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Recent progress on post-synthetic treatments of photoelectrodes for photoelectrochemical water splitting Yong Peng,ab Chun Hong Mak,ab Ji-Jung Kai,c Minshu Du, d Li Ji,*e Mingjian Yuan, f Xingli Zou,*g Hsin-Hui Shen,h Shella Permatasari Santoso, i Juan Carlos Colmenares *j and Hsien-Yi Hsu *ab For the global energy demand and climate change challenges, seeking renewable, sustainable energy sources is of great significance.

12**Photoelectrochemical (PEC) water splitting is one of the promising** technologies **for**

converting intermittent solar energy into storable hydrogen energy, to tackle these issues. As the core component in a PEC system, photoelectrodes have been modified by various strategies including nanostructuring, facet-engineering, elemental doping, and heterostructured engineering. Apart from these techniques, numerous effective post-synthetic treatments have also been used to facilely and powerfully boost the physicochemical properties of photoelectrodes, for the enhancement of their PEC performance. Among them, a number of post-treatments can selectively influence photoelectrode surface and subsurface areas, altering surface states that play crucial roles in the hydrogen/oxygen evolution reaction. In virtue of such post-treatments, we summarize recently reported post-synthetic treatments for enhanced PEC applications. Post-treatment methods are classified into three sections: chemical treatments, electrochemical and irradiation-based treatments, and post-annealing treatments. In the end, a summary and outlook section regarding the utilization of post-treatments for PEC applications have been provided. This review can provide inspiration for further studies about post-treatments, not only in the PEC water splitting field, but also in other aspects, such as electrolysis. aSchool of Energy and Environment, Department of Materials Science and Engineering, City University of Hong Kong, Kowloon Tong, Hong Kong, China. E-mail: sam.hyhsu@ cityu.edu.hk bShenzhen Research Institute of City University of Hong Kong, Shenzhen, 518057, China cDepartment of Mechanical Engineering, City University of Hong Kong, Kowloon Tong, Hong Kong, China dSchool of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, China eState Key Laboratory of ASIC and System, School of Microelectronics, Fudan University, Shanghai 200433, China. E-mail: lji@fudan.edu.cn fKey Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Renewable Energy Conversion and Storage Center (RECAST), College of Chemistry, Nankai University, Tianjin, 300071, P. R. China gState Key Laboratory of Advanced Special Steel, Shanghai Key Laboratory of Advanced Ferrometallurgy, School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China. E-mail: xlzou@shu.edu.cn hDepartment of Materials Science and Engineering, Faculty of Engineering, Monash University, Clayton, Victoria 3800, Australia iChemical Engineering Department, Widya Mandala Surabaya Catholic University, East Java, Indonesia jInstitute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw 01-224, Poland. E-mail: jcarloscolmenares@ichf.edu.pl 1. Introduction Hydrogen is envisioned as a clean, sustainable, and carbon- neutral energy source for the replacement of

44**fossil fuels to meet the** challenges **of** environmental concerns, the **energy** crisis, **and**

global warming issues in the future. Converting intermittent

44**solar energy to chemical energy stored in**

hydrogen is one of the promising technologies for large-scale hydrogen production by which to satisfy the ever-increasing energy demands of human society.25,26 It is estimated that capturing solar light at a solar-to-hydrogen (STH) efficiency of 10%, over an area of 250 000 km2 which corresponds to only 1% of the earth's desert area, is required to ful?ll one-third of the energy needs of the whole world in 2050.27 In light of this, solar water splitting technologies—including but not limited to photovoltaic-based electrolysis (PV-E), photoelectrochemical (PEC) water splitting, and photocatalytic (PC) water splitting— have been developed. The PV-E system primarily necessitates expensive photovol- taic devices, such as currently used silicon-based solar panels, for the conversion of solar energy to electricity. In comparison, PEC/PC water splitting, employing low-cost and effective pho- toresponsive materials, has drawn increased attention since the seminal demonstration by Honda and Fujishima in 1972.28 During PEC/PC water splitting, electrons in the valence band (VB) of a photocatalyst can be excited to the conduction band (CB) in response to light absorption.29–31 The

1**photogenerated electrons and holes** are then transported **from the** material bulk **to** its **surface**

. Finally, the

40**hydrogen evolution reaction (HER) and** the **oxygen evolution reaction (OER**

) can be realized at the surface of photoelectrodes and/or counter electrodes, respec- tively, as shown below. HER: 2H+ + 2e? / H2, EWred ¼ 0 V OER: 2H2O + 4h+ / O2 + 4H+, EWox ¼ 1.23 V Compared to PC water splitting, an extra small bias potential is generally required to be imposed on a single light-absorber photoelectrode, in order to overcome thermodynamic and kinetic barriers

1**for PEC water splitting (compared to**

this, ?nd ref. 32 for self-biased tandem cells

1**for PEC water splitting**). In spite **of** this, **the**

PEC system has the advantage of separated hydrogen and oxygen gases, which avoids dangerous mixing and makes the system facile for studying various photoelectrodes.33 In order to achieve practical PEC water splitting, the most important task is to develop efficient, robust, and cost-effective photoelectrodes. However, none of the present photocatalysts has satis?ed all these requirements. There is no doubt about the importance of developing new cutting-edge photo- responsive materials for PEC applications, yet this process is certainly hard and rather time-consuming. On the other hand, engineering/modi?cation of the existing materials to advance their bulk and surface/interface characteristics is feasible and useful. The bulk structure of photoelectrodes can be modulated by diverse strategies such as elemental doping, morphological engineering, facet regulating, heterojunction formation, and compositing engineering. Readers are directed to recently published excellent reviews, e.g., ref. 32, 34 and 35. Owing to the termination of lattice periodicity at the surface/ interface, it is impossible to avoid a surface state that determines surface/interface properties in photoelectrodes.36 Thus, an understanding of the surface state is of great signi?cance to the development of practical PEC applications. In detail, overall PEC performance, e.g., photocurrent density and solar-to-hydrogen efficiency, depends on the efficiencies of charge carrier forma- tion, separation, and injection. The charge formation and sepa- ration characteristics are highly subjected to the intrinsic structural and electronic characteristics of the photoelectrodes. In comparison, surface states such as chemical surroundings, chemical bondings, or atomic arrangements, could be relatively easily altered with powerful post-synthetic treatments. During PEC water splitting, HER and/or OER occur at the surface of photo-responsive materials. The interfacial properties of semiconductorksemiconductor, semiconductorkoverlayer, or photoelectrodekelectrolyte can substantially affect the PEC response. Therefore, it is desirable to utilize post-synthetic approaches to modify the interface/surface properties of photo- electrodes, in pursuit of boosted solar-to-hydrogen conversion performance in an inexpensive and robust manner. In consid- eration of the abovementioned, we analyze studies related to post-synthetic treatments and PEC water splitting in the recent ?ve years. In the review, we start with the introduction of facile chemical reduction and chemical modi?cation methods, fol- lowed by a discussion of unique electrochemical and interesting irradiation-based treatments, as well as versatile post-annealing treatments, for improving the performance of photoelectrodes. Finally, we end with an outlook for future work. 2. Chemical treatments Facile and effective chemical post-treatments can be used to modify photoelectrodes, which employ solution-based methods to process materials in most cases. This section is divided into two categories, chemical reduction and chemical modi?cation. The major differences between these two methods are that chemical reduction employs reducing agents, such as sodium borohydride (NaBH4), to react with photoresponsive materials in a vigorous manner. By comparison, chemical modi?cations are inclined to alter the surface states of the photoelectrodes via the formation of surface chemical bonds, without changing subsurface properties. Two points of view are emphasized as follows. (1) It is necessary to clarify that the classi?cation for certain cases is somewhat subjective, due to the lack of a clear boundary. (2) It is worth noting that we have arranged solid- and gas-based chemical reduction cases in the post-annealing part, because it is normally essential to activate the reaction between solid photoresponsive materials with solid/gas reducing agents at high temperature and/or high pressure. 2.1 Chemical reduction

Reducing agents undergo rapid reactions with the photo- electrode surfaces. Chemical reduction is low-cost, fast and reliable, and therefore it is a popular chemical method to create oxygen vacancies of the metal oxide photoelectrode families. 2.1.1 Sodium borohydride. As a strong reducing agent, sodium borohydride (NaBH4) has been extensively used to improve the photoactivity of various photoelectrodes, including TiO2, Fe2O3, BiVO4, SrTiO3, Bi2WO6, and BaSnO3. Firstly, NaBH4 treatment could conveniently create oxygen vacancies (Ovac) in photoelectrodes.37,38 Zheng et al. reported that Ovac could be introduced in black phosphorus (BP)- modi?ed TiO2 photoanodes by soaking them in a NaBH4 aqueous solution.37 The synergistic effect of Ovac and BP quantum dot sensitization was veri?ed by PEC measurements. Notably, the generated Ovac and BP sensitization could not only facilitate charge separation but also enhance the water oxida- tion reaction, by improving the activity and quantity of reactive sites. In another study, Shi et al. explored the synergistic interaction between plasmonic Au nanoparticles and Ovac.38 The NaBH4-treated amorphous black TiO2 photoanode maintained the Ovac, which could build intermediate energy levels. Such interband levels could facilitate the trapping and transfer of hot electrons generated from Au nanoparticles and thus improve electron–hole separation. In situ formation of surface hetero- phase could be realized using NaBH4.39 Metallic Bi-modi?ed Ovac-defective BiVO4 photoanodes could be obtained by one- step NaBH4 immersion treatment. The surface B–O bonds of BiVO4 photoanodes were destructed and Bi3+ atoms were reduced to Bi0 nanocrystals. At the same time, the formed Ovac could signi?cantly enhance charge carrier separation and bene?t the adsorption of water molecules, while the metallic Bi nanocrystals facilitate charge separation and consumption, due

1**to the surface plasmon resonance effect**. In situ formation **of the**

FeB overlayer on Fe2O3 could be generated by dipping the photoanode in an aqueous NaBH4 solution.40 The FeB layer could suppress charge carrier recom- bination in Fe2O3 and reduce interfacial resistance of electro- dekelectrolyte. In view of this, a twofold increase in photocurrent density could be observed. In comparison to this study,40 another report on the NaBH4 treatment of Fe2O3 showed that modi?cation of NaBH4 only contributed to a slight enhancement of photocurrent density.12 However, it is inter- esting to ? nd that, with both NaBH4 treatment and Co-Pi coating, the onset potential of the as-prepared Co-Pi/Fe2O3–NaBH4 photoanode decreased by 210 mV, compared to 110 mV of Co-Pi/Fe2O3. NaBH4 could induce surface states that serve as surface charge transfer and recombination sites. A?er Co-Pi coating, such surface states not only stored the accumulated holes but also served as a block layer to prevent the recombi- nation of photogenerated electrons with the oxidation inter- mediates in the Co-Pi cocatalyst (Fig. 1). Fig. 1 (a) Charge transfer pathway in bare Fe2O3, (b) NaBH4 treatment could induce surface states that serve as surface charge transfer (kct) and recombination (krec) sites, (c) only Co-Pi coating decreased the recombination rate (krec) but unfavorably impaired charge transfer (kct), (d) after coating Co-Pi on NaBH4-treated Fe2O3, surface states not only stored accumulated holes but also served as block layer to prevent recombinations.12

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. NaBH4 treatments are also bene?cial to bimetallic oxide semiconductors, such as strontium titanate (SrTiO3),2,17,41 bismuth tungstate (Bi2WO6),42 and barium stannate (BaSnO3).43 Shi et al. reported the formation of crystalline- core@amorphous-shell structured SrTiO3 photoelectrodes by NaBH4 treatment at 320 C.2 Owing

10**to the** localized **surface plasmon resonance effect and the**

high carrier density induced by Ovac, the treated photoanode exhibited an

38**enhanced photo- current density of** 170 **mA cm?2** under AM **1**

.5 G with an L-42 cutoff ?lter (Fig. 2a–c). Similarly, with $NaBH_4$ to process TiO_2/ $SrTiO_3$ heterostructure,17 surface amorphous structure and Ovac could be generated, which bene?ted the adsorption of hydroxide ions as well as the transfer of charge carriers (Fig. 2d). In addition to $SiTiO_3$, Ovac of Bi_2WO_6 could be prepared by a simple $NaBH_4$ etching process.42 The presence of Ovac could decrease charge transfer resistance and thus increase photo- current density. It is worth noting that an inappropriate amount of $NaBH_4$ could create excessive Ovac, which could serve as charge carrier recombination centers, undermining the photo- activity of the Bi_2WO_6 photoanode. Recently, Kim et al. reported that solution-based $NaBH_4$ treatment could induce Ovac in $BaSnO_3$ photoanodes, gradually narrowing the bandgap of $BaSnO_3$ from 3.11 eV to 1.81 eV.43 The amount of Ovac could be Fig. 2 (a) Transient photocurrent responses and (b) IPCE values of $SrTiO_3$ and r-$SrTiO_3$ photoelectrodes

31**at 1.23 V vs. RHE with an**

L-42 cutoff filter, and (c) localized surface plasmon resonance effect

43**enhanced PEC water splitting** of $SrTiO_3$ **under visible light**

.2 Modified

1**with permission from ref**. 2, **copyright** 2018 **American Chemical Society**. (d) **Schematic illustration of the**

synergistic effects between close contact TiO_2/$SrTiO_3$ heterojunction and $NaBH_4$-induced surface Ovac.17

13**Reprinted with permission from ref**. 17, **copyright 2019** Amer- ican **Chemical Society**. precisely controlled, and **the**

$BaSnO_3$ photoanode with 8.7% of Ovac exhibited the highest light absorption and best charge separation performance. A?er further coating FeOOH/NiOOH layered double oxide,

2**this photoanode exhibited a remarkable photocurrent of** 7.32 **mA cm?2 at 1.23 V** vs. **RHE**

. 2.1.2 Other reducing agents. In addition to sodium boro- hydride, a number of reducing agents such as lithium metal dissolved in ethylenediamine (Li-EDA), titanium(III) chloride ($TiCl_3$), sodium hypophosphite (NaH_2PO_2), and sodium sul?te (Na_2SO_3) have been used to modify the surface atomic arrangements and/or surface states of photoelectrodes. Li-EDA, as a strong reducing agent, has been employed to process TiO_2 3 and $BiVO_4$.14 Zhang et al. reported the formation of a controllable crystal-de?cient overlayer in rutile TiO_2 arrays by facile immersion in liquid Li-EDA for 5–120 s (Fig. 3a–e).3 The created overlayer not only resulted in enhanced

22**light absorption but also** improved **the conductivity**

of TiO2 by 50 times, bene?ting electron collection in the photoanode. As a result, the as-obtained TiO2 photoanode exhibited a

2**photocurrent density of** 2.0 **mA cm?2 at 1.23 V** vs. **RHE, four times higher than that of**

bare TiO2. Likewise, another study indicated that Li-EDA could induce the subsurface alteration of atomic arrangement in BiVO4 (Fig. 3f and g).14 The disordered surface layer, generated by a 5 s Li-EDA treatment, could alleviate charge carrier recombination at the BiVO4kelectrolyte interface,

1**leading to the increase of photocurrent**

density by 2.1 times. The enhanced

1**charge separation and** charge **transfer properties** were respon- sible **for the**

improved photoactivity of the Li-EDA-treated BiVO4 photoanode. Kim et al. demonstrated the effectiveness of a TiCl3-mediated treatment for TiO2 nanotubes.44 Both surface Ovac and the TiO2 nano-branch layer could be generated with the post-treatment,

18**which resulted in** an **improved charge** carrier density **and**

strengthened surface roughness, respec- tively. As a result, the

5**photocurrent density increased from 0**.83 **mA cm?2 to** 2.25 **mA cm?2 at 1.23 V** vs. **RHE**

. Another report by Liu et al. revealed that the concentration of Ovac in WO3 pho- toanodes could be controlled and was proportional to the amount of TiCl3.45 Enhanced PEC activity could be observed a?er treatments with certain concentrations of TiCl3, otherwise excessive Ovac might be generated to serve as surface defects for charge carrier recombination, resulting in unsatisfactory sepa- ration and transfer of charge carriers. Yang et al. investigated the thermodynamic and kinetic in?uence of Ovac on Fe2O3 photoanodes.46 Sodium hypo- phosphite (NaH2PO2) was used as a reductant to induce various amounts of Ovac in the photoanodes by adjusting the time of Fig. 3 (a–e) TEM images of Li-EDA-treated TiO2 nanowires for 5, 10, 20, 60, and 120 s, respectively. Scale bars 2 nm. Insets

37**are the FFT converted from the corresponding TEM images**

.3 (f and g) TEM images of (f) bare BiVO4 and (g) Li-EDA treated BiVO4.14 Modified

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2018, respectively,

3**WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim**. hydrothermal reactions. Notably, **a** prolonged time **of**

180 min could induce unfavorable bulk Ovac which had a negative effect on the photoactivity of Fe2O3. In comparison, the presence of surface Ovac decreased space charge region width, resulting in boosted charge separation and transfer. Additionally, from the perspective of kinetics, the surface Ovac could also improve the surface properties and hydrophilicity of the Fe2O3 photoanodes. In a similar manner, our group employed a mild reducing agent, sodium sul?te (Na2SO3), to modify the surface properties of the BiVO4 photoanodes.47 The facile immersion of BiVO4 ?lms in the Na2SO3 aqueous solution could create surface Ovac and disordered surface structure. Owing

2**to the** decreased **charge carrier recombination, the**

as-prepared sul?te-treated BiVO4 exhibited a

2**photocurrent density of** 2.2 **mA cm?2 at 1.23 V** vs. **RHE**, 1.7 times **higher than that of bare**

BiVO4. In addition to inorganic compounds, organic compounds could also be useful for chemical reduction treatments. For example, Long et al. reported the use of ethylene glycol for the reduction of CoOx-coated ZnO nanorods.48 A?er solvothermal reaction at 140 C for 8 h, the amount of Ovac in the photoelectrode was substantially increased, which acted as favorable trapping centers

1**for the migration of photogenerated holes**

at the elec- trodekelectrolyte interface. Consequently, the reduced CoOx- coated ZnO

7**photoanode exhibited a photocurrent density of 2**.1 **mA cm?2**

,

32**2.1 times higher than that of bare** ZnO nanorods **and**

1.6

10**times higher than that of** the CoOx-coated **ZnO** ones. Studies of the above chemical reduction treatments have been summarized in Table 1. It is facile and effective to employ chemical reduction methods for the post-treatments of various photoelectrodes. The physicochemical properties of the mate- rial, especially of the subsurface, can be selectively altered, depending on speci?c treating parameters. In most cases, an undesired structure (e.g., excessive Ovac) could be created with an excessive amount of reducing agents or reaction time. Therefore, adjusting reaction parameters (e.g., concentration of reducing agents, reaction time, and temperature) or employing other practical methods to precisely control the reaction process are expected. In addition, since the reducing agents used in the reported studies are primarily inorganic compounds, it might be suggested to screen suitable organic compounds as reducing agents to modify photoelectrodes for the pursuit of stable and effective photoactivity. Table 1 Chemical reduction of photoelectrodes for enhanced PEC performance Photocurrent density Materials Post-treatments (a mA cm?2 at b V vs. g; d times)c Ref. NaBH4 BPa/TiO2 TiO2 BiVO4 Fe2O3 Fe2O3 SrTiO3 TiO2/SrTiO3 Bi2WO6 BaSnO3 Li-EDAb TiO2 BiVO4 TiCl3 TiO2 WO3 NaH2PO2 Fe2O3 Na2SO3 BiVO4 Ethylene glycol Soaked in 0.1 M NaBH4 for 10–70 min 0.5 g of BiVO4 powders dispersed into 50 mL of 20 mg mL?1 Mixed with NaBH4 and heated at 360 C for 2 h NaBH4 and stirred for 30–60 min Dipped in 0.1 M NaBH4 for 40 min Immersed in 0.2 M NaBH4 for 10–30 min, followed by loading Co-Pi cocatalysts Mixed with 0.5 g of NaBH4 and heated at 320 C for 2 h in N2 Covered by 0.22 g of NaBH4 and heated at 320 C for 2 h in Ar 0.4 g of Bi2WO6 in 50 mL H2O mixed with 2.5–10 mL of 0.8 g L?1 NaBH4 under N2 for 3 h 0.5 g of BaSnO3 immersed in 130 mL of 1–7 M NaBH4 for 3 h followed by coating FeOOH/NiOOH cocatalysts Immersed in 0.69 mg mL?1 of Li-EDAb for 5–120 s Immersed in 0.05 M of Li-EDAb for less than 5 s Immersed in 10 mL of 17–68 mM of TiCl3 at 60–100 C for 5–40 min Dipped in 50–200 mg L?1 of TiCl3 for 25 s Hydrothermally heated in 1 M NaH2PO2 at 100 C for 60–180 min Immersed in 0.2 M Na2SO3 at 60 C for 24 h 1.12; 1.23; RHE; 3.0 1.33; 1.23; RHE; 3.1 1.00; 1.23; RHE; 8.3 37 38 39 1.65; 1.23; RHE; 2.2 1.29; 1.23; RHE; 1.5 40 12 1.71; 1.23; RHE; 3.1 0.32; 1.23; RHE; 1.5 1.90; 1.23; RHE; 2.7 2 17 42 7.32; 1.23; RHE; 7.3 43 1.70; 1.23; RHE; 3.4 2.30; 1.23; RHE; 2.1 2.25; 1.23; RHE; 2.7 0.82; 1.2; Ag/AgCl; 1.27 44 45 2.40; 1.6; RHE; 1.8 46 2.20; 1.23; RHE; 1.7 47 CoOx/ZnO Hydrothermally heated in 5 mmol NaOH dissolved in 10 mL 2.10; 1.23; RHE; 1.3 48 ethylene glycol at 140 C for 8 h a BP: black phosphorus. b Li-EDA: lithium metal dissolved in ethylenediamine. c

15**Photocurrent density** (a **mA cm?2 at** b **V vs**

. g; d times) ¼ 1.12; 1.23; RHE; 3.0, for example, means 1.12

20**mA cm?2 at 1.23 V vs. RHE**, 3.0 **times higher than the**

photocurrent density of relevant untreated sample, similarly herea?er. 2.2 Chemical modi?cation In comparison to the occurrence of strong reactions between reducing agents and photoelectrodes, the surface alteration induced by chemical modi?cation can usually be rather slow and gentle. Chemical modi?cation methods, including acid and alkaline treatments, contact-induced surface alternations, and in situ ion exchange are summarized as follows. 2.2.1 Acid and alkaline treatments. Facile acid or alkaline treatments have been used for effectively improving the PEC performance of hematite. Yang et al. immersed Fe2O3 photo- anodes in pure acetic acid (CH3COOH) for 5 min, followed by calcination treatment.49 The acid-treated Fe2O3 exhibited a considerably increased

5**photocurrent density, from 0**.3 **mA cm?2** of bare Fe2O3 **to** 1.2 **mA cm?2 at** 0.2 **V**

vs. Ag/AgCl, which was ascribed to the decreased charge recombination loss arising from an improved detrapping rate. The reduced charge recombination rate was also consistent with the observation of improved conductivity and enhanced charge separation effi- ciency. In addition to acetic acid, employing other acids, including HCl, HNO3, and H3PO4 for the post-treatment, could also improve the photoactivity of Fe2O3 photoanodes. As a comparison, other studies have indicated that the primary reason for the effectiveness of acid treatment should be the passivation of surface states50 or the suppression of back reac- tions.51 Apart from acid treatments, Zhang et al. reported the use of the alkaline solution for the modi?cation of Fe2O3.52 Spin-coating KOH solution on Fe2O3 followed by annealing could effectively modify the surface of Fe2O3 with numerous hydroxyl groups. The hydroxyl overlayer exhibited electrocatalyst-like properties, which accelerated water oxida- tion kinetics. Moreover, the valence band of the alkaline-treated Ti-doped Fe2O3 increased by 0.15 eV, indicating in situ forma- tion of a type II heterojunction along with the introduction of the hydroxyl-rich overlayer. In contrast to this method, the direct immersion of Fe2O3 in 1 M KOH was reported for self- passivation.53 In view of the passivating effect, improved donor density and increased surface charge transfer properties could be observed, which contributed to enhanced photoactivity. In addition to Fe2O3, photoelectrodes such as TiO2, CaTaO2N, and ZrO2 have also been treated with acid for PEC applications. Mao et al. reported the use of nitric acid for the treatment of TiO2 to introduce oxygen defects in the photo- anode.54 The induced oxygen defects could improve the intrinsic conductivity of the TiO2 photoanode, resulting in an enhancement in donor density. As a result, the acid-treated TiO2 exhibited a

10**photocurrent density of** 2.8 **mA cm?2 at** 0.**23 V** vs. Ag/ AgCl, **2**.5 **times higher than that of pristine**

TiO2. In comparison, the surface properties of CaTaO2N powders could be consider- ably altered with the treatment of aqua regia for only 20 s.55 As characterized by 1H and 14N solid-state nuclear magnetic reso- nance (NMR), the generation of abundant OH groups at the restructured surface of CaTaO2N could be detected. The acid modi?cation strategy resulted in an enhanced surface charge transfer efficiency in the CaTaO2N photoanode and yielded an increased photocurrent density by approximately four times. Another study by Rahman et al. demonstrated the effectiveness of using hydro?uoric (HF) acid for the treatment of ZrO2 hier- archical nanowires.56 The HF acid treatment enabled the generation of thin amorphous ZrO2 shells on crystalline ZrO2. As a result, an enhanced charge transport property and increased electrochemically active sites were obtained, along with the formation of Ovac. Consequently, the treated ZrO2 nanowires exhibited a signi?cantly improved

4**photocurrent density of** ?42.5 **mA cm?2 at** 0 **V vs. RHE, in comparison to** ? 12.9 **mA cm?2**

of pristine ZrO2 nanowires. Additionally, this simple post-treatment method could also be utilized to treat other photoelectrodes such as TiO2 and Ta2O5 for efficient PEC performance. 2.2.2 Contact-induced surface alternations. Contact- induced surface alternation using both inorganic and organic compounds

13**has been widely reported**. Wang **et al**. investigated **the** in?uence **of**

surface ?uorine-modi?cation on Fe2TiO5 pho- toanodes.10 A?er immersing Fe2TiO5 ?lms in a NH4F/H2O2 solution followed by an annealing process, Ti–F bonds on the surface could be created, as demonstrated by XPS analysis (Fig. 4a–d). The generated Ti–F bonds could facilitate the hole transfer process and approximately doubled the photocurrent density,

18**at 1.23 V vs. RHE. Another** report explored **the** syner- getic effects **of**

F- and Rh-based treatments on heterostructured Fe2TiO5/Fe2O3 photoanodes.57 Similar to the above, F- treatment also employed the NH4F/H2O2 immersion method followed by calcination, while Rh,F-treated samples were prepared by Rh- treatment—a photoassisted electrodeposition method. The F- treatment could modify the interface structure with the hydrogen-bond network for fast hole transfer, while the Rh- Fig. 4 (a) F

39**1s, (b**) Fe **2p, (c**) Ti **2p and (d) O 1s**

XPS spectra of pristine Fe2TiO5 (red line) and surface F-modified Fe2TiO5 (green line).10

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f) Tetrahedral [B(OH)4]? species as regulating ligand and passivator to accelerate hole transfer and reduce charge trapping: (e) without and (f) with borate modification.19 Modi- fied

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Authors. treatment enhanced catalytic performance. In addition to ?uorine ions, other common ions, such as phosphate (PO4?) and borate (BO3?) ions, can also be effective for surface modi- ?cation. Meng et al. reported the immersion of BiVO4

41**photo- anodes in a borate buffer solution**

at room temperature.19 Remarkably, the borate-treated BiVO4 photoanode exhibited

22**an onset potential** shi? **of** 320 **mV and**

a substantially enhanced

4**photocurrent density of** 3.5 **mA cm?2 at 1.23 V vs. RHE**, compared **to** 1.6 **mA cm?2** of **the** pristine **BiVO4**

. Their characterizations indicated

33**that the bulk** nature **of the** BiVO4 photoanode **remained unchanged** a?er **the**

post- treatment, while the reason for enhanced PEC performance was ascribed to the absorption of

28**tetrahedral [B(OH)4]? species near the active sites**, which served as **a** regulating ligand and passivator to accelerate hole transfer and reduce charge trap- ping during water oxidation reaction (Fig. 4e and f).

30**It is worth noting that the** surface **structure** may **not**

be so stable, as overnight immersion in pure water could undermine the PEC performance of the treated BiVO4. In another report, phosphate ions were exploited to functionalize Ti-doped Fe2O3 photo- anodes by a cost-effective dip-annealing method.58 The photo- anodes were post-treated with immersion into a Na3PO4 solution followed by calcination in N2. This phosphate func- tionalization not only lowered the onset potential by suppress- ing electron–hole recombination, but also improved surface water oxidation kinetics, resulting in an enhancement in photocurrent density. Likewise, Sahu et al. reported the co- modi?cation of Fe2O3 photoanodes by titanium doping and phosphate treatment.59 The co-modi?cation signi?cantly improved

5**the photocurrent density from 0**.45 **mA cm?2** of untreated Fe2O3 **to** 2.56 **mA cm?2**

of co-modi?ed Fe2O3, arising from the increased charge carrier density (10 fold) and improved charge transfer characteristic. With the introduction of light treatment, the interaction between phosphate ions and BiVO4 photoanodes was studied.60 A 25–30 nm thick layer was generated with a dip-and-pull method under illumination, which led to the formation of bismuth phosphate endowed with a negative charge. Interestingly, such a negatively charged structure may function as a passivation layer for the deactiva- tion of surface states of BiVO4, revealing the importance of selecting a suitable electrolyte for practical PEC water splitting. In addition to inorganic compounds, employing organic matter such as methanol, 1,2-ethanedithiol, and thioacetamide for chemical modi?cation is also efficacious. For example, Xiao et al. explored the roles of distinct surface defects generated by methanol or HCl treatments in Fe2O3 photoanodes.1 Interest- ingly, methanol treatment at 180 C for 10 h induced a hydrox- ylated surface on Fe2O3, while HCl treatment at 95 C for 1 h created abundant chemisorbed oxygen on the photoanode. Methanol treatment improved the charge carrier density and surface hydrophilicity of Fe2O3, resulting in enhanced photo- activity. In contrast, HCl treatment barely affected carrier density and hydrophobicity. Instead, surface states were altered with the treatment of HCl, which promoted surface charge transfer and suppressed bulk recombination of charge carriers, thereby lowering the onset potential (Fig. 5a). The photocurrent density of the photoanode was optimized to 3.0 mA cm?2 at Fig. 5 (a) Schematic illustration of surface states induced by methanol and HCl treatments as well as the combination with the cocatalyst FeCoW to enhance PEC performance.1

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) Room-temperature pho- toluminescence and time-resolved photoluminescence spectra of untreated and EDT-treated GaN nanowires.13 Reprinted with permis- sion from ref. 13,

18**2017 American Chemical Society. (c**) Schematic illustration **of the** formation mechanism **for**

grooved pyramid-like morphology (left), and the generation of various structures by maneuvering the rate of cation exchange with an increased amount of thiourea (right).23 Modified

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.

1**1.23 V vs. RHE** with **the** addition **of**

cocatalysts. Varadhan et al. employed 1,2-ethanedithiol (EDT) for the surface passivation of GaN nanowires.13 A 5 min EDT treatment followed by loading Pt cocatalyst could improve the charge carrier separation efficiency of the photocathode by changing its ?at-band and band-edge potentials. Additionally, the EDT treatment could also increase carrier lifetime by suppressing unfavorable surface –OH and –O bonds (Fig. 5b).

32**As a result, a** considerably enhanced **photocurrent of** ?31 **mA cm?2 at** ?0.2 **V** vs. **RHE** of **the**

EDT-treated GaN could be attained. Another study employed thioacetamide as an etching reagent to alleviate surface trap states and Fermi pinning in WO3 photoanodes, which resulted in a decreased onset potential.61 Moreover, the in?uence of additional loading of the cocatalyst FeOOH layer and introducing the passivating layer Ga2O3 were evaluated. The onset potential values of different structures indicated that the interfacial properties of photoelectrodes could greatly affect their PEC performance. These chemical modi? cation approaches have been shown to be effective in altering the photophysical and electrochemical properties at the surface/interface of photoelectrodes by, for example, creating new chemical bonds. Both inorganic and organic compounds are useful for enhancing metal-oxide as well as non-metal-oxide semiconductor photoelectrodes. Exploring the mechanism of these PEC enhancements can also promote our understanding of surface PEC water splitting reactions. 2.2.3 In situ ion exchange. Chemical treatments affect charge carrier behaviors of electrodes by altering surface states and surface physicochemical properties. From time to time, new materials/compositions are created onto pristine elec- trodes with chemical treatments, including the ion-exchange method. Recently, solution-based in situ ion exchange

42**has been regarded as an effective approach to** generate **the**

hetero- structure on pristine photoelectrodes. Note that this section does not include studies on the direct synthesis of photo- electrodes via ion exchange; for example, see ref. 62. As reported by Chong et al.,63 elemental Co was incorporated into a calcium hydroxyapatite structure (Ca10(PO4)6(OH)2, Ca- HAP) by immersing the Ca-HAP, which was coated onto Fe2O3, in a Co(NO3)2 solution. The resultant Co-HAP-loaded Fe2O3 exhibited a signi?cant enhancement (9.8 times) in photocurrent density, owing to the extraction of holes from Fe2O3 by PO43?, active Co sites for surface hole transfer, arising from the 2D structure of Co(OH)2, the electrochemically active surface area (ECSA) was maximized and larger electrode/ electrolyte interface was provided for reaction. The ECSA was increased from 0.051 mF cm?2 of Fe2O3 and 0.065 mF cm?2 of HAP/Fe2O3 to 0.13 mF cm?2 of Co-HAP/Fe2O3. Chen et al. fabricated a BiVO4/Bi2S3 heterojunction by immersing BiVO4- loaded conductive glass in a thiourea solution for a hydro- thermal reaction.64 By varying precursor sulfur, the convergence of Bi2S3 on BiVO4 nanorods could be tuned. The highest photocurrent density of the BiVO4/Bi2S3 heterojunction was 1.43

4**mA cm?2 at 1.23 V vs. RHE, compared to** 0.25 **mA cm?2 of** bare **BiVO4**, because of **the**

enhanced absorption by Bi2S3 and Table 2 Various chemical modification approaches to treat photoelectrodes

18**for PEC water splitting Photocurrent density** Materials Post-treatment (**a**

4**mA cm?2 at** b **V vs**

. g; d times) Ref. Acid and alkaline treatments Fe2O3 Ti-doped Fe2O3 Ti-doped Fe2O3 TiO2 CaTaO2N ZrO2 Ti-doped Fe2O3 Immersed in pure acetic acid for 5 min followed

37**by annealing at** 450 **C for 30 min in air**

Spin-coated with KOH, dried at 70

26**C for** 12 **h, and** calcined **at** 400 **C for** 2 h **in**

air Soaked in 1 M KOH at 80 C for 30 min Hydrothermally heated in 0.1 M HNO3 at 80 C for 1 h 0.2 g of CaTaO2N added into 4 mL of aqua regia stirred for 20 s Soaked in 0.01 M HF acid for 1 h Hydrothermally heated in 0.1 M HCl at 95 C for 1 h Contact-induced surface alternations Fe2TiO5 Immersed in 0.2 M NH4F with H2O2 at 60 C for 10 min,

5**followed by annealing at** 200 **C for** 20 min **in air**

Fe2TiO5/Fe2O3 Immersed in NH4F/H2O2 solution at 60 C for 5 min BiVO4 Immersed

36**in 0.5 M borate buffer (pH 9.3**

) for 12 h Ti-doped Fe2O3 Immersed in 0.2 M Na3PO4 for 10 min, air-dried at 100

26**C for** 1 **h, and** sintered **at** 250 **C for** 2 h **in**

N2 Ti-doped Fe2O3 Immersed in 0.5 M Na2HPO4 for 10 min, then annealed at 350 C for 1 h Ti-doped Fe2O3 Hydrothermally heated in 10 mL methanol at 180 C for 10 h GaN Immersed in 1,2-ethanedithiol for 5 min WO3 Immersed in 5 mg mL?1 thioacetamide at 80 C for 20 min In situ ion exchange Ca-HAPa coated Fe2O3 BiVO4 ZnO In2S3 Cu7S4 Immersed in 50 mL of 0.01 M Co(NO3)2 solution at 40 C for 40 min Hydrothermally heated in 12–24 mg mL?1 of thiourea in aqueous solution at 170 C for 6 h, followed by washing and vacuum-drying at 200 C for 2 h Immersed in 0.32 M Na2S aqueous solution, and heated at 60

C for 8 or 18 h in a water bath Solvothermally heated in a mixture (15 mM Cu(NO3)2 and 0–45 mM thiourea in ethylene glycol) at 200

31**C for** 12 **h, followed by annealing** at 400 C **for** 30 **min**

in Ar Cu7S4 mixed with 4 mL of toluene and then swi?ly adding to a well-mixed complex solution containing InCl3, followed by heating at 50 C for 2 h a Ca-HAP: calcium hydroxyapatite. 1.2; 0.2; Ag/AgCl; 4.0 49 2.14; 1.6; RHE; 2.3 52 3.7; 1.5; RHE; 1.8 53 2.8; 0.23; Ag/AgCl; 2.5 54 0.025; 1.2; RHE; 4.0 55 ?42.5; 0; RHE; 3.3 56 2.0; 1.23; RHE; 1.3 1 0.4; 1.23; RHE; 2.2 10 1.0; 1.0; RHE; 2.6 57 3.5; 1.23; RHE; 2.2 19 1.56; 1.23; RHE; 1.7 58 2.56; 1.23; RHE; 1.7 59 2.2; 1.23; RHE; 1.5 ?31; ?0.2; RHE; >31 0.27; 1.2; RHE; 1.2 2.25; 1.23; RHE; 9.8 63 1.43; 1.23; RHE; 5.7 64 0.60; 0.5; Ag/AgCl; 1.5 65 N/A 23 0.06; 0.3; RHE; N/A 66 the efficient charge transfer resulting from the type II hetero- junction. Another study revealed the preparation of ZnO/ZnS core/shell nanorods by immersing ZnO nanorods in a Na2S solution.65 As a result of such chemical sul?dation treatment, both the surface roughness of the ZnO/ZnS and the crystallo- graphic quality of the ZnOkZnS interface were improved. The ZnO/ZnS heterojunction exhibited a

4**photocurrent density of** 0.60 **mA cm?2 at** 0.5 **V vs**. Ag/AgCl, compared **to** 0.39 **mA cm?2** of **bare** ZnO **photoanode**

. Feng et al. reported the synthesis of a p- CuInS2 or n-CuIn5S8 junction by solvothermally heating In2S3 in a Cu(NO3)2/thiourea solution.23 By adjusting the amount of thiourea to control the cation exchange rate, the In2S3 could be controllably converted to various structures, including Cu1.81S, CuInS2/CuIn5S8, p-CuInS2, and n-CuIn5S8 (Fig. 5c). With the addition of cocatalysts Pt and CoOx on the p-CuInS2 and n- CuIn5S8, respectively, self-biased PEC water splitting could be realized. Another study revealed that, by immersing Cu7S4 nanocrystals in an In-included solution, hollow Table 3 Electrochemical treatments of photoelectrodes for improved PEC activity Materials Post-treatment TiO2 Electrochemically reduced at a bias (?1.3, ?1.5 or ?1.8 V) for 5–20 min in 1 M KOH supporting electrolyte TiO2 Reduced at a bias voltage of ?1.35 V in dark for 10–60 s in 1 M NaOH TiO2 Reduced at a

5**potential of ?0**.5 **V** vs. **RHE in 0**.05 **M**

H2SO4 for 35–55 min Ni,Si-codoped TiO2 Cathodically polarized at 5 V for 10 min in various electrolytes (0.5 mM H2SO4, 0.3 M Na2SO4 or 0.1 M KOH) TiO2 Cathodically reduced at 4 V for 20 min

27**in 0.1 M Na2SO4** TiO2 Reduced **at a potential of** ?1.8 V **vs. Ag/AgCl**

in 1 M NaOH for 10 s BiVO4 Cathodically reduced at a potential of ?0.1 V vs. RHE

39**in 1 M potassium borate electrolyte (pH 9.5**

) Mo-doped BiVO4 Reduced at various potentials (?0.6, ?0.

24**8, ?1.0 and ?1.2 V** vs. **Ag/AgCl**

) for 5 min

27**in 0.1 M Na2SO4** BiVO4 Reduced **at a potential of** ?0.8 V **vs. Ag/AgCl**

in 0.5 M Na2SO4 for 30 s Nb,Sn-codoped Fe2O3 Electrochemically activated by Ti-doped Fe2O3 Fe2O3 WO3 ZnO GaN p-InP a three-times cathodic scanning (

22**from 1.0 to 0**.2 **V vs. RHE**

) followed by a three-times anodic scanning (

22**from 1.0 to** 2.2 **V vs. RHE**

) in 1 M KOH Reduced

40**at a potential of** ?1.2 **V vs**. SCE **for** 1000 s in **1**

M NaOH Potentiostatically reduced at ?1.5 to ?0.8 V for 10 s, or cyclically reduced between ?0.8 V and ?1.5 V, followed by a stabilization process Reduced

1**at a potential of ?0**.8 **V vs. Ag/AgCl**

in 0.5 M Na2SO4 for 30 s

2**followed by annealing at** 300 **C for** 5 **min**

using a hotplate Reduced at a potential of ?1.2 V vs. Ag/AgCl in 0.5 M Na2SO4 for 30 s Electrochemically etched at a voltage of 15 V for 10 min in an ethanol/hydro?uoric acid solution Cathodically reduced at potentials from open-circuit potential to ?0.06 V under illumination with intermittent passivation under dark condition

15**Photocurrent density** (a **mA cm?2 at** b **V vs**

. g; d times) 0.53; 0.6; Ag/AgCl; 3.1 0.70; 0.4; Ag/AgCl; 2.0 2.5; 1.23; RHE; 3.1 2.41; 0; Ag/AgCl; 2.2 2.74; 0; Ag/AgCl; 3.4 2.4; 0; Ag/AgCl; 3.2 2.5; 1.23; RHE; 10 4.3; 1.5; RHE; 4.3 0.21; 1.0; Ag/AgCl; 3.5 3.05; 1.23; RHE; 1.6 0.62; 0.6; SCE; 1.93 N/A 0.53; 1.0; Ag/AgCl; 6.6 1.2; 1.0; Ag/AgCl; 1.3 4.0; 1.2; Ag/AgCl; 5.3 25; 0; RHE; 8.3 Ref. 76 77 78 79 81 82 4 83 82 84 nanododecahedron-structured CuInS2 nanocrystals could be generated.66

1**As a result of the** enhanced **light-harvesting** prop- erties, **the**

CuInS2 photocathode showed an optimal photocur- rent

11**density of 0**.06 **mA cm?2 at 0**.3 **V vs. RHE**

. These chemical modi?cation approaches have been summarized in Table 2. It can be observed that various surface modi?cation methods can substantially enhance the PEC activity of various photoelectrodes. Noticeably, beyond improving photoactivity, the chemical modi?cation also is of crucial signi?cance in aiding our understanding of the inter- action among the surface structures of photoelectrodes, elec- trolyte composition, and light irradiation. 3. Electrochemical and irradiation- based treatments 3.1 Electrochemical treatments Compared to chemical treatments, electrochemical treatments are not only simple and effective, but also can be performed in a controllable and reproducible manner. It is worth noting that the electrochemical reaction process could be precisely tuned and optimized by adjusting operation parameters. The elec- trochemical treatment methods have been summarized in Table 3. As a representative of photoelectrodes, anatase and rutile TiO2 photoanodes have been modi?ed with various methods. Several fabrication approaches, such as hydrogenation,67–70 plasma treatments,71–74 and chemical reduction,70,75 have been con?rmed to create self-doped Ti3+-incorporated TiO2. In addition to these methods, electrochemical reduction as an effective approach has been studied to improve the photophysical and photo- electrochemical properties of TiO2. Song et al. prepared Ti3+-self- doped TiO2 by reducing it at cathodic potential.76

29**Owing to the** enhanced **light absorption**, improved conductivity **and** increased **charge**

transfer rate, the self-doped TiO2 exhibited an enhanced

11**photocurrent density of 0**.525 **mA cm?2 at 0**.6 **V vs. Ag/AgCl**

, 3.1

10**times higher than that of pristine TiO2**

nanotubes. Signi?cantly, another study demonstrated that the surface TiIIIO(OH) structure could be created with the assistance of electrochemical reduction at a bias more negative than the ?at-band potential of TiO2.77 It is interesting to note that, unlike previously reported reduced surface states, the electrochemically proton-doped TiO2 photo- anode exhibited an increased surface state density (i.e., Ti–OH), which served to capture photogenerated electrons and suppress charge carrier recombination. The as-prepared TiO2 exhibited

11**a photocurrent density of 0**.70 **mA cm?2 at 0.4 V vs. Ag/AgCl**

, two

41**times higher than that of bare** TiO2. **In** addition, **it** was proved **that**

electrochemical reduction could induce a type II structure, which enhances charge separation and transport78 as well as creates self-doped Ti3+ accompanied by increasing the amount of Ovac in the TiO2 photoanode.79–81 These studies validate that electrochemical treatments not only can affect the surface/ interface properties of TiO_2, but also improve its bulk attributes from time to time. Wang et al. reported the electrochemical reduction of various metal oxide photoanodes, including WO_3, TiO_2, $BiVO_4$, and Fig. 6 (a) UV-visible spectra, (b) electrochemical impedance spectra, (c) Mott–Schottky curves, and (d) chopped J–V curves of bare $BiVO_4$ (I) and electrochemically reduced $BiVO_4$ (II) in 1 M KPi buffer with 0.2 M Na_2SO_3 (pH 9.5).4

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f) TEM images for Fe_2O_3 nanorods (e) before and (f) after electrochemical reduction, showing more individual nanowires.15 Modified

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Owner Societies. ZnO.82 With the electrochemical treatments, Ovac could be controllably introduced in these photoanodes. As a result of the improved charge separation and injection properties, all these electrochemically treated photoanodes exhibited substantially improved PEC performance. Another study comprehensively explored the effects of electrochemical reduction on the pho- toactivity of $BiVO_4$ photoanodes.4 A?er electrochemical reduc- tion

1**at 0**.1 **V vs. RHE for**

only 150 s, the as-treated $BiVO_4$

1**exhibited a 10-fold increase in photocurrent density**

. The signi?cantly

1**enhanced PEC activity** was **attributed to the** generation **of**

Ovac, which substantially facilitated bulk and surface charge separation (Fig. 6a–d). In another study, by imposing Mo-doped $BiVO_4$ photoanodes with various bias potentials, the contrary roles of as-created Ovac and quasioxygen vacancies were explored.83 It was revealed that the Ovac gener- ated

1**at a bias of** ?1.2 **V vs. Ag/AgCl** were detrimental **to**

PEC performance. In comparison, the quasioxygen vacancies formed

1**at a bias of ?0.8 V vs. Ag/AgCl**

could increase charge carrier density and thus improve the

2**photocurrent density** to **4**.3 **mA cm?2 at 1**.5 **V** vs. **RHE, 4.3**

4**times higher than that of** untreated **BiVO4**

photoanodes. For Fe2O3 photoanodes, the passivation of an Nb- and Sn- codoped Fe2O3 photoanode using an electrochemical activa- tion method was realized.84 A?er cathodic scanning three times, followed by anodic scanning three times, the as-treated Fe2O3

21**exhibited a** photocurrent **density of** 3.05 **mA cm?2 at 1.23 V** vs. **RHE, which is** 1.6 **times higher than that of bare**

Fe2O3. The

10**enhanced performance could be attributed to the**

etching of surface dangling defects, the enriched Nb–O and Sn–O bonds that passivated the surface states, and the creation of Fe2+ and Ovac, which improved conductivity. In spite of the effectiveness of employing electrochemical reduction treatment to boost Fe2O3, the fundamental mechanism has not been well-understood. In view of this, Zhang et al. reported their work in which they constructed a new charge carrier dynamics model to explore surface-state mediated charge transfer and recom- bination.85 Their results indicated that a new type of surface state, generated by the electrochemical reduction of Fe2O3. The new surface state is peaked at 0.1 VSCE which is 0.05 VSCE lower than the bare Fe2O3. Such shi? in surface state favours the overlapping of unoccupied surface state of electrodes and ?lled levels of the redox couple, leading to increased charge transfer rate constant and enhanced surface water oxidation process. Additionally, the negatively shi?ed ?at-band potential resulted in reduced electron density,

20**leading to the reduction of the** charge **recombination rate**. By contrast, **the**

report by Cibrev et al. pointed out

20**that the enhanced PEC performance of**

elec- trochemically reduced Fe2O3, an eight-fold increase in transient photocurrent, should be primarily ascribed to the n-type doping (e.g., the generation of Fe2+ or other polaron species) as well as to the change in ?lm morphology (Fig. 6e and f).15 In addition to metal oxide photoelectrodes, III–V semi- conductors can also be tailored using electrochemical treat- ments, and the reports of n-GaN and p-InP are two examples.86–88 Cao et al. reported the electrochemical etching of GaN-based thin ?lms in an ethanol/hydro?uoric acid solution, with the intention of peeling off mesoporous InGaN/GaN layers.86 A?er transferring the free-standing GaN-based layers on the n-Si substrate, the as-prepared photoanode exhibited a low turn-on voltage and high efficiency, which could be attributed to the increase of surface area and the relaxation of stress. The etched sample was reported with speci?c area (SBET) with 3.97 m2 g?1. In another study by Goryachev et al.,87 the combination of cathodic scanning with open circuit/dark resting for the treatment of p-InP photocathodes allowed a 27- fold increase in photocurrent density. Moreover, with an online electrochemical mass spectrometry technique, the in?uence of the employed electrolytes (i.e., H2SO4 or HCl) on the surface passivation was examined. It appeared that InOx and InPOx at the material surface could be generated when using H2SO4 as an electrolyte, while insoluble InCl was formed when using HCl as an electrolyte. The results indicated the need to evaluate fara- daic efficiencies of reactions (e.g., HER and OER) using chemical-speci?c techniques. 3.2 Irradiation-based treatments Light/irradiation treatments are effective for modifying photo- electrodes, such as BiVO4 and Fe2O3. This facile method exhibits simplicity and effectiveness and can avoid extra complex material processing steps in the optimization of practical PEC water splitting systems. Irradiation treatments for BiVO4 photoanodes have been presented. For instance, a?er exposure to UV radiation in the air for 20 h, the surface of BiVO4 could be cured.89 UV light-induced passivation of surface states (e.g., dangling oxygen) reduced the charge trapping possibility, as re?ected by an increased charge carrier density. Additionally, the cathodic shi? of ?at-band potential also contributed to the wide separation of

15**quasi- Fermi levels of electrons and holes, which**

bene?ted charge separation. As a result, the as-treated BiVO4 exhibited a photo- current

2**density of 1**.1 **mA cm?2 at 1**.2 **V** vs. **RHE**, 2.2 times **higher than that of bare**

BiVO4, accompanied by a remarkable shi? of onset potential (400 mV). Likewise, illuminating BiVO4

1**in a 0.1 M** KPi buffer with **AM 1.5 G**

light under an open-circuit condition,5 known as photocharging, could induce a 4.4-fold

34**increase in photocurrent density** (3.3 **mA cm?2 at 1.23 V** vs. **RHE for**

as-illuminated BiVO4)

11**and a cathodic** shi? **of onset potential**

(300 mV). It was shown

33**that the light-induced** passivation **of surface**

states could result in an increased photovoltage by eliminating detrimental Fermi level pinning (Fig. 7a and b), responsible for the enhanced PEC performance. Their follow-up study further revealed that the pH of exposed electrolytes has a great in?uence on such photocharging effects.9 Illuminating BiVO4 photoanodes at pH 10 under open-circuit conditions achieved

4**a high photocurrent density of** 4.3 **mA cm?2 at 1.23 V vs. RHE**, while **the** photocurrent density **of** processed BiVO4 photoanodes at pH 4 remained unchanged, as 1.0

2mA cm?2 at 1.23 V vs. RHE. It has been suggested that the

formation of Fig. 7 (a) Electronic band diagrams for BiVO4

6under open-circuit conditions: dark, without illumination

; light, with illumination; SuS, with photocharging-induced surface states. (b) Equilibrium potentials and photovoltage values of BiVO4 photoanodes under open-circuit conditions. Untreated sample in 0.1 M KPi electrolyte (H2O) or a hole scavenger (H2O2), or photocharged sample in 0.1 M KPi electrolyte (H2Ophoto).5

14Reprinted with permission from ref. 5, copyright 2016 The Royal Society of Chemistry. Fig. 8 (a

)

12Band diagrams of BiVO4 in the dark and under illumination before and after photocharging treatment, including the simplified photocharging mechanism model

.9

7Reprinted with permission from ref. 9, copyright 2017 The Royal Society of Chemistry. (b

)

6Effect of photocharging on the bandgap region and the Fermi level of BiVO4. Hydroxide (dark sample) and bismuth borate (photocharged sample) surface layers have a valence band closer to the Fermi level, intro- ducing band bending at the surface. The band bending directs elec- trons toward the bulk of BiVO4, leading to a reduced electron concentration in the space charge region for photocharged BiVO4. The

6effect of photocharging on a BiVO4 photoanode in contact with an electrolyte under illumination is shown. The additional band bending improves the charge separation, leading to the unrivaled PEC properties of the photocharged BiVO4

.22

13**Reprinted with permission from ref**. 22, **copyright 2019 American Chemical Society**. photoanodes in **a**

Na2SO3/KBi solution for only 10 min under illumination could induce considerable amounts of surface Ovac at the surfaces.91 Because these surface Ovac could contribute to the formation of interband states, as indicated by DFT calcu- lations,

19**improved charge** separation **efficiency at the** BiVO4- kelectrolyte **interface**

was observed. As a result, the photoetched BiVO4

2**exhibited a photocurrent density of 3**.55 **mA cm?2 at** 0.6 **V** vs. **RHE**, two times **higher than** that **of**

untreated BiVO4. In a similar way, Yin

34**et al. reported the use of** sul?te **to**

treat BiVO4 photoanodes under illumination.93 It was revealed that the photogenerated holes could be consumed by sul?te ions that were oxidized to sulfate ions, while the remaining electrons could reduce V5+ to V4+ and thus indirectly create Ovac in BiVO4 photoanodes, rather than directly invoking the formation of Ovac by reaction between holes and lattice oxygen. Remarkably, the self-reduced BiVO4

2**exhibited a photocurrent density of** 3.18 **mA cm?2 at 1.23 V** vs. **RHE**, compared **to 1**.44 **mA cm?2**

of the bare one. In addition to BiVO4, other photoelectrodes, such as Fe2O3, WO3, CuWO4, and TiO2, can also be distinct a?er irradiation treatments. Xie et al. investigated the in?uence of stability tests under long-term illumination on the PEC performance of Ti- doped Fe2O3.6 Their results indicated an improvement in photocurrent density and a cathodic shi? of onset potential a?er illumination for 12–70 h. The enhanced photoactivity was attributed to the generation of FeOOH, which acted as a cocat- alyst to facilitate hole transfer (Fig. 9a). In spite of this, in contrast to the generation of Fe2+, Deng et al. revealed that high-valence Fe(IV), created by illumination for 30–150 min

19**at a bias of 1.23 V vs. RHE**

and detected by O

1**K-edge X-ray absorption spectroscopy**

(XAS) (Fig. 9b), should be responsible for the

12**active water oxidation intermediates and/or the** change **of surface**

chemistry, which enhanced the electrocatalysis reaction (Fig. 8a), should be the reasons for the boosted PEC water splitting performance. Firet et al. further investigated the surface chemistry of BiVO4 during photocharging.22 Notably, by employing

6**ambient-pressure X-ray Raman scattering**

spectros- copy as a tool, the researchers demonstrated that a BiVO4 surface could adsorb electrolyte anion species, generating

6**a bismuth borate layer under** illumination. **The**

light-induced heterojunction structure could lead to

33**additional band** bend **in the space charge region**

, thus resulting

6**in an improved charge separation** efficiency **and** a suppressed **charge**

recom- bination rate (Fig. 8b). Another study particularly employed

6**intensity-modulated photocurrent spectroscopy (IMPS) to investigate the** impact **of**

photocharging on both bulk and surface properties of BiVO4.90 With this technique, the 1.91-

7**fold increase in the photocurrent density at 1**.2 **V** vs. **RHE** has been ascribed **to**

a 45% improvement in surface charge transfer efficiency as well as to a 46% improvement in bulk charge separation efficiency. Additionally, two examples are presented to demonstrate the importance of an immersion solution during the photocharging process.91–93 As reported by Feng et al., immersing BiVO4 Fig. 9 (a) XPS O 1s spectra of Ti-doped Fe2O3 photoanodes after 18 and 70 h stability testing and photoelectrochemically deposited FeOOH on Ti-doped Fe2O3.6

15**Reprinted with permission from ref.** 6, **copyright 2018 American Chemical Society. (b**

) O K-edge XAS spectra of pristine Fe2TiO5/Fe2O3 film (black curve), a photocharged Fe2TiO5/ Fe2O3 film for 60 min (red curve), and a discharged Fe2TiO5/Fe2O3 film for 10 min (blue curve), respectively. (c) Schematic illustration of photocharging and discharging of Fe2TiO5/Fe2O3.20 Modified

1**with permission from ref**. 20, **copyright** 2018 **American Chemical Society**. increased **photocurrent density**

.20 Importantly, the Fe(IV) species could restore to Fe(III) at light switch-off, pointing out the importance of exploring effective methods to preserve the created advantageous surface structures (Fig. 9c). Li

2**et al**. examined **the impact of** UV light exposure **on the PEC** performance **of**

WO3 photoanodes.94 A?er UV irradiation in the air for 4 h, the UV-radiated WO3 exhibited

10**a photocurrent density of** 0.69 **mA cm?2 at 1.23 V** vs. **RHE**, 1.3 times **higher than that of**

untreated WO3. Different from the occurrence of surface chemistry changes in photoelectrodes such as BiVO4 (the formation of bismuth borate)22 and Fe2O3 (the generation of FeOOH or Fe(IV)),6,20 this work revealed that the light exposure only led to a high ?lm porosity and thus a

30**high speci?c surface area, which is** responsible **for**

the enhancement in photoactivity of WO3. The surface area was not measured, the increasement of surface area was determined by the porous formation on SEM images. In another work, Breuhaus-Alvarez et al. analyzed the interaction between the photochromism effect and PEC prop- erties of WO3 photoanodes.95 It was demonstrated that the PEC decay of WO3 should be related to the change of surface chemistry instead of to the dissolution of WO3 itself, because the PEC performance of WO3 photoelectrodes could be fully recovered by illumination under the open-circuit condition in the electrolyte. The report highlighted the importance of exploring the in?uence of intercalation/deintercalation behav- iors on photoelectrodes. Photocharging treatments could also enhance the photo- activity of CuWO4.96 Prolonged exposure to 1 sun illumination for 15 h doubled the photocurrent density of CuWO4

1**at 1.23 V vs. RHE. The** formation **of a**

heterostructured copper borate layer

6**at the** CuWO4 **surface, which** facilitated **charge separation and suppressed** charge **recombination**, should be **the** reason for **the**

enhanced photoactivity. This work, together with other photocharging studies, suggests a complex metal oxide elec- trodekelectrolyte interface,6,22 demanding more efforts to study interfacial properties for realizing practical PEC water splitting. Additionally, pulsed laser irradiation could also be useful for the treatment of photoelectrodes, such as TiO2 nanotubes.97 The as-optimized TiO2 photoanode exhibited a 1.

29**6-fold increase in photocurrent density**, which **was** ascribed **to**

an increased charge carrier donor density and reduced deep trapping states. These irradiation-based treatments are summarized in Table 4. It can be seen that the surroundings of the photoelectrodes (e.g., air or electrolyte of different compositions) during the irradiation treatments have a signi?cant in?uence on the resultant PEC responses. This indicates that bene?cial Table 4 Various irradiation-based treatments of photoelectrodes for PEC applications Materials BiVO4 BiVO4 BiVO4 BiVO4 BiVO4 BiVO4 Ti-doped Fe2O3 Fe2TiO5/Fe2O3 WO3 CuWO4 TiO2 Post-treatment Exposed to UV radiation (185 and 254 nm, 10 mW cm?2) in the air for 20 h Exposed to AM 1.5 light in

38**a 0.1 M phosphate buffer (pH 7**.2) **under**

open-circuit condition for 10 h Exposed to

16**AM 1.5** light **in a** 0.1 **M** phosphate–**borate**–acetate **buffer**

(

12**pH 4, 7** or **10**) under **open-circuit** condition **for**

10 h Illuminated by AM 1.5 light (1 sun) in a 0.5 M phosphate buffer under open-circuit condition for 3 h Illuminated by

16**AM 1.5 G** light **in a 1 M** potassium **borate**

containing 0.2 M Na2SO3 for 10 min without external bias Irradiated by

16**AM 1.5 G** light **in a** 0.2 **M** Na2SO3 solution **for**

40 min Exposed to 100 mW

7**cm?2** light **in 1 M** NaOH **at 1.23 V** vs. **RHE**

for 70 h Exposed to 1 sun light

29**in 1 M** NaOH **at 1.23 V vs. RHE**

for 30–150 min Exposed to UV radiation (185 and 254 nm, 10 mW cm?2) in air for 4 h Exposed to

16AM 1.5 light in a 0.3 M borate buffer

with 0.1 M NaClO4 (pH 7.5) for 15 h under open-circuit condition Irradiated by a 248 nm pulsed laser when immersing in DI water for 60 s a Measured in

51 M potassium borate buffer (pH 9.0) containing 0.2 M

Na2SO3.

15Photocurrent density (a mA cm?2 at b V vs

. g; d times) 1.1; 1.2; RHE; 2.2 3.3; 1.23; RHE; 4.1 4.3; 1.23; RHE; 3.9 1.0; 1.23; RHE; 2.0 3.55a; 0.6; RHE; 2.0 3.18; 1.23; RHE; 2.2 0.32; 1.23; RHE; 1.2 2.02; 1.23; RHE; 1.2 0.69; 1.23; RHE; 1.3 0.06; 1.23; RHE; 2.0 0.36; 1.23; RHE; 1.6 Ref. 89 5 9 90 91 97 structures could be generated as the photochemical reactions transpire. On the ?ip side, it should be acknowledged that, in general, these structures may not be so stable when standing still in the electrolyte under dark/illumination conditions. Exploring advanced techniques to scrutinize the formation and diminishing of the structures and seeking effective methods by which to preserve them are therefore of crucial importance. 4. Post-annealing treatments Post-annealing modi?cation is always an effective method for changing the surface and bulk properties of photoelectrodes. In this section, gas-based annealing under various atmospheres, such as H2,7,98–107 NH3,18,108–114 N2,115–117 Ar,118,119 CO,120 O2,24,121,122 and (NH4)2S,123 and other unique annealing techniques including solid-based annealing, employing S,124 Mg16 and Zn,125,126 and ?ame annealing11,127 as well as vacuum anneal- ing21,128 have been introduced. It should be noted that this section does not include studies of the two-step annealing process, for instance, dip-coating followed by annealing,129 to avoid complexity and confusion. 4.1 Gas annealing 4.1.1 Hydrogen annealing. Since the report of Chen et al. in 2011,130 hydrogen annealing, also called hydrogenation, has been extensively explored for the treatment of TiO2. In general, the enhanced photoactivity of hydrogenated TiO2 can be ascribed to extra visible light absorption as well as to the opti- mized surface structures for reducing charge recombination and enhancing charge transfer.131–136 By contrast, Mohajernia et al. reported the annealing of TiO2 in the Ar/H2 atmosphere.105 They found that the enhanced PEC performance should be dominantly attributed to strongly improved conductivity (i.e., semimetallic properties) as a result of the formation of Ovac and Ti3+, and slightly due to the enhancement in light absorption. Another study also reported the high conductivity of anatase TiO2 post-annealed in the Ar/H2 atmosphere.106 High-temperature annealing at 650–850 C not only induced the creation of Ovac and Ti3+ species but also rendered the generation of various phases, including Ti2O3, TiO, Ti4O7, and rutile TiO2. Owing to limited interfacial charge recombination and a two-order enhancement in charge carrier density, the as- prepared TiO2 photoanode exhibited a 2.4-fold increase in photocurrent density. Recently, Liu et al. compared the stability of hydrogenated and cathodically reduced TiO2 photoanodes.107 It was revealed that black TiO2, resulting from hydrogenation treatment, was of high stability during an electrochemical oxidation test. In comparison, the same experiment could easily degenerate cathodically reduced TiO2. The study of Liu et al. proves the reliability of post-annealing treatments. In addition to TiO2, photoelectrodes such as WO3, SrTiO3, and ZnFe2O4 could be hydrogenated as well. Zhang et al. revealed that surface Ovac in WO3, created by hydrogenation,

19could serve as recombination centers for photogenerated charge carriers

.7 Interestingly, an ozone treatment was employed to cure these surface defects while reserving bene?- cial bulk Ovac (Fig. 10a). The treatments eventually resulted in a cathodic shi? of

2**0.15 V and a photocurrent density of** 2.25 **mA cm?2**

(Fig. 10b). The introduction of Ovac for intrinsic doping Fig. 10 (

7**a) Schematic of the synthesis process of**

H2-annealed WO3 (H–WO3), H2-annealed WO3 followed by ozone treatment (HO–WO3), and only ozone-treated WO3 (O–WO3), and (b) J–t curves of bare WO3, H–WO3, HO–WO3, and O–WO3 photoanodes

35**under AM 1.5 G at 1.23 V vs. RHE**

.7

14**Reprinted with permission from ref**. 7, **copyright** 2018 **The Royal Society of Chemistry**. (c) **The** crystal phase **of**

generated nitrated products from Nb2O5 depends on O2 concentration and reaction temperature in the nitrogen annealing process.18

7**Reprinted with permission from** ref. 18, **copyright** 2018 **Elsevier Ltd**. (d) **Schematic illustration of** two routes for **the**

formation of CuO from Cu2O.24

3**Reprinted with permission from ref**. 24, **copyright** 2019 **Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim**

. could enhance the PEC activity of photoelectrodes. Also, hydrogen intercalation could provide an opportunity to tune the absorption characteristics and charge carrier behaviors in photoelectrodes. In the study by Gu et al., the synergetic effects between Ovac and intercalated hydrogen in WO3 were investigated.101 Ovac was generated by hydrogenation treatment, while a subsequent two-step photoelectrochemical treatment was employed to realize hydrogen intercalation. Owing to boosted spatial charge separation efficiency resulting from oxygen- de?cient defects and hydrogen-intercalated structures, the as- treated WO3 photoanode

1**exhibited a high photocurrent density of 2**.94 **mA cm?2 at 1.23 V vs. RHE**

. Hydrogenation could also drive the conversion of the WO3 semiconductor to a semi- metallic compound,102 similar to that in the report of TiO2.106 The creation of Ovac, as a result of the hydrogenation, not only increased conductivity but also narrowed the

42**band structure of the photoanode**, allowing **the**

absorption of infrared light. The as-produced WO3 exhibited a

8**photocurrent density of 0**.21 **mA cm?2** 1.2 **V** vs. **Ag/AgCl**

under infrared light and a dark current

10**density of 0**.14 **mA cm?2**. Yan **et al**. investigated **the**

synergistic effect of combining heterojunction with hydrogenation.99 The as-prepared hydrogenated SrTiO3/TiO2 heterojunction exhibi- ted

7**a photocurrent density of** 0.48 **mA cm?2 at 1**.0 **V** vs. SCE, **3**.0 times **of**

that of hydrogenated TiO2 and 1.

1**5 times** of **that of bare** SrTiO3/**TiO2**

. The enhanced

7**PEC performance was** due **to the improved**

light absorption as well as to the increased charge carrier density. Kim et al. presented a series of strategies to process ZnFe2O4 photoanodes.100 Hydrogen

5**annealing at** 200 **C for 2 h**

, as one of these strategies, improved the photocurrent density

5**from 0.22 mA cm?2 to 0.79 mA cm?2 at 1.23 V** vs. **RHE**, owing to **the**

generated Ovac, which increased majority carrier density. As summarized in Table 5, hydrogen annealing is an effective and robust approach for modifying various photoelectrodes. It is widely accepted that this treatment can easily introduce surface and/or bulk Ovac in photo-responsive materials, bene?ting charge transport and transfer. 4.1.2 Annealing in other gases. Ammonia (NH3) is a useful chemical for realizing the nitridation of various photo- electrodes, such as Ta2OxNy,109 NbON,18 SrNbO2N,108 Ta3N5 (ref. 113) and TiO2.114 Zhang et al. investigated the roles of internal electric ?elds and charge transport behaviors in type II Ta2OxNy/ TiO2 heterostructures obtained by the ammonization of Ta2O5/ TiO2.109 The as-prepared

Ta2OxNy/TiO2 was endowed with improved hydrophilicity, decreased overpotential, as well as enhanced bulk charge separation and transport properties.

4**As a result, the as-prepared photoanode** exhibited **a photocurrent density of** 1.32 **mA cm?2 at 1.23 V vs. RHE**

, 12 times and 4.

19**3 times higher than that of bare**

TiO2 and Ta2O5/TiO2 photo- electrodes, respectively. Another study explored the role of small amounts of oxygen mixed in ammonia.18 Interestingly, NbON (of Nb5+) could be generated with the presence of 0.05–0.40% oxygen during the nitridation of Nb2O5 (Nb5+). The mixed oxygen avoided the generation of unfavorable NbOxNy (Nb2+ and Nb3+) resulting from the reduction of Nb, proving the relevance between oxygen and the synthesis of oxynitrides (Fig. 10c). The study of Tamura et al. provided a special path for realizing the nitridation of photoelectrodes. Kodera et al. examined and compared the nitridation mechanisms of Sr2Nb2O7 and SrNbO3 to SrNbO2N.108 It was shown that the reaction between Sr2Nb2O7 and NH3 involved both the intro- duction of nitrogen and the extraction of oxygen, leading to lattice shrinkage and thus to a porous structure. In comparison, the nitridation of SrNbO3 only introduced the N element into the photoelectrode, resulting in lattice expansion and phase separation. In another work, Ta3N5 photoanodes were prepared from Ta foil by an electrochemical anodization method fol- lowed by post-annealing in a N2/NH3 gas mixture.113 Annealing at a temperature of 1000 C resulted in the highest photocurrent density, due to high crystallinity, broad light absorption, as well as the formation of a conductive interlayer between substrates. In addition to nitridation, ammonia annealing has the ability to motivate the chemical reduction of photoelectrodes without the introduction of elemental nitrogen.

30**For example**, Xu **et al. demonstrated** that **the** post-annealing **of**

TiO2 in Ar/NH3 could introduce Ovac and Ti3+ species in the photoanode without concurrent nitrogen doping,114 similar to the reported WO3?x by Liu et al.137 As a consequence of enhanced visible light absorption, increased charge carrier density and reduced ?at- band potential, the as-obtained TiO2 exhibited a four-fold enhancement in photocurrent density. The work of Xu et al. clari?ed the contribution and roles of exclusive Ovac without substitutional N dopants. Various gases, such as CO,120 N2,115 Ar,118,119 and O2,24,121 can be used for efficient post-synthetic annealing treatments. Zhang et al. investigated H2 or CO as an annealing gas for the treat- ment of BiVO4.120 The H2 annealing primarily introduced hydrogen donors in BiVO4, which improved minority carrier (i.e., holes) transport. In contrast, CO annealing exclusively induced Ovac, resulting in enhanced majority carrier (i.e., elec- trons) transport. Owing to the decreased polaron hopping barrier, the conductivity of the CO-annealed photoanode was improved, thus promoting PEC responses. It is extensively recognized that broadening light absorption and improving charge separation efficiency should be the main contributions of Ovac. In spite of this, Lv et al. especially explored the role of Ovac in charge injection.115 They introduced Ovac in TiO2 by a one-step annealing treatment. Both the theoretical and experimental studies proved that Ovac chie?y increased elec- trochemically active surface area and reactivity, which acceler- ated hole transfer and reduced overpotential, ?nally resulting in a 5.8-fold increase in photocurrent density. Seo et al. explored a new route by which to fabricate high-performance BaNbO2N photoanodes,118,119 which included moderate nitridation fol- lowed by post-annealing in Ar ?ow. The as-prepared Ar- annealed BaNbO2N exhibited a 5-fold enhancement in PEC performance, which should be ascribed to increased crystal- linity and reduced surface defect density. In comparison, post- annealing BaNbO2N in NH3 could increase crystallinity but unfavorably increased the number of surface defects. Wang et al. annealed Cu2O photocathodes in pure oxygen to generate copper vacancies in CuO (Fig. 10d).24 Both theoretical and experimental results indicated the formation of metal vacancies in CuO. As a result of enhanced majority carrier density and Table 5 Various post-annealing treatments for photoelectrodes Photocurrent density Materials Post-treatment (a mA cm?2 at b V vs. g; d times) Ref. Hydrogen annealing TiO2 Annealed in H2 (10% in Ar) at 450–550 C TiO2 Annealed in H2 (5% in Ar) at 650–850 C for 5–120 min WO3 Annealed in H2 (60 sccm) at 350 C for 10–60 min, followed by O3 treatment (40 sccm) at 100 C for 10–60 min WO3 Annealed in H2 (5% in Ar, 100 mL min?1) at 400

31**C for 2 h, followed by**

electrochemically oxidized at 1.5 V vs. Ag/AgCl under light for 4 h, and then reduced

1**at ?0**.5 **V vs. Ag/AgCl under**

dark for 30 s WO3 Annealed in pure H2 (20 mL min?1) at 250–450 C for 20–360 min SrTiO3/TiO2 Annealed in pure H2 at 300–400 C for 30 or 60 min ZnFe2O4 Annealed under H2 atmosphere at 200 C for 2 h Ammonia annealing Ta2O5/TiO2 Annealed in NH3 (100 mL min?1) at 500 C for 30 min Nb2O5 Annealed in NH3/O2/N2 (20% of NH3 and 0–0.80% of O2, 500 sccm) at 600–750 C for 1 h Sr2Nb2O7 0.5 g of Sr2Nb2O7 heated under NH3 (250 mL min?1) at 900 C for 1–40 h SrNbO3 0.5 g of SrNbO3 heated under NH3 (250 mL min?1) at 900 C for 1–40 h TaOx Annealed in NH3 (10% in N2, 40 mL min?1) at 600–1000 C for 3 h TiO2 Annealed in NH3 (100 sccm) at 450 C for 7.5 min

5**followed by annealing** in Ar **at** 450 **C for** 1–4 **h** Annealing **in**

other gases BiVO4 Annealed in pure CO (20 sccm) at 300 C for 20 min TiO2 Annealed under N2 atmosphere at 800 C for 2 h BaNbO2N Annealed in pure Ar (100 mL min?1) at 400–800 C for 10–120 min Cu2O Annealed in N2/O2 mixed gas (200 mL min?1, ratio changed from 0 to 9)

43**at 450 C for 2 h** WO3 **Annealed in**

controlled oxygen pressure (95 mTorr) at 500 C for 200–600 s Solid-based annealing Fe2O3 Annealed in the air at 400 C for 20 min with upstream S powder BiVO4 Annealed in N2 at 370

26**C for 2 h and** then in air **at** 450 **C for** 15 **min**

with PVDFc aside TiO2 Ground with Mg powder, sealed and annealed at 500 C for 10 h, followed by washing, ?ltering and drying Ni-doped TiO2 Annealed in Ar at 500 C for 4 h with upstream Zn particles heated at 700 C Si-doped TiO2 Annealed in Ar at 500 C for 4 h with upstream Zn particles heated at 700 C CuO Heated in an enclosed graphitic cylinder (1 torr) at 300 C for 1 h C3N4 Ground with LiCl/KCl mixture,

5**followed by annealing at** 550 **C for** 24 **h**

under N2, then washing with HCl or NH3 solution Flame annealing CuFe2O4 TiO2 Annealed in an oxygen-rich ?ame region (>980 C) for 16 min Repeatedly spin-coated with precursor solution ten times and then heated in a n-butane ?ame for 25 s Vacuum annealing ZnO Annealed in vacuum (<1 mTorr) at 100–700 C for 1 h SnO2/In2O3 Annealed in an ultrahigh vacuum system (5 10?8 Pa) a Measured under infrared light (>800 nm). b Measured

5**in 0.1 M** phosphate **buffer containing 0**.1 **M**

H2O2. c PVDF: polyvinylidene ?uoride. 0.6; 1.2; RHE; 5.5 0.54; 1.23; RHE; 2.4 2.25; 1.23; RHE; 2.0 2.94; 1.23; RHE; 2.3 0.21a; 1.2; Ag/AgCl; N/A 0.48; 1.0; SCE; 1.5 0.79; 1.23; RHE; 3.6 1.32; 1.23; RHE; 4.3 0.6b; 1.23; RHE; N/A N/A N/A 0.25; 1.23; RHE; N/A 0.93; 1.23; RHE; 4.0 2.25; 1.23; RHE; 1.5 1.02; 1.23; RHE; 5.8 5.0; 1.23; RHE; 5.0 ?1.8; 0.1; RHE; 2.0 1.81; 1.23; RHE; 2.0 1.42; 1.23; RHE; 2.45 0.28; 1.23; RHE; 1.4 3.0; 1.0; RHE; 5.0 2.06; 0; Ag/AgCl; 2.2 1.78; 0; Ag/AgCl; 2.3 ?0.75; 0; RHE; 1.5 ?0.5; 0; RHE; 5.0 ?1.82; 0.4; RHE; 3.5 1.17; 1.23; RHE; 4.5 0.6; 1.23; RHE; 20 N/A 105 106 7 101 102 99 100 109 18 108 108 113 114 120 115 118 24 121 124 8 16 126 125 138 139 11 127 128 21 reduced charge transfer resistance, the as-prepared CuO exhibited

1**a photocurrent density of ?1**.8 **mA cm?2 at 0**.1 **V vs**

. SHE, two times higher than that of the CuO annealed in synthetic air. Another work by Cen et al. examined the in?uence of annealing WO3 under controlled oxygen pressure (95 mTorr).121 The treatment enhanced charge carrier density, leading to

2**a photocurrent density of** 1.81 **mA cm?2 at 1.23 V** vs. **RHE**, two times **higher than** that **of** untreated WO3. **4.2**

Other post-annealing treatments 4.2.1 Solid annealing. In addition to gas-based post- annealing treatment, the reaction between photoelectrodes and solid chemicals can be realized at a high temperature, known as solid-based annealing in the review. Gas annealing treatment seems to be a direct method to create unique surface structure to the materials; however, the choice of the gas is limited. Notably, the improper setup of gas annealing treatment is dangerous and fatal while using H2 and NH3. Besides, various pressure applied in the annealing system offers different performance of the photoelectrode. In the following content, solid-based annealing, vacuum annealing, and ?ame annealing are introduced in addition to gas-based post-annealing treat- ment. These studies have been summarized in Table 5.

36**For example**, Zhang **et al. investigated the PEC** properties **of** S-doped Fe2O3 **nanorods**

.124 Elemental S was doped in Fe2O3 by employing S powder upstream during the annealing process, similar to tube-furnace chemical vapor deposition. As a result of the enhanced electron mobility

1**by the** nonmetal **doping, the** S- **doped Fe2O3**

7**exhibited a photocurrent density of** 1.42 **mA cm?2 at 1.23 V** vs. **RHE**. Rohloff **et al**. applied **a** low-cost solid–vapor reaction route to incorporate elemental F into BiVO4 by annealing the photoanode close to F-rich organic polymers (PVDF) in an N2 atmosphere (Fig. 11a).8 This F-modi?cation treatment primarily affected the charge transfer efficiency at the BiVO4kelectrolyte interface by increasing catalytic efficiency. In another study, by Xu et al., metal-reduction methods—safer than hydrogenation—were used to reduce TiO2 photoanodes.16 Among various metals such as Zn, Al, and Mg (Fig. 11b),

24**Fig. 11 (a) Schematic illustration of the** synthesis **of**

F-incorporated BiVO4.8 Reprinted

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)

14**UV-visible absorption spectra and** corresponding digital photographs **of**

colored TiO2 reduced by (b) various metals and (c) various dosages of Mg.16 Reprinted

1**with permission from ref**. 16, **copyright 2017 The Royal Society of Chemistry**

. annealing with Mg powder could controllably alter the color of TiO2 from light blue, to dark blue, and to black (Fig. 11c). The highest photocurrent density of the Mg-reduced TiO2 photo- anode attained 3.1

7**mA cm?2 at 1**.0 **V** vs. **RHE**, ?ve **times higher than that of** the **bare**

one, owing to the generation of Ovac and Ti3+ species. Dong et al. explored co-doped strategies (Si/Ti3+ or Ni/Ti3+) for improving the conductivity and charge transport of TiO2.125,126 In one study, a?er Zn metal reduction in argon at 700 C for 4 h, the resultant black Si-doped TiO2

1**exhibited a photocurrent** density **of 1**.78 **mA cm?2 at 0 V vs. Ag/AgCl**, 5.1 **and**

1.9

10**times higher than that of bare TiO2**

and black Si-free TiO2, respectively.125 Banerjee

11**et al. reported the** formation **of** an **amorphous**

Cu2?xO overlayer for the passivation of CuO.138 By annealing CuO in an enclosed graphitic cylinder at 300 C for 30–120 min, the as-prepared Cu2?xO/Cu2O/CuO exhibited a

2**photocurrent density of** ?0.75 **mA cm?2 at** 0 **V** vs. **RHE**, 1.**5** times **higher than that of bare**

CuO. The enhanced photoactivity and stability were ascribed

21**to the formation of** a **type II** heter- ojunction and **the**

bene?cial electron trapping by the amor- phous Cu2?xO overlayer. In another study, Wang et al. annealed carbon nitride with the presence of salts, including CuCl2, KCl, and LiCl.139 This salt-melt method not only introduced free CuCl species that could act as type II heterostructure but only incorporated coordinated Cu atoms, which enhanced visible light absorption, resulting in a signi?cantly improved PEC performance. 4.2.2 Flame annealing. As a special post-annealing strategy, ?ame treatments are endowed with the advantages of high temperature (easily to reach 1000 C), fast heating rate, and short process time. These studies have been summarized in Table 5. Park et al. compared the effects of ?ame annealing with furnace annealing on a photocathode CuFe2O4 (Fig. 12a and b).11 The ?ame-treated CuFe2O4 exhibited

10**a photocurrent density of 1**.82 **mA cm?2 at** 0.4 **V** vs. **RHE**, 3.5 times **higher than that of** furnace-annealed CuFe2O4. **The**

enhanced photoactivity was attributed to reduced bandgap which allowed more light absorption, increased porosity which enlarged the electro- chemically active surface area (Fig. 12c and d) by a factor of 2.78, and eliminated Ovac which lowered undesirable charge recom- bination. Chen et al. explored the ex situ doping of TiO2 by spin- coating W and Sn dopants on the photoanode followed by ?ame annealing.127 The incorporation depth of Sn and W ions could be tuned by ?ame treatment time. Owing to the easy activation of water molecules by the co-existed W and Sn atoms, the ?ame- treated TiO2 exhibited a 4.5-fold improvement in photoactivity, along with a cathodic shi? of onset potential (450 mV). 4.2.3 Vacuum annealing. In addition to gas annealing, vacuum annealing sometimes results in unique changes of photoelectrodes. These studies have been summarized in Table 5. For example, unfavorable hydroxyl groups at the surface of ZnO could be eliminated by post-annealing the photoanodes in a vacuum below 1 mTorr at 200–700 C.128 Increasing the post- annealing temperature to 700 C could induce the generation of Ovac, which acted as shallow donors and increased free charge carrier density. Consequently, the as-annealed ZnO exhibited Fig. 12 (a and b) Schematic illustration of CuFe2O4 on FTO annealed by (a) furnace annealing conditions with the formation of dense film and (b) flame annealing conditions with the formation of the porous structure. (c and d) Top and cross-section SEM images of the (c) furnace-annealed CuFe2O4 and (d) flame-annealed CuFe2O4.11 Modified

1**with permission from ref**. 11, **copyright** 2019 **American Chemical Society**. (e) A series **of** in situ **TEM** images **of**

indium metal/SnO2 nanowires during annealing in an ultra-high vacuum system.21

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7**a photocurrent density of 0**.6 **mA cm?2 at 1.23 V** vs. **RHE**, 20 times **higher than that of**

untreated ZnO. In another report by Liu et al.,21 the SnO2/In2O3 heterojunction was heated in the vacuum range from 100 Pa in the air to 5 10?8 Pa, which determined the amount of Ovac. In situ TEM observation was performed to explore detailed changes during annealing (Fig. 12e). The creation of Ovac in the vacuum-annealed SnO2?x/ In2O3?y photoelectrode should be responsible for the 1.6-fold increase in H2 production. 5. Summary and outlook The preparation of efficient and robust semiconductor photo-electrodes by facile post-synthetic treatments could accelerate the potentially industrial PEC water splitting application for the development of sustainable energy conversion technology. This review summarizes advances in post-synthetic treatments for PEC applications reported in this ?eld in the past ?ve years, focusing on the details of the various post-treatment methods and the resultant improved PEC performance. Various effective strategies, of which most are surface modi?cation methods, have also been introduced. Despite that the great progress has been made in developing post-synthetic treatment methods for improving photoelectrodes, there is still considerable distance to go before the industrial-scale application of PEC water splitting. The following is a detailed discussion of current limitations, challenges and prospects for future development in the ?eld of post-treatments of photoelectrodes

24**for PEC water splitting** technology. First, **it is** worthy **to** notice that **the**

PEC stability of the resultant post-treated photoelectrodes is, from time to time, not satisfactory. The photoactivity of chemically treated photo- electrodes, such as borate-treated BiVO4,19 can be reversed or easily undermined alongside the PEC measurement process in just a few hours. Another typical example is that illuminating BiVO4 photoanodes under open-circuit conditions can enhance PEC photoactivity, but the photoanode standing still in the electrolyte overnight can undesirably lead to the receding of photocurrent density to its initial level.5 Thus, it is of signi?- cance for researchers to explore the intrinsic properties of post- treatment-induced surface structure changes and think of useful methods by which to avoid the diminishing of these functional structures, such as by coating protective/passivation/ cocatalyst layers, in the pursuit of long-term stability. Although chemical treatment is a facile, efficient and low- cost method

28**to change the defect chemistry at the surface and in the bulk of** semiconductor, **it**

has an obvious limitation on material choice. The main target for chemical reduction method is to create oxygen vacancies on the surface of the metal oxide. Metal ions that are easily to be reduced may not be applicable. The misuse of chemical reduction method can damage the crystallinity of the materials. As reported, electro- chemical treatments on the photoelectrode can be quantita- tively controlled, so that researchers could modify the material in a more precise scale. However, the operational parameters, such as an applied potential and the corresponding electrolyte, were complex and totally different unless same material has been used. Such unclear and limited record on electrochemical treatments can restrict the progress by using electrochemical treatments. An in-depth investigation, e.g., in situ X-ray diffraction pattern analysis and in situ Ramen spectrometer analysis, of photoelectrodes using electrochemical treatments can help scientists to understand the kinetics and dynamics of electrochemical treatments. Irradiation-based treatment has an obvious limitation on its slow treatment process. In the normal cases, it requires 10 hour irradiation. Some methodologies require the treatment process work under open-circuit condi- tion. A 248 nm pulse laser can effectively reduce the irradiation duration from hours to seconds, but it is a high-cost solution. Post-annealing treatment is a very high-cost method. During the process, it consumes a lot of gas.

Some preparation method is dangerous, for instance, hydrogen annealing treatment. The leak of gas into the H2-?lled furnace tube can cause explosion. Solid-based annealing may cause contamination to the tube due to evaporation of solid sample. Frequent replacement of quartz tubes can greatly increase the cost. Post-synthetically modi?ed surface structure changes in photoelectrodes can directly interact with electrolytes, in a manner similar to the electrolysis of water. As an important component in a PEC system, electrolytes and their impact on PEC performance undeniably cannot be ignored. It has been reported that the composition and chemical properties (e.g., pH) of electrolytes have tremendous impacts.9,22,140–145 For example, the relation between PEC performance and the varia- tion of electrolyte composition has been investigated for BiVO4 photoanodes, proving that the pH and cation size signi?cantly in?uence the solar water oxidation reaction.141 In addition, during the PEC process, various intermediates may be gener- ated when employing different electrolytes, and the one that primarily in?uences OER/HER efficiencies should be explored. It is usually envisioned that post-synthetic treatments for surface modi?cation should only alter the surface properties of metal oxide photoanodes. However, from time to time, the bulk properties,

11**such as light absorption and charge separation**

efficiencies, could be improved or impaired. It is of interest and signi?cance to explore the reasons why surface structural changes or surface state alternations have such great in?uence on these bulk structures, in order to gain an in-depth under- standing of the structure–property–performance relationships. A large number of post-treatments exclusively in?uence the surface physicochemical properties of photoelectrodes. Thus, it is important to develop cutting-edge techniques by which to precisely characterize surface chemistry changes; for example, the destruction of chemical bonds and the formation of new bonds is of critical importance for a deep understanding of the roles of surface atomic arrangements. Furthermore, it is worth noting that the illumination involved during PEC measure- ments makes it harder to capture such changes, as some alternations might be easily reverted back to initial states. Thus, in situ techniques that provide opportunities to observe these possibly generated structure changes should be promoted. The development of such techniques can also broaden our under- standing of the relation between photocorrosion and irradia- tion treatments, a ?eld that is inadequately studied at the moment, because of a lack of understanding of the detailed impact of irradiation on photoelectrode surfaces and bulk structures. Without such knowledge, applying these post- treatments to improve the performance and stability of photo- electrodes in a pertinent manner seems to be difficult. Accordingly, in addition to photo-responsive semiconductor materials, an in-depth understanding of the photophysical (e.g., light absorption, and charge formation, and charge separation) and photoelectrochemical (e.g., photoredox activity, electro- chemical resistance, and diffusion behaviors) properties of solid/solid and solid/liquid interfaces are suggested to be ach- ieved by utilizing in situ characterization techniques under dark and light conditions, which will de?nitely provide

23**new insights into the** advancement **of next-generation** PEC semiconductor **materials for** commercial **applications in the emerging ?eld of** electrocatalytical, photocatalytical, **and** photoelectrocatalytic technologies. **Conflicts of interest There are no con?icts to declare**

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