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Surface Modification of Hematite Photoanodes with CeO_x Co-catalyst for Improved Photoelectrochemical Water Oxidation Kinetics

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Abstract: Hematite is a promising photoanode for solar water splitting via photoelectrochemical (PEC) cell, but its performance is still limited by the slow kinetics of water oxidation reaction (or oxygen evolution reaction, OER). Surface modification of hematite photoanode with suitable water oxidation co-catalyst is a key strategy for improving the kinetics of water oxidation reaction. In this work, we demonstrate the deposition of CeO_x overlayer on the surface of hematite photoanode by a water-based solution method using ceric ammonium nitrate (CAN) complex followed by heat treatment. The photocurrent of CeO_x-modified hematite is 3 times higher than that of pristine hematite (at 1.23 V vs. RHE) under AM 1.5 G, 1 sun conditions. Through hole scavenger measurements, Tafel plot analysis and electrochemical impedance spectroscopic studies, it is concluded that CeO_x overlayer increases the hole injection efficiency, improves the surface catalytic activity, and enhances the charge transfer across the photoanode/electrolyte interface. These observations are attributed to the synergistic effects of Ce³⁺/Ce⁴⁺ redox species in CeO_x and the oxygen vacancies. Our work elucidates the role of CeO_x as an efficient co-catalyst overlayer to improve the OER kinetics of photoanodes.

Introduction

The steady growth of energy demand and the depletion of Earth's fossil fuel resources are major challenges facing humanity in the 21st century. More importantly, CO₂ emission from the combustion of fossil fuels is the main contributor of global warming.^[1] To reduce these challenges, hydrogen has been proposed as a green chemical fuel to be an alternative energy source and to meet the future global energy demands.^[2] Photoelectrochemical (PEC) cell is one of the most promising technologies to produce hydrogen via water splitting, and thus achieving storable and sustainable transportation fuel.^[3] Although various metal oxides including α-Fe₂O₃,^[4] TiO₂,^[5] ZnO,^[6] and BiVO₄^[7] have been commonly used as photoanodes for PEC water splitting, the ideal

material is still elusive. Hematite, α-Fe₂O₃ has some features making it a potential photoanode candidate for PEC water splitting, including a narrow bandgap 2.2 eV,^[8] low cost, high chemical stability and suitable valence band to drive water oxidation reaction.^[9] Nevertheless, the PEC performance of hematite is still limited by several challenging issues such as short hole diffusion length (2–4 nm),^[10] poor conductivity,^[11] and sluggish oxygen evolution reaction (OER kinetics).^[12] Therefore, a variety of strategies have been adopted to overcome these issues including: nanostructuring,^[13] elemental doping,^[14] and surface coating with oxygen evolution co-catalyst.^[15] The latter approach is of particular interest because OER is the bottleneck of water splitting reaction and limits the efficiency of photoanode materials.^[16] Owing to the slow kinetics of water oxidation reaction, most of the photogenerated holes are accumulated at the surface and may recombine with photogenerated electrons. As a result, a larger hole injection barrier is necessary to be removed to drive water splitting reaction.^[17] Several reports have focused on lowering the activation energy of water oxidation and accelerating the surface reaction kinetics. For instance, numerous metal oxide OER catalysts such as NiOOH,^[18] FeOOH,^[19] and Co₃O₄^[20] have been loaded on the surface of hematite photoanode and significantly improved the PEC performance for water splitting. A number of studies have indicated that addition of Ce to metal oxides enhances OER activity.^[21] For example, a new Ce-rich quaternary oxide (Ni-Fe-Co-Ce)O_x was discovered as efficient OER catalyst using high-throughput methods.^[22] Coupling of this Ce-rich family with BiVO₄ photoanode using high-throughput methods has enhanced the PEC performance towards water splitting.^[23] Lim *et al.*, has reported that the incorporation of Ce into the Ni-based co-catalyst activates the OER catalytic activity of hematite photoanode under illumination.^[24] Bu *et al.*, has observed photocurrent enhancement of P-doped hematite by 1.4 times when coated with Ce_xPO₄.^[25] Even though these studies have reported the synergistic effect of Ce in mixed metal oxides co-catalyst, the behavior of CeO_x was not well studied. Ceria (cerium oxide, CeO_x) is a rare earth metal oxide material that has been assessed for various catalytic applications including oxygen evolution electrocatalysis.^[26] It has favorable properties, including superior catalytic oxidation performance, abundant oxygen vacancy defects and the high oxygen storage/release capacity^[27] due to the ease of transition between Ce⁴⁺ and Ce³⁺ oxidation states.^[28] In addition, CeO_x has strong electronic interaction with other matrices and promotes the formation of oxygen vacancies at the contact surface which are desirable for high electrocatalytic performance. Therefore, coupling hematite photoanode with CeO_x is proposed to be an efficient way to reduce the hole injection barrier and promote the surface reaction kinetics. However, the aforementioned study of Lim and

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coworkers found that no significant change was observed in the photocurrent response of hematite upon loading CeO_x without Ni.^[24] Thus, finding an appropriate method for the deposition of CeO_x on the surface of hematite is challenging. Recently, Mahmoud *et al.* has reported water-based solution process to deposit thin TiO_2 overlayer on hematite photoanode using titanium bis(ammonium lactate) dihydroxide (TALH) complex based on the surface chemistry on hematite.^[29] The photocurrent of TiO_2 -modified hematite was enhanced by 4.5 times. Therefore, a thin overlayer film of different metal oxides can be deposited based on the same approach.

In this work, CeO_x overlayer was successfully deposited on hematite photoanode by water-based solution process using ceric ammonium nitrate (CAN) complex as a precursor followed by heat treatment. Interestingly, CeO_x -modified hematite exhibits an improved photocurrent density of 0.6 mA cm^{-2} which is 3 times higher than that of pristine hematite photoanode at 1.23 V vs. RHE under AM 1.5, 1 sun conditions. The origin of the significant enhancement of CeO_x -modified hematite has been explored and discussed using hole scavenger measurements, Tafel plot analysis and electrochemical impedance spectroscopic studies.

Results and Discussion

Scheme 1 shows the preparation steps of pristine and CeO_x -modified hematite photoanodes. Firstly, hematite photoanodes were prepared with nanorods morphology^[30] to shorten the diffusion distance of photogenerated holes and decrease the chance of recombination.^[9] $\beta\text{-FeOOH}$ nanorod array was grown on FTO substrates by hydrothermal reaction and converted to $\alpha\text{-Fe}_2\text{O}_3$ (denoted as pristine hematite) by consecutive two-step annealing, 550°C for 2h and 750°C for 20 min. CeO_x was deposited on the surface of hematite photoanode using CAN complex based on the surface chemistry of hematite. Hematite was immersed in aqueous solution containing negatively charged CAN molecules at a low pH value ($\text{pH} = 2.5$). The behavior of hematite in an aqueous solution is governed by its point of zero charge, pH_{PZC} (7.5–9.5).^[31] When the pH of a solution is lower than pH_{PZC} , the surface of hematite is positively charged. Therefore, the adsorption of negatively charged CAN molecules on positively charged hematite surface is favorable due to electrostatic interaction. During thermal treatment at a relatively low temperature (200°C for 1h), CeO_x was formed on the surface of hematite after the decomposition of CAN complex.^[32] As interface optimization is an important step to achieve the maximum PEC performance, the surface coverage of hematite photoanodes by CeO_x was investigated by varying immersion time and CAN concentration (Figure S1, S2). The optimal CeO_x coverage on hematite was observed in 4 mM CAN solution for 1 h, which was subsequently characterized in more details.

Scheme 1. Illustration for the preparation of pristine and CeO_x -modified hematite.

Surface-sensitive technique X-ray photoelectron spectroscopy (XPS) was performed to identify the surface composition and chemical state of Fe and Ce. Figure S3a shows the XPS spectrum of $\text{Fe}2p$. Two distinct peaks at 711 and 724.2 eV were assigned to $\text{Fe}2p_{1/2}$ and $\text{Fe}2p_{3/2}$, respectively. The shakeup satellite peak observed at 718.6 eV indicates that the Fe^{3+} is the dominant. The core level spectrum of $\text{Ce}3d$ level in CeO_x -modified hematite is shown in Figure 1. The peaks at binding energies of 901.5, 903.8, 907.9 and 917.2 eV are ascribed to $\text{Ce}3d_{3/2}$ spin-orbit states and those at 882.9, 885.5, 889.0 and 898.8 eV are ascribed to $\text{Ce}3d_{5/2}$ spin-orbit states. The peaks at 903.8 and 885.5 eV are assigned to Ce^{3+} , while the other six peaks are characteristic of Ce^{4+} , which are consistent with the literature value of CeO_2 .^[33] Hence, the presence of CeO_x on the surface of hematite photoanode is confirmed and Ce^{3+} and Ce^{4+} oxidation states co-existed through fitting results of XPS spectra. The formation of Ce^{3+} species at the surface is more likely to occur due to the decomposition of ceric ammonium nitrate which is in good agreement with previous reports.^[34] The presence of Ce^{3+} implies the formation of oxygen vacancies to maintain the charge neutrality. The vacancies could promote the adsorption of hydroxyl species on the surface of modified hematite photoanode more than that of pristine hematite and thus contribute further to enhanced OER activity.^[35]

Figure 1. XPS spectra of Ce 3d core level existing in CeO_x -modified hematite.

This statement is further supported by the $\text{O}1s$ spectrum which is shown in Figure S3b. The XPS of $\text{O}1s$ spectrum consists of three clear peaks reflecting different chemical environments. The first peak observed at $\sim 529.9 \text{ eV}$ is associated with the oxygen atoms bonded to metal ion species (M-O) in the crystal lattice (O_L , in

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Fe_2O_3 and CeO_x).^[36] The peak observed at 531.37 is assigned to the oxygen atoms in the vicinity of oxygen vacancies (O_v).^[37] The last peak at 533.06 eV can be attributed to surface adsorbed oxygen such as hydroxyl groups (M-OH) and/or water molecules (O_{OH}).^[37b]

The XRD patterns of hematite samples are shown in Figure 2. All the characteristic peaks indicated by star symbol are attributed to hematite, $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS No.33-0664), confirming the successful conversion of $\beta\text{-FeOOH}$ to $\alpha\text{-Fe}_2\text{O}_3$. The diffraction peaks located at $2\theta = 35.7^\circ$, 40.9° , 49.7° , 54.7° can be attributed to (110), (113), (024) and (116) crystal planes of hematite, respectively.^[38] The most intense peak located at 35.7° represents the preferential growth of hematite in the [110] direction.^[14] Such preferential growth is desirable for electron transfer process because the electron mobility along (001) basal plane is 4 orders of magnitude higher than in the orthogonal plane.^[39] All other XRD peaks were indexed to FTO substrates (marked by square).

Figure 2. XRD patterns for pristine and CeO_x -modified hematite photoanodes. Hematite peaks are marked by * symbols (JCPDS 33-0664) and the other peaks marked by □ belong to FTO substrates (JCPDS 46-1088).

For CeO_x -modified hematite, no CeO_x peak was observed (Figure 2), indicating the co-catalyst layer is either too thin or amorphous. SEM image of pristine hematite is shown in Figure 3a. The SEM images of as-grown $\beta\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$ films after one-step annealing (550°C) are shown in Figure S4. Pristine hematite

consists of condensed particles with a rod-like morphology and average diameters of 90 nm. There is no significant change on the morphology of CeO_x -modified hematite as compared to the pristine hematite (Figure 3b). Even though the cross-section SEM was conducted, CeO_x overlayer cannot be clearly distinguished, suggesting that it is extremely thin. The thin CeO_x overlayer does not affect the absorption spectra of hematite as shown by UV-Vis spectra (Fig S5).

Figure 3. Top view SEM images of (a) pristine and (b) CeO_x -modified hematite.

To evaluate the photoelectrochemical water oxidation, the photocurrent response of pristine and CeO_x -modified hematite photoanodes was measured in 1.0 M NaOH under AM 1.5, 1 sun conditions as shown in Figure 4a. Interestingly, the hematite photoanodes loaded with CeO_x showed photocurrent density up to 3 times higher than that of the pristine one. To confirm that the enhanced photocurrent density is not merely a result of post heat-treatment, pristine hematite photoanodes were subjected to post heat-treatment but without CeO_x overlayer. The photocurrent does not change as shown in Figure S6. Incident photon-to-current conversion efficiency (IPCE) measurements were further performed to calculate the photocurrent generated by monochromatic light of various wavelengths ranging from 350 to 650 nm at a potential of 1.23 V vs. RHE (Figure 4b). The IPCE of CeO_x -modified hematite exhibits significant enhancement in the entire absorption range by a factor of approximately 3 compared to that of pristine hematite, which is consistent with the photocurrent response shown in Figure 4a. The IPCE of pristine and CeO_x -modified hematite exhibit similar IPCE onset, which is in good accordance with the band gap of hematite. We hypothesized that this significant enhancement upon CeO_x deposition on the surface of hematite may be attributed to either catalytic properties of CeO_x that facilitates charge transfer or creation of heterojunction at the interface with hematite.^[40]

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Figure 4. a) Photocurrent-potential curves of pristine and CeO_x-modified hematite measured under AM1.5G, 1 sun conditions. b) IPCE of pristine and CeO_x-modified hematite photoanodes measured at 1.23 V vs. RHE. c) Surface catalysis efficiency and d) charge separation efficiency of pristine and CeO_x-modified hematite photoanodes.

To gain mechanistic insight into the role of CeO_x on hematite photoanodes, PEC measurements were performed in the presence of sodium sulfite (0.5 M) as an efficient hole scavenger. It is assumed that surface recombination is completely suppressed (i.e., ~100% catalytic efficiency) upon the presence of hole scavenger because the oxidation of sulfite is much more thermodynamically and kinetically favorable than water.^[41] Therefore, all holes arriving at the surface are rapidly injected into the electrolyte across the photoanode/electrolyte interface. In Figure S7, the photocurrent measured with hole scavenger for pristine and CeO_x-modified hematite is almost the same, suggesting an equal number of holes arrive at the photoanode/electrolyte interface for both photoanodes. It is also supported by the similar charge separation efficiency. The photocurrent of CeO_x-modified hematite for water oxidation without hole scavenger is lower because a fraction of the holes recombines via surface states existing on the surface of hematite.

It was also observed that onset potential is approximately equal to 0.63 V for both hematite photoanodes with and without hole scavenger. It indicates that surface modification with CeO_x keeps the band bending of hematite relatively unchanged because it is limited by the flat-band potential.^[42]

The efficiency of surface charge transfer (η_{catalysis} which is related to surface hole injection) was also calculated to quantify the contribution of CeO_x to improve the surface reaction kinetics. The η_{catalysis} was calculated by the photocurrent ratio of water oxidation to that of sulfite oxidation. Figure 4c shows that the η_{catalysis} values for pristine hematite are low (~25%-30%) over the entire potential range, illustrating severe surface recombination. In contrast, the η_{catalysis} of CeO_x-modified hematite is significantly enhanced reaching 76% at 1.23 V vs. RHE, and the enhancement ratio is in good agreement with photocurrent response shown in Figure 4a. This significant η_{catalysis} improvement demonstrates that CeO_x can greatly reduce surface charge recombination and facilitates the

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charge injection at the photoanode/electrolyte interface. Moreover, the charge separation efficiency of pristine and CeO_x-modified hematite was calculated as shown in Figure 4d. The charge separation efficiency is less than 10% of the total photon flux absorbed by the material indicating that more than 90% of the photogenerated charge carriers undergo recombination in the bulk. This low charge separation efficiency is a significant limitation for hematite photoanodes regardless its nanostructure morphology.^[43] The rather insignificant change of charge separation efficiencies of pristine and CeO_x-modified hematite excludes the possibility of heterojunction formation between hematite and CeO_x for improved PEC performance.

To further support that CeO_x deposition on the surface of hematite photoanode improves the surface reaction kinetics, a steady-state Tafel plot analysis was performed. In photoelectrochemical reactions, Tafel plots may not be valid because photogenerated charge recombination has to be considered besides electrochemical kinetics. Thus, Tafel plots were derived from LSV measurements performed in the dark. As shown in Figure 5, CeO_x-modified hematite electrodes have a lower Tafel slope of 73 mV/decade than 90 mV/decade of pristine hematite, indicating more favorable surface reaction kinetics during OER catalysis. The Tafel slope value of CeO_x-modified hematite is closer to 60 mV/decade which is associated with a rate-limiting step following the first electron transfer.^[33c]

Figure 5. Tafel slope values of pristine and CeO_x-modified hematite photoanodes.

To further understand the hole transfer kinetics across the photoanode/electrolyte interface, electrochemical impedance spectroscopy (EIS) measurements were performed. Figure 6a shows the Nyquist plots of hematite photoanodes at 1.23 V vs. RHE under illumination. Obviously, the arc diameter of CeO_x-modified hematite is smaller than that of pristine hematite, indicating improved charge transfer in CeO_x-modified hematite photoanode which explains the high photocurrent observed after modification in Figure 4a. EIS data were further fitted with an appropriate equivalent circuit to estimate the physical parameters responsible for charge transfer process across the photoanode/electrolyte interface (Figure 6b). In the proposed

equivalent circuit, R_s represents the solution resistance, $R_{ct,bulk}$ represents the trapping charge resistance inside hematite photoanode, while $R_{ct,trap}$ represents the resistance of charge transfer through the photoanode/electrolyte interface. The capacitances C_{bulk} and C_{trap} are related to the space charge capacitance of the bulk hematite and the capacitance associated with the surface states, respectively.^[44] Table 1 shows the EIS fitting parameters obtained using equivalent circuit model. $R_{ct,bulk}$ does not show a significant change after surface modification with CeO_x overlayer indicating the conductivity of both hematite photoanodes remains relatively the same. On the other hand, $R_{ct,trap}$ is significantly decreased from 2976 to 620 Ω upon loading CeO_x. This indicates that the photogenerated holes on CeO_x-modified hematite are easily injected into electrolyte compared to that of pristine hematite photoanode. Moreover, as C_{trap} of CeO_x-modified hematite is higher than that for pristine hematite, it suggests that more holes are accumulated at the interface and consequently more holes are injected into the electrolyte and participate in water oxidation.

All of these confirm the surface catalytic effect of CeO_x on improving PEC water oxidation.

Figure 6. (a) Complex-plane impedance plots (Nyquist plots) of pristine and CeO_x-modified hematite photoanodes at 1.23 V vs. RHE under AM 1.5, 1 sun conditions in 1.0 M NaOH, (b) equivalent circuit.

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Table 1. Fitting parameters of Nyquist plots for pristine and CeO_x-modified hematite photoanodes.

	R_s Ω	$R_{ct,bulk}$ Ω	C_{bulk} μF	$R_{ct,trap}$ Ω	C_{trap} μF
Pristine hematite	70	160	1.2	2976	7.3
CeO _x -modified hematite	60	128	2.3	620	10.6

Mott-Schottky measurements were also conducted to determine any change in the band positions following the deposition of CeO_x on the surface of hematite (Figure S8). Both hematite photoanodes exhibit the same flat-band potential close to 0.64 V vs. RHE, which is in good agreement with onset potential measured either with or without hole scavenger. This indicates that the flat-band potential is independent of the CeO_x overlayer, which proves that CeO_x overlayer keeps the band positions unchanged. This behavior is consistent with previous reports of Co-Pi co-catalyst modified BiVO₄ and hematite photoanodes.^[45] Based on the discussion above, CeO_x overlayer has changed the surface catalytic properties of hematite photoanode. We hypothesize that the vacancies in CeO_x overlayer and the Ce³⁺/Ce⁴⁺ redox transformations are the key factors in enhancing the catalytic surface properties of hematite photoanode.

Generally, the electrocatalytic OER process in basic medium includes the adsorption of OH⁻ on the surface forming various intermediates and eventually producing O₂ gas.^[27] As CeO_x is a nonstoichiometric structure containing oxygen vacancies which are generated from the transformation between Ce³⁺ and Ce⁴⁺, these vacancies could promote the adsorption of OH⁻ on the surface to form intermediates.^[27] The presence of CeO_x on the surface of hematite tends to bind the intermediates much stronger than normal oxide sites and thus facilitates the water oxidation to produce O₂.^[27, 35]

During photoelectrochemical reaction, if the photogenerated holes are trapped in the surface states of hematite,^[46] they may recombine with the photogenerated electrons instead of oxidizing water. The active redox species Ce³⁺/Ce⁴⁺ and the existence of oxygen vacancies in CeO_x co-catalyst may synergistically facilitate the hole trapping and migration.^[47] The oxygen vacancies could facilitate the adsorption of water onto the surface of catalyst as the adsorption of water is more favorable for low coordination sites, i.e., Ce³⁺ site. Also, the Ce³⁺ species near oxygen vacancy act as hole-trapping sites^[42, 48] which could facilitate hole transfer to oxidize adsorbed water.^[49] In brief, Ce³⁺ species will be oxidized by holes to higher oxidation state Ce⁴⁺. Afterwards, Ce⁴⁺ will be reduced back to Ce³⁺ state by getting an electron from water molecule (i.e., water oxidation). The modification of pristine hematite with CeO_x co-catalyst in this study records 200 % photocurrent enhancement (ΔJ_{ph}) for pristine hematite at 1.23 V vs. RHE which is among the highest values achieved in the literature for hematite coupled with co-catalysts without dopants or heterojunction formation (see Table S1). Therefore, we conclude that the CeO_x layer could facilitate the hole trapping and transfer for improved water oxidation kinetics.

Conclusions

In summary, the surface reaction kinetics of hematite photoanodes are improved by the deposition of CeO_x overlayer employing water-based solution process using CAN complex as precursor followed by heat treatment. In comparison with pristine hematite, the photocurrent of CeO_x-modified hematite is significantly enhanced by 3 times at 1.23 V vs. RHE under AM 1.5, 1 sun conditions. CeO_x overlayer increases the surface catalytic efficiency (hole injection) across the photoanode/electrolyte interface, reduces charge recombination and promotes surface holes for water oxidation. The catalytic activity of CeO_x is attributed to the coexistence of Ce³⁺/Ce⁴⁺ on the surface of hematite and the oxygen vacancies generated as a result of maintaining charge neutrality.

Experimental Section

Synthesis of hematite photoanode

Hematite films were fabricated by hydrothermal method as previously reported^[14] but with minor modification. Firstly, fluorine-doped tin oxide (FTO, 1 x 1.5 cm) glass substrates were cleaned using an ultrasonic bath in acetone, followed by ethanol and de-ionized water for 15 min for each solvent and then dried in a stream of N₂. The precursor solution was an aqueous solution of ferric chloride, 0.15 M and sodium nitrate, 1.0 M. A 10 mL of this solution was transferred directly to the autoclave reactor (Teflon-lined stainless-steel vessel, 20 mL volume), where the FTO substrates were placed inside the reactor at a slight angle and the FTO side is facing down. The autoclave reactor was kept in the oven at 100 °C for 1 h resulting in the growth of a uniform layer of FeOOH on FTO substrates. The substrates were then rinsed with water and further annealed in air at 550 °C and 750 °C for 2 hours and 20 minutes, respectively to obtain Fe₂O₃ nanorods on FTO substrate. The ramping rate for each annealing step was 300 °C/h.

Modification of hematite photoanode with CeO_x

The hematite photoanodes were dipped in various concentrations (2, 4, 6 mmol L⁻¹) of ceric ammonium nitrate (CAN) solution. After being dipped for different time periods 30, 60, 90 min, the films were rinsed with water to remove the excess unbonded CAN molecules and then heated up to 200 °C for 1 h.

Characterization

XRD patterns of hematite samples were recorded on using Shimadzu thin film X-ray diffractometer with Cu-K α radiation of $\lambda = 0.1540$ nm. SEM images of hematite samples were examined by FE-SEM (JEOL-7600F). X-ray photoelectron spectroscopy (XPS) analysis was performed using VGESCALAB 2201-XL instrument provided with a monochromatic Al K α (1486.7 eV) x-ray source and the operational base pressure is lower than 5×10^{-10} mbar. Light absorption spectra were measured by Lambda 750S UV/Vis/NIR spectrophotometer, PerkinElmer, equipped with 60 mm integrating sphere.

Electrochemical and photoelectrochemical measurements

All PEC measurements were conducted by using CHI 660D electrochemical workstation (CH instruments, inc.) in a three-electrode

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setup. The working electrode is the photoanode material, while reference and counter electrodes are Ag/AgCl (KCl, 3.0 M) and Pt coil, respectively. A 150 W xenon solar simulator (67005, Newport.) was used as a light source which is capped by a solar filter (KG-3) to simulate the AM1.5G spectrum. The light intensity was calibrated with Si solar cell to be 1 sun, i.e., 100 mW cm⁻² prior to all photoelectrochemical measurements. Sodium hydroxide (NaOH, 1.0 M) was used as electrolyte for all measurements

IPCE data were collected with monochromator and the light from Xenon lamp together with an AM 1.5 G filter set. The monochromatic light intensity was determined using calibrated Si-diode after applying bias on the device by Keithley source meter Keithley and measuring the photocurrent. The IPCE values were calculated at each certain wavelength as described previously in the literature.^[14]

Polarization data for Tafel plots were obtained by linear sweep voltammetry, LSV with low scan rate 1 mV/s. The potential values were R compensated (the solution resistance was determined from impedance measurements). The potential values were iR compensated (the solution resistance was determined from impedance measurements).

Nyquist and Mott-Schottky measurements were performed using autolab potentiostat (Metrohm, PGSTAT 302N). The former was collected at

constant DC potential value of 1.23 V vs. RHE with AC signal amplitude 10 mV within frequency range 10 kHz to 0.1 Hz and the intensity of light was 100 mW cm⁻². Mott-Schottky measurements were recorded over potential range of 0.7 to 1.4 V vs. RHE at a frequency of 100 Hz but without illumination.

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Keywords: hematite photoanode • water splitting • CeO_x • Co-catalyst •

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Text for Table of Contents

CeO_x was deposited for the first time on the surface of hematite photoanode to improve the surface kinetics of water oxidation reaction. The photocurrent has increased 3 times compared to pristine hematite. CeO_x was able to increase the surface catalysis efficiency and keep the separation efficiency unchanged. It is assumed that oxygen vacancies in CeO_x increases the adsorption of hydroxyl groups to form intermediates and also facilitate the hole transfer process for O_2 evolution.

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Title Surface Modification of Hematite
Photoanodes with CeO_x Co-catalyst
Overlayer for Improved Water
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