheme solar water splitting system, combining two photocatalysts responsible for the independent oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) through an electron transfer assisted

by electron mediators, has been extensively studied for the solar hydrogen production [6–9]. As the redox potential of the shuttle mediator is located between the conduction band (CB) of the OER photocatalyst and the valence band (VB) of the HER photocatalyst, the forward electron transfer reaction is easily hindered by the redox reactions (so-called “backward reactions”) of the shuttle mediators, resulting in a lower efficiency of the solar-to-hydrogen conversion [10–14]. Avoiding the backward reaction therefore becomes one of the crucial issues in constructing an efficient Z-scheme water splitting system. By

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making channels for gas production and diffusion [10], constructing selective cocatalysts [11], and modifying the surface of photocatalyst [13], the backward reactions are inhibited to some extent; however, such approaches are still limited.

The redox couple $\text{Fe}(\text{CN})_6^{4-/3-}$ is an efficient electron mediator frequently employed in photosystem II (PSII)-integrated biotic-abiotic hybrid Z-scheme water splitting systems, which have received much attention owing to the application of the excellent natural water oxidation enzyme (PSII) in solar energy conversion, and also for the research on the basic scientific issues in water splitting [15–17]. $\text{Fe}(\text{CN})_6^{3-}$, as an efficient exogenous electron acceptor of PSII, is capable of extracting the photogenerated electrons from the reducing side of PSII during the light-driven water oxidation process without triggering any undesirable side reactions, and the produced $\text{Fe}(\text{CN})_6^{4-}$ then transfers the electrons to the artificial component for water reduction. However, the backward reactions caused by the shuttle mediators have also been encountered in the $\text{Fe}(\text{CN})_6^{4-/3-}$ -mediated biotic-abiotic hybrid systems. Even though the OER is almost unaffected owing to the highly selective active sites of PSII for water oxidation and $\text{Fe}(\text{CN})_6^{3-}$ reduction [18–20], the inhibition of HER on the semiconductor photocatalyst happens easily, which limits the usability of the combination of PSII and artificial materials for solar water splitting.

In the present study, ZrO_2/TaON was employed as the HER photocatalyst to construct a PSII- ZrO_2/TaON hybrid Z-scheme water splitting system, and PtCrO_x particles were loaded on ZrO_2/TaON as HER cocatalysts. We found that the backward reaction of hydrogen oxidation by $\text{Fe}(\text{CN})_6^{3-}$ can be catalyzed and accelerated remarkably on the metallic Pt cocatalyst; however, it was not catalyzed on the oxide PtCrO_x due to a weak adsorption and activation of H_2 . The higher oxidation states of Pt^{II} and Pt^{IV} in PtCrO_x were well-sustained during the HER, and might be stabilized by the coordination of the surrounding CrO_x species that protect Pt^{II} and Pt^{IV} from being reduced into metallic Pt even on aggregation of the photogenerated electrons. Therefore, a long-term hydrogen evolution took place on PtCrO_x -loaded ZrO_2/TaON , with $\text{Fe}(\text{CN})_6^{4-}$ as the electron donor. Finally, Z-scheme overall water splitting was achieved successfully through the $\text{Fe}(\text{CN})_6^{3-/4-}$ -assisted electron transfer from PSII to PtCrO_x -loaded ZrO_2/TaON . This work paves a new way to inhibit the backward reaction caused by the electron mediator, $\text{Fe}(\text{CN})_6^{3-/4-}$, for an efficient electron transfer between PSII and the artificial photocatalyst in the Z-scheme water splitting system.

2. Experimental

2.1. Preparation of ZrO_2/TaON

ZrO_2/TaON was synthesized as reported previously [21]. Typically, Ta_2O_5 and $\text{ZrO}(\text{NO}_3)_2$ were mixed with a 0.1 molar ratio of Zr/Ta in a small amount of methanol, dried at 70 °C for 1 h, and subsequently heated in air at 800 °C for 2 h to yield a $\text{ZrO}_2/\text{Ta}_2\text{O}_5$ composite. ZrO_2/TaON was obtained by nitridation of the as-prepared $\text{ZrO}_2/\text{Ta}_2\text{O}_5$ powder at 900 °C under a flow

of NH_3 (20 mL min⁻¹) for 20 h.

2.2. Photodeposition of cocatalysts

Metallic Pt particles (1 wt% Pt) and the mixed oxide, PtCrO_x (1 wt% Pt, Cr: according to the different Cr/Pt mass ratios), were loaded on the surface of ZrO_2/TaON by photodeposition. ZrO_2/TaON (0.2 g) was dispersed in a 100 mL aqueous solution containing 20 vol% methanol as the electron donor, to which the calculated volume of concentrated $(\text{NH}_4)_2\text{PtCl}_6$ and K_2CrO_4 solution was added as precursors. The photodeposition process was carried out under the full-spectrum irradiation of a Xenon lamp for 6 h at 15 °C in a Pyrex-top irradiation type reaction vessel connected to a closed gas circulation system. After photodeposition, the resultant powder was washed with distilled water and dried overnight at 65 °C in an oven.

2.3. Preparation of electrodes

$\text{ZrO}_2/\text{TaON}/\text{FTO}$ electrodes were prepared by the electrophoresis method. ZrO_2/TaON powder (20 mg) was dispersed in 25 mL acetone containing 15 mg I_2 under an ultrasonic treatment for 10 min. FTO plates (1 cm × 2 cm) were used as substrates after they were ultrasonically washed in acetone, isopropanol, ethanol, and water successively. Two FTO plates were connected to a two-electrode system with their conductive layers face to face, and the as-prepared $\text{ZrO}_2/\text{TaON}/\text{I}_2$ solution was used as the electrolyte. A pulsing voltage of 20 V was applied 10 times, each time lasting for 10 s with an interval of 10 s, upon which, ZrO_2/TaON powder got deposited onto the FTO anode. The electrode was dried at 65 °C in an oven for 2 h. The cocatalysts, Pt and PtCrO_x , were then photo-deposited onto the $\text{ZrO}_2/\text{TaON}/\text{FTO}$ surface. First, the $\text{ZrO}_2/\text{TaON}/\text{FTO}$ plate was placed at the bottom of a beaker and 25 mL $(\text{NH}_4)_2\text{PtCl}_6$ -methanol mixed aqueous solution, with the mass of the Pt element being 0.25 mg, or 25 mL $(\text{NH}_4)_2\text{PtCl}_6/\text{K}_2\text{CrO}_4$ -methanol mixed aqueous solution, with the mass of the Pt and Cr elements being 0.25 and 0.125 mg, respectively, was added for the respective deposition of Pt or PtCrO_x . The volume proportion of methanol in the mixed solutions is 20%. Photodeposition was carried out under the light of a Xenon lamp ($\lambda \geq 420$ nm) for 4 h at 15 °C. The electrode was carefully washed with distilled water and then dried at 65 °C in an oven for 2 h.

2.4. Preparation of the PSII core complex

PSII core complex was isolated from the thermophilic cyanobacterium *T. vulcanus* as described previously [22,23], and finally dispersed in an MES solution (30 mM MES, 20 mM NaCl, 3 mM CaCl_2 , pH = 6.0). The concentration of Chl *a* (denoted as $[\text{Chl } a]$) in the PSII sample was obtained according to the equation $[\text{Chl } a] = A_{665} \times 13.4 \times \text{dilution factor}$, in which A_{665} is the UV-Vis absorbance of the sample at 665 nm in methanol [24]. $[\text{Chl } a]$ was employed for calculating the quantity of the PSII centers by using 35 Chl *a*/PSII [25]. Steady-state O_2 evolution of the prepared PSII sample was measured with a Clark-type

electrode at 30 °C with 0.5 mM phenyl-*p*-benzoquinone and 0.5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ as the electron acceptors, and the O_2 evolution rate exceeded $3000 \mu\text{mol O}_2 (\text{mg of Chl})^{-1} \text{h}^{-1}$ under a saturated illumination.

2.5. Characterization of photocatalysts

Morphologies of the cocatalysts were examined by high resolution transmission electron microscopy (HR-TEM, JEOL JEM-2000EX) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM, JEM-ARM200F). Electronic states of the cocatalysts were examined by X-ray photoelectron spectroscopy (XPS) measurements on a VG ESCALAB MK2 spectroscope under a monochromatized Al K α excitation.

2.6. Measurements of photocatalytic reactions and dark backward reactions

For the photocatalytic half reactions and the overall water splitting reactions, a homemade airtight vessel with a top quartz window was utilized. Before irradiation, the vessel containing the reaction solution was connected to a vacuum/inert gas line to replace the air in the headspace with the Ar gas, and then placed in a thermostatic water bath with the temperature kept at 25 °C for the subsequent photocatalytic reaction. The gas produced during the reaction was monitored by injecting the headspace samples into a gas chromatography instrument (Agilent GC 7890, USA, 5A zeolite column and Ar carrier gas).

The dark backward reaction between hydrogen and $\text{Fe}(\text{CN})_6^{3-}$ was carried out in the same homemade airtight vessel. For each reaction, either no photocatalyst or 40 mg of it was dispersed in 20 mL of the PBS buffer (pH = 6) containing 2 mM $\text{Fe}(\text{CN})_6^{3-}$. The vessel containing the reaction solution was filled with Ar gas and sealed when quantitative hydrogen gas was injected in for the backward reaction; however, it was not sealed when the reaction solution was bubbled with hydrogen gas.

2.7. Electrochemical measurements

The electrochemical performances of the $\text{ZrO}_2/\text{TaON}/\text{FTO}$ and the cocatalyst-loaded $\text{ZrO}_2/\text{TaON}/\text{FTO}$ electrodes were measured in a three-electrode setup, where Pt electrode and the saturated calomel electrode (SCE) were employed as the counter and reference electrodes, respectively. The PBS buffer (100 mM phosphate, 15 mM NaCl, pH = 6) containing 5 mM $\text{Fe}(\text{CN})_6^{3-}$ was used as the electrolyte. Linear sweep voltammetry (LSV) was carried out in the range of 0.2 to -1.2 V vs. SCE at a scan rate of 50 mV s^{-1} on a CHI 760D electrochemical workstation (Shanghai Chenhua Instruments, China). Electrochemical impedance spectroscopy (EIS) was carried out at the potential of -0.2 V vs. SCE , with the AC potential frequency ranging from 0.1 Hz to 200 kHz on a PARSTAT 2273 workstation (Princeton Applied Research).

3. Results and discussion

3.1. Photocatalytic activities for hydrogen evolution

ZrO_2 -modified TaON (ZrO_2/TaON), with the band gap of 2.5 eV, has been previously demonstrated as a good photocatalyst for hydrogen production [26–28]. In the present study, ZrO_2/TaON was employed to collaborate with the natural PSII core complex to construct a bio-artificial Z-scheme water splitting system. The redox mediator couple $\text{Fe}(\text{CN})_6^{4-/3-}$ was used to transfer the electrons from PSII to the semiconductor photocatalyst. Pt and PtCrO_x particles with different Cr/Pt mass ratios were loaded on ZrO_2/TaON as cocatalysts through the photodeposition method described above. Fig. 1(a) depicts the time courses of hydrogen evolution on the cocatalyst-loaded ZrO_2/TaON samples. Hydrogen evolution on the Pt-loaded sample was negligible, whereas the activities increased notably on the PtCrO_x -loaded samples, reaching a maximum value at a Cr/Pt ratio of 0.5. Furthermore, the PtCrO_x (Cr/Pt = 0.5)-loaded sample was able to display a long-term hydrogen evolution for 9 h until the electron donor, $\text{Fe}(\text{CN})_6^{4-}$, was consumed com-

Fig. 1. Hydrogen evolution performances of cocatalyst-loaded ZrO_2/TaON . (a) Time course of hydrogen evolution on cocatalyst-loaded ZrO_2/TaON with different Cr/Pt mass ratios; (b) Long-term hydrogen evolution on $\text{PtCrO}_x(0.5)\text{-ZrO}_2/\text{TaON}$. For each reaction, 20 mg photocatalyst was dispersed in 20 mL PBS buffer (pH = 6) containing 10 mM $\text{Fe}(\text{CN})_6^{4-}$ as the electron donor. Light source: 300 W Xenon lamp ($\lambda \geq 420 \text{ nm}$).

pletely (Fig. 1(b)). As a control experiment, when only CrO_x was loaded on ZrO_2/TaON without addition of the Pt precursor during photodeposition, no hydrogen was detected in the HER with $\text{Fe}(\text{CN})_6^{4-}$ as the donor on this Pt-absent sample, which indicates that the Pt species in PtCrO_x is indispensable for hydrogen production.

3.2. Composition and morphology of the cocatalysts

To investigate the relationship between the photocatalytic activity and the composition and structure of the cocatalysts, the electronic states and morphologies of the Pt and Cr species on ZrO_2/TaON were characterized by XPS and HR-TEM. Fig. 2(a) shows the XPS spectra of Pt 4f of the as-prepared samples with different Cr/Pt ratios. For the Pt-only loaded sample (Cr/Pt = 0), the spectrum is mainly attributed to the Pt^0 species at the binding energies of ca. 70.2 ($4f_{7/2}$) and 73.6 eV ($4f_{5/2}$), and the small fitted peaks centered at ca. 72.3 ($4f_{7/2}$) and 75.7 eV ($4f_{5/2}$) are attributed to the Pt^{II} species. With the addition of the Cr species, the XPS peaks due to Pt^{II} and Pt^{IV} (ca. 74.5 eV for $4f_{7/2}$, 77.9 eV for $4f_{5/2}$) became dominant, whereas those due to Pt^0 decreased remarkably. There is a gradual change in the spectra with the increasing Cr/Pt ratio; the Pt^0 peaks at the low binding energy disappear, whereas the Pt^{IV} peaks at the higher binding energy grow up, until reaching a stable proportion of Pt^{II} and Pt^{IV} after the Cr/Pt ratio is higher than 0.5. The Cr 2p spectra in all of the PtCrO_x -loaded samples show the same peaks at the binding energies of ca. 576.5 and 586.4 eV, corresponding to the $2p_{3/2}$ and $2p_{1/2}$ electrons, respectively, of the Cr_2O_3 species (Fig. S1). Accordingly, it could be speculated that the chemical state of Pt was regulated by the CrO_x species during the photodeposition process, and the HER activity of $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$ is sensitive to the chemical state of Pt.

XPS spectra after the HER with $\text{Fe}(\text{CN})_6^{4-}$ as the electron donor were also recorded. For $\text{Pt-ZrO}_2/\text{TaON}$, the proportion of

the Pt peak at the high binding energy increased slightly after the photoreaction (Fig. S2(a)), probably due to the adsorption of hexacyanoferrate on Pt through the highly polar CN^- , as also found by some researchers that a surface species containing Pt-CN was formed after the redox reaction of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ on the Pt electrode [29–31]. For $\text{PtCrO}_x(0.5)\text{-ZrO}_2/\text{TaON}$, the electronic states of Pt and Cr were well-sustained after the photoreaction (Fig. S2(b)), indicating the stable configuration of PtCrO_x during the proton reduction process, which is consistent with the stable HER performance. It is well-known that the photogenerated electrons aggregate on the HER cocatalyst for proton production, but the high oxidation states of Pt^{II} and Pt^{IV} in the PtCrO_x cocatalyst could still be well-sustained without being reduced into metallic Pt during the HER process. The coordination function of the CrO_x species to Pt^{II} and Pt^{IV} might contribute to the good stability of PtCrO_x .

Morphologies of the cocatalysts were observed by HR-TEM. In the absence of Cr, metallic Pt particles with a diameter of ~5 nm and a lattice fringe of Pt (111) were observed on the ZrO_2/TaON surface (Fig. 2(b)). Upon addition of Cr, amorphous PtCrO_x clusters without any distinct lattice fringe formed on the substrate, with a size of ~2 nm, much smaller than the Pt particles (Fig. S3). It was noted that on the sample with a low Cr/Pt ratio of 0.2, a spot of the metallic Pt particles could still be found (inset of Fig. S3(a)), in agreement with the small proportion of the Pt^0 XPS peaks. This suggests that during the photodeposition process, the redundant Pt precursor that did not form PtCrO_x was finally reduced into metallic Pt particles. Considering the limitation of resolution of HR-TEM, the small PtCrO_x particles on $\text{PtCrO}_x(0.5)\text{-ZrO}_2/\text{TaON}$ were further confirmed by HAADF-STEM, and small bright dots were found to distribute in the PtCrO_x clusters, which are considered as the Pt species with a heavy atomic weight (Fig. 2(c)). Compared with the metallic Pt particles, the PtCrO_x clusters are able to provide more active sites for the proton reduction due to the larger surface area of smaller particles.

Fig. 2. Valence states and morphologies of the cocatalysts. (a) XPS spectra of Pt 4f of cocatalysts with different Cr/Pt mass ratios; (b) HR-TEM image of $\text{Pt-ZrO}_2/\text{TaON}$; (c) HAADF-STEM image of $\text{PtCrO}_x(0.5)\text{-ZrO}_2/\text{TaON}$.

3.3. Backward reactions on different cocatalysts

When $\text{Fe}(\text{CN})_6^{4-}$ acts as an electron donor in the HER, hydrogen evolution is accompanied by the production of $\text{Fe}(\text{CN})_6^{3-}$. The forward activity might be hindered by the backward reactions shown in Eqs. (1) and (2).

It can be noted that both the backward reactions involve the reduction of $\text{Fe}(\text{CN})_6^{3-}$ and ultimately affect hydrogen production. In the case of Eq. (1), $\text{Fe}(\text{CN})_6^{3-}$ competitively reacts with the photogenerated electrons which are expected to reduce protons for hydrogen production, while in the case of Eq. (2), the produced hydrogen gas might be consumed due to hydrogen oxidation by $\text{Fe}(\text{CN})_6^{3-}$.

Some control experiments were carried out to investigate the backward reactions in the HER. Hydrogen evolution on $\text{Pt-ZrO}_2/\text{TaON}$ with methanol as an electron donor was measured both in the absence and presence of $\text{Fe}(\text{CN})_6^{3-}$. As shown in Fig. S4(a), the activity declined by seven times after adding 1

mM $\text{Fe}(\text{CN})_6^{3-}$, and $\text{Fe}(\text{CN})_6^{3-}$ was reduced to $\text{Fe}(\text{CN})_6^{4-}$, as indicated by the UV-Vis absorption spectrum (Fig. S4(b)). Subsequently, the decline in hydrogen evolution on $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$ as a function of $\text{Fe}(\text{CN})_6^{3-}$ concentration was investigated. To avoid light being blocked by the $\text{Fe}(\text{CN})_6^{3-}$ solution, the lamp was equipped with a long-pass filter ($\lambda \geq 480$ nm). As shown in Fig. S5, among the three samples with different Cr/Pt mass ratios (0.2, 0.35, and 0.5), $\text{PtCrO}_x(0.5)\text{-ZrO}_2/\text{TaON}$ showed the slowest activity decline along with the increasing $\text{Fe}(\text{CN})_6^{3-}$ concentration, while hydrogen production on $\text{PtCrO}_x(0.2)\text{-ZrO}_2/\text{TaON}$, which contained a spot of the metallic Pt cocatalyst, was almost quenched in 5 mM $\text{Fe}(\text{CN})_6^{3-}$. These results indicate that the presence of $\text{Fe}(\text{CN})_6^{3-}$ indeed lowers the hydrogen production activity, especially for the photocatalyst loaded with metallic Pt. $\text{PtCrO}_x(0.5)\text{-ZrO}_2/\text{TaON}$ containing only the Pt^{II} and Pt^{IV} species shows the best capability to block the backward reaction.

Furthermore, the redox reaction between hydrogen and $\text{Fe}(\text{CN})_6^{3-}$ was investigated in the dark in the presence and absence of photocatalysts. The corresponding changes in the amount of hydrogen and the $\text{Fe}(\text{CN})_6^{3-}$ concentration are shown in Fig. 3(a) and Fig. S6, respectively. It was found that both, the amount of hydrogen and the concentration of $\text{Fe}(\text{CN})_6^{3-}$, remained unchanged if there was no photocatalyst in the solution, indicating that the redox reaction did not take place. Even in the presence of $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$ ($\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$ hereafter represents the sample with a Cr/Pt mass ratio of 0.5, unless otherwise noted), the redox reaction did not take place. However, in the presence of $\text{Pt-ZrO}_2/\text{TaON}$, the amount of hydrogen decreased obviously and $\text{Fe}(\text{CN})_6^{3-}$ was transformed into $\text{Fe}(\text{CN})_6^{4-}$. To ensure sufficient contact between hydrogen, $\text{Fe}(\text{CN})_6^{3-}$, and the photocatalyst, hydrogen was bubbled into the reaction solution. Similarly, as shown in Fig. 3(b), $\text{Fe}(\text{CN})_6^{3-}$ remained unchanged in the absence of the photocatalyst or in the presence of $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$, whereas almost all $\text{Fe}(\text{CN})_6^{3-}$ in the solution was reduced in 15 min in the presence of $\text{Pt-ZrO}_2/\text{TaON}$. These results indicate that the kinetically controlled backward reaction of hydrogen oxidation by $\text{Fe}(\text{CN})_6^{3-}$ was remarkably

accelerated via the catalytic action of the metallic Pt particles, resulting in the remarkable hydrogen loss in the HER. On the contrary, PtCrO_x oxide did not catalyze this backward reaction; thus, hydrogen could evolve even in the presence of $\text{Fe}(\text{CN})_6^{3-}$.

Subsequently, surface interactions between the cocatalysts (Pt and PtCrO_x) and the reactants ($\text{Fe}(\text{CN})_6^{3-}$ and hydrogen) were investigated to understand their different catalytic behavior. Zeta potentials of $\text{Pt-ZrO}_2/\text{TaON}$ and $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$ in the reaction buffer solution (PBS buffer, pH = 6) were found to be about -24 and -19 mV, respectively, suggesting that there are no electrostatic attractions between $\text{Fe}(\text{CN})_6^{3-}$ ions and the electronegative photocatalyst surface. The adsorption tests showed that there is no chemical or physical adsorption of $\text{Fe}(\text{CN})_6^{3-}$ on the surface of both $\text{Pt-ZrO}_2/\text{TaON}$ and $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$. Moreover, it has been well-convicted that hydrogen molecules can be chemisorbed on the metallic Pt surface strongly and dissociate into highly active atomic H^* [32–35]. In contrast, the adsorption and activation of hydrogen molecules on the metal oxide surface was reported to be much weaker [35]. Therefore, it is reasonable to speculate that the difference in the catalytic behavior of Pt and PtCrO_x in hydrogen oxidation by $\text{Fe}(\text{CN})_6^{3-}$ is mainly due to the different adsorption and activation performances of hydrogen on their surfaces.

3.4. Electrochemical reduction performances of different cocatalysts

To obtain further insights into the function of cocatalysts on the forward and backward reactions, the electrochemical behavior of proton and $\text{Fe}(\text{CN})_6^{3-}$ reduction was measured for ZrO_2/TaON , $\text{Pt-ZrO}_2/\text{TaON}$, and $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$ -covered FTO electrodes. In Fig. 4(a), the LSV curves show that the reduction peaks of $\text{Fe}(\text{CN})_6^{3-}$ emerge at more positive potentials than those of hydrogen evolution for all the samples. The Pt-loaded sample exhibits the highest hydrogen evolution current, but the most positive onset potential for $\text{Fe}(\text{CN})_6^{3-}$ reduction. For the PtCrO_x -loaded sample, the proton reduction performance is not so good, but it possesses the most negative

Fig. 3. Backward reaction performances between hydrogen and $\text{Fe}(\text{CN})_6^{3-}$. (a) Decline percentage of 7 μmol hydrogen in the dark reaction in 2 mM $\text{Fe}(\text{CN})_6^{3-}$ with different photocatalysts; (b) Decline percentage of 2 mM $\text{Fe}(\text{CN})_6^{3-}$ in the dark reaction under H_2 bubbling with different photocatalysts.

Fig. 4. Electrochemical performances of cocatalyst-loaded ZrO₂/TaON electrodes. (a) LSV curves for the reduction of both Fe(CN)₆³⁻ and proton; (b) EIS performances of the electrodes in the electrochemical Fe(CN)₆³⁻ reduction at -0.2 V (vs. SCE).

onset potential for Fe(CN)₆³⁻ reduction. To further clarify the charge transfer of Fe(CN)₆³⁻ reduction at the solution-electrode interface, EIS was performed at an applied potential of -0.2 V vs. SCE, which is negative enough for Fe(CN)₆³⁻ reduction, but not for proton reduction. The Nyquist curves are shown in Fig. 4(b) and the values of the charge transfer resistance (*R*_{ct}) are given in Table S1. The order of *R*_{ct} (PtCrO_x > bare > Pt) also confirms the favorable kinetics of Fe(CN)₆³⁻ reduction on metallic Pt and the unfavorable kinetics of Fe(CN)₆³⁻ reduction on PtCrO_x. As a consequence, even though PtCrO_x is not as good as Pt in catalyzing proton reduction, it conducts the slowest Fe(CN)₆³⁻ reduction, which is more important for achieving sustainable hydrogen evolution.

3.5. Overall water splitting in PSII-integrated hybrid Z-scheme system

Finally, a PSII-integrated hybrid Z-scheme system was constructed for the overall water splitting reaction with PtCrO_x-ZrO₂/TaON as the HER photocatalyst and Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ as the electron mediator. The water oxidation rate of PSII has been demonstrated to be greatly dependent on the concentration of the exogenous electron accep-

tor, Fe(CN)₆³⁻, in the previous work [16]. Benefiting from the high selectivity of the Mn₄CaO₅ cluster and Q_B pocket of PSII for water oxidation and Fe(CN)₆³⁻ reduction, no backward reactions or other side reactions were observed.

During the overall water splitting process, the initial H₂ and O₂ evolution rates are kinetically controlled and strongly dependent on the concentration of the electron donor or acceptor. As shown in Fig. 5(a), when 100% Fe(CN)₆³⁻ (10 mM Fe(CN)₆³⁻) was used as the initial electron mediator with no Fe(CN)₆⁴⁻ supplied, O₂ evolution by PSII is considerably high, whereas H₂ evolution by PtCrO_x-ZrO₂/TaON is much less, which is comprehensible as the concentration of transformed Fe(CN)₆⁴⁻ is definitely low. On the contrary, O₂ is much more slowly produced than H₂ when 100% Fe(CN)₆⁴⁻ was used initially. It is predictable that the stoichiometric ratio of H₂ to O₂ would approach 2:1 at some point, along with the concentration change of the mediator ions during the water splitting process. However, taking into consideration the gradual photodegradation of PSII, it is better to offer an optimal concentration of the shuttle ions at the initial stage for the stoichiometric water splitting. To simulate the mutual transformation of Fe(CN)₆^{4-/3-} during the water splitting process, the total concentration of the shuttle ions was fixed at 10 mM, and their

Fig. 5. (a) Overall water splitting activities dependent on the percentage of Fe(CN)₆⁴⁻. The total concentration of Fe(CN)₆³⁻ and Fe(CN)₆⁴⁻ is 10 mM. (b) Time course of overall water splitting activity at 80% Fe(CN)₆⁴⁻ (8 mM Fe(CN)₆⁴⁻, 2 mM Fe(CN)₆³⁻). 20 mg Cr/Pt (0.5)-ZrO₂/TaON and 150 μg Chl of PSII were dispersed in 20 ml PBS buffer (pH = 6). Temperature: 25 °C. Light source: AM 1.5G.

relative proportions were modulated to several possible points with the percentage of $\text{Fe}(\text{CN})_6^{4-}$ being 80%, 70%, and 20%. As expected, hydrogen evolution decreased and oxygen evolution increased regularly with the decline of the $\text{Fe}(\text{CN})_6^{4-}$ proportion, and the stoichiometric splitting of water into ca. 20 $\mu\text{mol H}_2 \text{ h}^{-1}$ and 10 $\mu\text{mol O}_2 \text{ h}^{-1}$ was achieved at 8 mM $\text{Fe}(\text{CN})_6^{4-}$ and 2 mM $\text{Fe}(\text{CN})_6^{3-}$. The corresponding time courses of gas evolution are shown in Fig. 5(b).

3.6. Proposed mechanisms for the blockage of the backward reactions

In this PSII- $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$ Z-scheme system, due to the original favorable water oxidation performance of PSII, the key point to realize a successful overall water splitting in the presence of both $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ lies in the improved HER on $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$ without any major backward reactions. According to the results and analyses above, the mechanisms of the generation and suppression of $\text{Fe}(\text{CN})_6^{3-}$ reduction involved in the backward reactions on metallic Pt and oxide PtCrO_x cocatalysts can be proposed reasonably. Owing to the negligible interactions between $\text{Fe}(\text{CN})_6^{3-}$ and the surfaces of the two photocatalysts, hydrogen oxidation by $\text{Fe}(\text{CN})_6^{3-}$ (Eq. (2)) is considered as the major backward reaction to block the forward HER. As shown in Fig. 6(a), metallic Pt loaded on ZrO_2/TaON not only catalyzes proton reduction to produce hydrogen, but also catalyzes the backward reaction that results in hydrogen oxidation by $\text{Fe}(\text{CN})_6^{3-}$ due to the activation of adsorbed hydrogen. Therefore, molecular H_2 and H^* interme-

diate can be oxidized by $\text{Fe}(\text{CN})_6^{3-}$ rapidly, with a negligible amount of hydrogen gas being evolved. However, for the $\text{PtCrO}_x\text{-loaded ZrO}_2/\text{TaON}$ sample, hydrogen adsorption on PtCrO_x is much weaker so that the backward reaction would not be catalyzed (Fig. 6(b)). Although the proton reduction on PtCrO_x is not so efficient as that on metallic Pt, the net hydrogen production performance on $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$ becomes much better than that on $\text{Pt-ZrO}_2/\text{TaON}$ due to the relatively better suppressed backward reactions. In addition, stable PtCrO_x during the photocatalytic reduction process with no reduction of the Pt^{II} and Pt^{IV} species helps to maintain sustainable hydrogen production. As a consequence, Z-scheme overall water splitting into H_2 and O_2 can be realized by combining PSII with $\text{PtCrO}_x\text{-ZrO}_2/\text{TaON}$ via the $\text{Fe}(\text{CN})_6^{3-/4-}$ -mediated forward electron transfer (Fig. 6(c)).

4. Conclusions

In summary, the present work has demonstrated the suppression of the backward hydrogen oxidation reactions caused by the electron shuttle, $\text{Fe}(\text{CN})_6^{3-}$, in a PSII- ZrO_2/TaON hybrid system for Z-scheme water splitting. Serious hydrogen oxidation by $\text{Fe}(\text{CN})_6^{3-}$ took place under the catalysis of the metallic Pt cocatalyst loaded on ZrO_2/TaON and blocked the forward HER. By introducing the oxide PtCrO_x which contains stable Pt^{II} and Pt^{IV} species to replace metallic Pt as the cocatalyst, hydrogen oxidation was greatly suppressed owing to the lack of adsorption and activation of hydrogen on PtCrO_x , thus leading to a remarkable enhancement in the hydrogen producing activity.

Fig. 6. Schematic representation of the generation and suppression of the backward reaction on Pt-loaded ZrO_2/TaON (a), $\text{PtCrO}_x\text{-loaded ZrO}_2/\text{TaON}$ (b), and the PSII- ZrO_2/TaON hybrid Z-scheme (c) overall water splitting process.

Graphical Abstract

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Blocking backward reaction on hydrogen evolution cocatalyst in a photosystem II hybrid Z-scheme water splitting system

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Hydrogen evolution cocatalyst, PtCrO_x, is loaded on ZrO₂/TaON to block the backward hydrogen oxidation reaction by Fe(CN)₆³⁻, promoting the overall water splitting in a photosystem II-ZrO₂/TaON hybrid Z-scheme water splitting system.

This work provides new opportunities for the inhibition of the backward reaction when using Fe(CN)₆^{3-/4-} as the electron shuttle to build the PSII-semiconductor hybrid water splitting system.

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光系统II杂化Z型水分解体系中产氢助催化剂上逆反应的抑制

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摘要: 光催化Z型水分解反应有望发展成为一种生产太阳氢能的有效方法. 将具有优异水氧化性能的自然光系统II与人工半导体产氢材料进行耦合, 以构建生物-人工杂化光催化Z型水分解反应体系, 对于深入理解自然光合作用原理和促进人工太阳能转化具有重要意义. 由于 $\text{Fe}(\text{CN})_6^{3-}$ 可从光系统II接受电子, 因此氧化还原电对 $\text{Fe}(\text{CN})_6^{3-/4-}$ 成为研究光系统II基杂化Z型水分解体系时常用的电子传递. 然而, 在该Z型水分解反应中, 正向的产氢反应经常受到由 $\text{Fe}(\text{CN})_6^{3-}$ 引起的逆反应的阻碍, 致使水分解过程中产氢产氧失衡, 不能实现有效的全分解水反应. 本文通过在光系统II杂化Z型水分解体系的人工光催化剂 ZrO_2/TaON 上沉积产氢助催化剂 PtCrO_x , 有效抑制了逆反应的发生, 从而使体系实现了全分解水反应.

实验发现, 在光催化剂 ZrO_2/TaON 上沉积金属Pt作为产氢助催化剂时, 以 $\text{Fe}(\text{CN})_6^{4-}$ 为电子供体的光催化产氢半反应基本没有产氢活性, 而当沉积氧化物 PtCrO_x 作为产氢助催化剂时, 产氢半反应活性可提高至 $\sim 35 \mu\text{mol h}^{-1}$. 进一步研究发现, 这种产氢活性的差异主要是由于两种不同助催化剂对于 $\text{Fe}(\text{CN})_6^{3-}$ 引起的氢气氧化逆反应的催化行为不同. 金属Pt表面对于氢气具有吸附和活化作用, 光催化反应中产生的氢气和 $\text{Fe}(\text{CN})_6^{3-}$ 在Pt- ZrO_2/TaON 催化作用下发生快速的氧化还原逆反应; 而由于 PtCrO_x 表面对氢气的吸附和活化作用较弱, 上述氢气氧化的逆反应在 PtCrO_x - ZrO_2/TaON 存在时不发生. 此外, 在产氢过程中, 光生电子虽然迁移到助催化剂 PtCrO_x 上, 但 PtCrO_x 中高氧化态的 Pt^{II} 和 Pt^{IV} 并未被还原, 因此使 PtCrO_x - ZrO_2/TaON 具有稳定的光催化产氢反应活性.

基于 PtCrO_x - ZrO_2/TaON 在 $\text{Fe}(\text{CN})_6^{4-}$ 作为电子供体时有效的产氢半反应, 我们以 $\text{Fe}(\text{CN})_6^{3-/4-}$ 作为电子传递, 将光系统II与 PtCrO_x - ZrO_2/TaON 耦合构建了生物-人工杂化Z型全分解水体系, 通过调节 $\text{Fe}(\text{CN})_6^{3-/4-}$ 的初始浓度, 最终实现了杂化体系的全分解水反应, 产氢和产氧活性分别为 $\sim 20 \mu\text{mol H}_2 \text{h}^{-1}$ 和 $\sim 10 \mu\text{mol O}_2 \text{h}^{-1}$. 这为理解和抑制以 $\text{Fe}(\text{CN})_6^{3-/4-}$ 作为电子传递体的光系统II-人工杂化Z型水分解体系中的逆反应提供了新的思路.

关键词: 水分解; 助催化剂; 逆反应; 氢气氧化; 光系统II

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