SPECIAL TOPIC: Heterojunction in Photocatalysts

Synergistically regulating d-band centers of heterojunction redox sites by ligand effect for photocatalytic H₂ evolution

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ABSTRACT Stiff transportation behaviors in kinetics for photo-excited charges from their generation sites to corresponding redox sites as well as subsequent large reaction overpotential of these charges with intermediates during splitting H₂O have not been solved yet, which extremely hinders solar photon energy conversion into H₂ (STH). Herein, CeO₂ nanowires-anchored Ni₃P nanoparticles were built to solve the above dynamical issues by synchronously modifying d-band centers (ε_d) with ligand effect. Photon-excited electrons and holes were separately propelled to Ni₃P as the reductive site and CeO₂ as the oxidative site within the spontaneously formed localized electric field for the dehydrogenation and coupling of active oxyhydrogen intermediates, respectively, characterized by in situ diffuse reflectance infrared Fourier transform spectroscopy and Hall effect tests. Consequently, a STH of 1.13% was achieved at room temperature under AM 1.5G irradiation. The study supplies a unique insight to enhance STH over heterojunction photocatalysts by synchronously tuning ε_d.

Keywords: heterojunction, d-band center, H₂O splitting, H₂ energy, photocatalysis

INTRODUCTION

The transformation of solar photon energy into clean fuels via artificial photocatalytic technology is a prospective and potential strategy to solve critical energy issues, in which photocatalytic H₂O splitting has received wide research interest for supplying sustainable and clean H₂ energy [1–8]. It is explored that photocatalytic solar energy conversion procedure mainly involves three steps [9–12]: (i) photon-irradiated yield of electrons (e⁻) and holes (h⁺); (ii) individual movement behavior of e⁻ and h⁺ from the yield sites to surface redox active sites; (iii) surface redox reaction of these charge carriers with H₂O. Nevertheless, step (iii) is still subject to the high overpotential and slow desorption rates of gas products, and these two limitations are essentially constrained by too weak or too strong adsorption of photocatalysts to oxyhydrogen intermediates (e.g., *OH, *O, and *OOH) in H₂O splitting [13–16].

The d-band center (ε_d) catalytic model discovered and put forward by Hammer & Nørskov has been preliminarily performed to majorize the chemical adsorption to oxyhydrogen intermediates and explore the corresponding reaction principle as well as forecast the feasibility in constructing electro- or photoelectron-catalysts [17–25]. Nowadays, adjusting the center position of ε_d to be close to the Fermi level using ligand effect and/or strain effect has been confirmed to be effective for boosting the efficiency of solar conversion into H₂ energy (STH). However, photocatalysts with only a unitary ε_d can merely satisfy the requirement of oxidation or reduction reactions [26–33], and thus it is undoubtedly not probable to simultaneously reconcile the needs of oxidation and reduction reactions. Thereby, it is ideally required that two different ε_d can be performed to chemically adsorb H* and oxyhydrogen intermediates for photocatalytic reduction and oxidation, respectively. Herein, growing Ni₃P nanoparticles on oxygen vacancies of CeO₂ nanowires (Ni₃P/CeO₂) with synchronously adjusted ε_d of both Ce and Ni by ligand effect had been achieved for solar photon energy transformation into H₂ fuel by H₂O splitting under visible irradiation. The ε_d of Ce and ε_d of Ni showed an increasing and decreasing tendency near their respective intrinsic Fermi level due to the decreased and increased coordination of Ce and Ni by ligand effect. Therefore, the rising ε_d of Ce favored the chemical adsorption of oxyhydrogen (*OH and *O) on CeO₂, while the declining ε_d of Ni facilitated the preferential adsorption of *H on Ni₃P. Under irradiation with AM 1.5G solar simulator, e⁻ and h⁺ were boosted to migrate and gather separately on Ni₃P and CeO₂ with the action of localized electric field (LEF) induced by their Fermi level difference, wherein charges reacted with those active intermediates to generate H₂ energy and O₂ by dehydrogenation and coupling processes, characterized via Hall effect tests and in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS). Finally, a STH of 1.13% was completed over the optimized ε_d in Ni₃P/CeO₂ by ligand effect.

EXPERIMENTAL SECTION

CeO₂ nanowires were prepared by the hydrothermal methods (Scheme S1) [34,35]. CeCl₃ (3.7 mmol) was dissolved in 35 mL of NaCl aqueous solution (0.11 mol L⁻¹) which could facilitate the product to grow uniformly and anisotropically with high aspect ratios. Then 40 mL of NaOH solution (11.6 mol L⁻¹) was added drop by drop. After stirring for 30 min at room tem-

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perature, the mixture was transferred to a hydrothermal reactor, and heated up to and then kept at 180°C for 18 h. When cooling to room temperature, the solid sample was collected and dried for further usage after filtration and washing several times with water and ethanol.

Ni$_2$P/CeO$_2$ sample was synthesized by a one-step hydrothermal method. The fresh prepared CeO$_2$ (0.8 g) was homogeneously dispersed in 60 mL of ethanol aqueous solution (1:1 volume ratio) containing a certain concentration of red phosphorus and C$_4$H$_6$O$_4$Ni·4H$_2$O as P and Ni sources (molar ratio of P to Ni was 10:1). The suspension was then poured into a hydrothermal reactor, and heated and kept at 140°C for 12 h. After the reaction was completed, the solid product was washed with water and ethanol repeatedly and dried at 70°C. Ni$_2$P loading was modified by increasing the dosage of Ni precursor from 0.54, 0.86, to 1.10 mmol, and the samples were named as Ni$_2$P/CeO$_2$-1, Ni$_2$P/CeO$_2$-2, and Ni$_2$P/CeO$_2$-3, respectively.

RESULTS AND DISCUSSION

Macromorphology and microstructure

CeO$_2$ nanowires with a diameter of ~50 nm and a length of 1–2 μm presented a slender, sturdy and smooth wire morphology in the transmission electron microscope (TEM) (Fig. 1a). The exposed crystal facet was confirmed as (111) of fluorite cubic CeO$_2$ by the accurately measured lattice spacing of 0.312 nm in high resolution TEM (HRTEM) and the typical peaks in X-ray diffraction (XRD) (Fig. 1b–d and Fig. S1a). With Ni$_2$P loading, some nanoparticles with sizes of 10–20 nm appeared on the surface of CeO$_2$ nanowires (Fig. 1e), and with increasing the content of Ni$_2$P, the gradually intensified diffraction peaks at 40.80°, 44.60°, and 54.23° indicated the generation of hexagonal Ni$_2$P (JCPDS: 03-0953) (Fig. S1a) [36]. Ulteriorly, the exposed lattice spacing of 0.169 nm was assigned as (300) facet for Ni$_2$P (Fig. 1f–i), and it should be mentioned that there was no clear boundary between CeO$_2$(111) and Ni$_2$P (300) from HRTEM observation. In X-ray photoelectron spectroscopy (XPS), O 1s signal could be fitted into three peaks at 529.2, 530.8, and 532.5 eV, which corresponded to the lattice oxygen (O$_{\text{l}}$), oxygen vacancy (O$_{\text{v}}$), and adsorbed oxygen (O$_{\text{ads}}$) (Fig. 1j) [37]. Noticeably, the concentration of O$_{\text{v}}$ diminished while that of O$_{\text{l}}$ augmented after Ni$_2$P growth on CeO$_2$. This might be attributed to the disengagement behavior of oxygen atoms from CeO$_2$ crystal structure unit during the second hydrothermal treatment for loading Ni$_2$P; moreover, the finite spectrum for Ce 3d mutually corroborated with the change of O$_{\text{v}}$, as reflected by the increasing proportion of Ce$^{3+}$ group in Ce species for Ni$_2$P/CeO$_2$ compared with CeO$_2$. These O$_{\text{v}}$ hence provided preferential anchor sites for Ni$_2$P nucleation and growth, which was beneficial to build a smooth charge transfer route between Ni$_2$P and CeO$_2$. In addition, the binding energy for Ce$^{4+}$ group shifted negatively from 883.1 eV in CeO$_2$ to 882.7 eV in Ni$_2$P/CeO$_2$-2, while conversely the signals for Ni 2p$_{1/2}$ and Ni 2p$_{3/2}$ migrated positively from 856.2/852.8 eV (pristine Ni$_2$P) to 856.6/853.2 eV (Ni$_2$P/CeO$_2$-2) (Fig. 1k, l) [38]. The above characterization results suggested the electron-giving behavior from Ni$_2$P to CeO$_2$ through the low barrier interface within Ni$_2$P/CeO$_2$ heterojunction induced by the different Fermi
levels between them [39]. In line with work function (Φ) calculation, Φ for CeO₂ and Ni₃P corresponded to 5.98 and 5.35 eV [40], and thereby Ni₃P displayed a lower Φ but a higher Fermi level than CeO₂ (Fig. S1b and Equation S1). Thereby, electrons preferentially transferred from Ni₃P with a high Fermi level to CeO₂ with a low one through O₂ as bridges driven by their Fermi level difference after the growth of Ni₃P on CeO₂. Furthermore, the decrease of O₂ resulted in the declined coordination of Ce in CeO₂, and thus ε₂ of Ce rose; meanwhile, along with the formation and charge exchange of Ni₃P on the O₂ sites, the number of P ligands increased compared with the pristine Ni₃P due to the positive charge accumulation, which resulted in a declined ε₂ of Ni in Ni₃P/CeO₂. The rising ε₂ of Ce and the declining ε₂ of Ni immediately favored the chemical adsorption of the key active oxyhydrogen (e.g., *OH, *O, and/or *OOH) to Ni₃P/CeO₂ [41]. In Fig. 2a of in situ DRIFTS, the signals of oxyhydrogen intermediates on Ni₃P/CeO₂ at ~3580, 3500–3400, ~3200, and ~1320, and ~980 cm⁻¹ belonged to H₂O molecule adsorption, H₂O—OH— and *-OH—H–, low-frequency and flexural vibration HO—*, and stretching-vibration *–O, respectively [42–45]. Instead, these peaks could not be detected over CeO₂ nanowires. Thereupon, Ni₃P/CeO₂ heterojunction with the modified ε₂ of both Ce and Ni by ligand effect conduced to the chemical adsorption of oxyhydrogen intermediates in kinetics.

**Charge carrier transfer dynamics within LEF**

The transportation of electrons brought about the gather zones for positive and negative charges on CeO₂ and Ni₃P within the action of their Fermi level difference, inducing the generation of LEF in Ni₃P/CeO₂. Macroscopically, LEF could be characterized by Kelvin probe force microscope (KPFM) and expressed as surface contact potential (SCP), which showed continuous change ups and downs over Ni₃P/CeO₂-2 with a mean SCP value of 138.8 mV (Fig. 2b and Fig. S1c). Besides, the LEF as a whole could also be tested using electrochemical polarization measurements (Fig. 2c, Fig. S1d, e, and Equations S2–S6) [46]. In Fig. 2c, LEF intensity varied from 0.0442 (CeO₂) to 0.0466 (Ni₃P/CeO₂-2). It was known that the distribution for e⁻ and h⁺ followed the Boltzmann rule over semiconductor photocatalyst. By introducing current and magnetic fields, e⁻ and h⁺ would be driven within the Lorentz forces [47]. In this scenario, e⁻ tended to congregate on Ni₃P as a reductive site and h⁺ on CeO₂ as an oxidative site. In Fig. 2d, the detected densities for e⁻ and h⁺ varied with following a roller coaster tendency, i.e., Ni₃P/CeO₂-2 > Ni₃P/CeO₂-1 > Ni₃P/CeO₂-3 > CeO₂, wherein the optimal charge densities of 1.95 × 10¹¹ and 1.53 × 10¹¹ cm⁻³ for e⁻ and h⁺ had been detected over Ni₃P/CeO₂-2. Noticeably, this trend was consistent with the intensity ranking of LEF over heterojunction, and thus without the influence of Lorentz forces, efficient separation and migration as well as application for charges in the optoelectronic system, could still be achieved under the spontaneous LEF promotion. Under photoexcitation, e⁻ was excited and jumped from the ground state to the first or second excited singlet state. Within the action of LEF, e⁻ and h⁺ were timely and effectively transferred to the first or second excited singlet state of Ni₃P/CeO₂ surface, and thus the charge recombination

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**Figure 2**  (a) Fourier transform infrared spectroscopy (FTIR) spectra for CeO₂ and Ni₃P/CeO₂-2. (b) KPFM potential image for Ni₃P/CeO₂-2. (c) LEF intensities of the samples. (d) Hall effect parameters. (e) Photo-current signals. (f) Chopping J-V curves and (g) the derived ABPCE. (h) LSV curves for H₂O splitting over catalyst electrodes and (i) the derived Tafel slope plots.
probability declined, as reflected by the clear decrease in fluorescence intensity of Ni$_2$P/CeO$_2$ on the basis of CeO$_2$ (Fig. S1f). When electrolyte was used as a charge transfer medium, the movement for $e^-$ and h$^+$ formed a circuit [48], and thus an obvious, sustained, and stable photocurrent appeared in both transient current density ($J$)-time ($t$) and chopped $J$-voltage ($V$) tests (Fig. 2e, f). Furthermore, by deriving from $J$-$V$ signal, Ni$_2$P/CeO$_2$-2 devoted the significant efficiency of the applied bias photon to current (ABPCE) (Fig. 2g and Equation S7). Beyond that, active oxyhydrogen intermediates for H$_2$O splitting were quickly and easily adsorbed on Ni$_2$P/CeO$_2$-2 because of the adjusted $\epsilon_4$ in kinetics, bringing about a declined overpotential for H$_2$O splitting over catalyst electrode through the smooth charge transfer route between Ni$_2$P and CeO$_2$ (Fig. 2h). Thereby in linear sweep voltammogram (LSV) tests, the onset reaction potential for H$_2$O splitting was remarkably decreased over Ni$_2$P/CeO$_2$-2 with an enlarged electro-chemical reactive region and hydrophilicity compared with CeO$_2$ (Fig. 2h and Fig. S2); additionally, Tafel value was lowered to 143.97 mV dec$^{-1}$, revealing that $^*$H adsorption was the rate-determining step for H$_2$O splitting (Fig. 2i) [49].

The electron transfer and separation dynamics behavior were then investigated by femtosecond transient absorption spectrum (fs-TAS) (Fig. 3). It was found that there were mainly three regions within the probe detection range of 340–600 nm including a common cyan region at ~345 nm caused by pump laser (Fig. 3a). The highly visible red and yellow positive signal from wavelength of 350–400 nm and delay time of 1.5–224.0 ps was assigned as the excited state absorption. Another inconspicuous but important negative region with cyan and green colors marked for attention from 421–520 nm was jointly assigned as the overlap of ground state bleaching (GSB) and stimulated emission (SE) processes (Fig. 3a, b). Within the GSB and SE region, three probe wavelengths of 417, 455, and 490 nm were selected to fit for typical charge lifetime and dynamic processes investigation (Fig. 3c–e). It was found that all curves conformed to a three-exponential fit, which provided the charge lifetime spans of 0.9–1.1, 9.3–15.4, and 516.0–635.0 ps covering three wavelengths (Fig. S3). These three states corresponded to three dynamics processes, i.e., electron transition (0.9–1.1 ps), trapping by active sites (9.3–15.4 ps), and exciton cooling (516.0–635.0 ps) (Fig. 3f). Notably, the electron transition and trapping behaviors were finished in very fast time spans from ~1 to a dozen ps, which should be attributed to the promotion effect of LEP formed within Ni$_2$P/CeO$_2$. Thereby, it was seen that a smooth kinetics transportation behavior for charges from generation point to active sites had been realized within Ni$_2$P/CeO$_2$-2 and solar energy conversion into H$_2$ in photocatalytic H$_2$O splitting would certainly be accelerated combined with the improved adsorption to intermediates originating from the modulated $\epsilon_4$ of Ni and Ce in Ni$_2$P/CeO$_2$.

Photocatalytic H$_2$O splitting and principle

Impact factors of the photocatalysis tests for H$_2$O splitting reaction such as H$_2$O quality, irradiation area, cooling system, O$_2$ evacuation, half photocatalysis for H$_2$O splitting, and mass effect of photocatalyst were confirmed in advance (Table S1 and Fig. S4a, b) [50–52]. In Fig. 4a, the photon-excited output for H$_2$ and O$_2$ with a mole ratio of 2:1 constantly increased under long-lasting illumination of 3 h over Ni$_2$P/CeO$_2$ heterojunction photocatalysts ($\lambda \geq 350$ nm, 300 W Xe lamp) (Fig. 4a), while H$_2$ and O$_2$ could not be detected over the pristine monomer photocatalysts from beginning to the end. Among Ni$_2$P/CeO$_2$ heterojunctions, it was observed that the productivity for H$_2$ and O$_2$ over Ni$_2$P/CeO$_2$-2 displayed a linearity rise with the highest gradient, and product generation velocities of 116.00 and 58.00 $\mu$mol h$^{-1}$ for H$_2$ and O$_2$ had been completed, accordingly. When the Xe lamp was equipped with band-pass filters, quantum efficiency (QE) for H$_2$ generation over Ni$_2$P/CeO$_2$-2 was 9.63%, 7.36%, and 1.10% under monochromatic light irradiation at $\lambda = 350$, 400, and 420 nm, respectively (Fig. 4b and Equation S8). Apart from the QE, STH was also tested by the Xe lamp fitted with AM 1.5 G as a solar simulator, and the productivities of 38.60 and 19.30 $\mu$mol h$^{-1}$ for H$_2$ and O$_2$ with STH of 1.13% were obtained over Ni$_2$P/CeO$_2$-2 at room temperature (Fig. 4c, Fig. S4c, and Equation S9). Afterwards, Ni$_2$P/CeO$_2$-2 was
continuously performed to evaluate its cyclic stability, and the result exhibited that Ni$_2$P/CeO$_2$-2 bestowed on a steady catalytic behavior in the H$_2$O splitting cycling tests combined with its stable macroscopic, microstructural, and optoelectronic properties (Fig. 4d and Fig. S4d, e). To further go a step to explore the possibility of increasing STH, the thermal influence from the solar simulator on STH was discussed as well. Within the temperature range from 25 to 65°C, the STH exhibited a sustained rise from 1.13% to 2.11%, maybe because the generated H$_2$ and O$_2$ clusters were prone to grow and release in dynamics from Ni$_2$P (reductive site) and CeO$_2$ (oxidative site) at an appropriately high temperature; on the contrary, when further increasing reaction temperature, the counter-reaction (i.e., recombination reaction between H$_2$ and O$_2$) occurred and intensified easily due to the activation of gas molecules at much high temperature (e.g., 75 and 85°C) [53]. Based on the similar catalytic conditions as much as possible, a performance comparison chart was built between the reported materials and Ni$_2$P/CeO$_2$-2 system (Fig. 4e and Table S2). It was found that Ni$_2$P/CeO$_2$-2 still maintained a relatively advantageous capability within these released results [15,20,40,54–63]. Therefore, under the modulation of the ligand effect, an increased ε$_d$ of Ce in CeO$_2$ facilitated the chemisorption of oxyhydrogen intermediates to Ce sites, while a decreased ε$_d$ of Ni in Ni$_2$P was conducive to the chemisorption of *H on the Ni sites. Combined with the separation of photoexcited e$^-$ and h$^+$ in space with the action of LEF, i.e., e$^-$ gathered on Ni$_2$P and h$^+$ on CeO$_2$, H$_2$, and O$_2$ were released smoothly from the Ni$_2$P/CeO$_2$ system with a high rate and stability.

Further, the kinetic principle and the derived reaction model over Ni$_2$P/CeO$_2$ for the splitting reaction were subsequently explored by in situ DRIFTS. In Fig. 5a, it was noted that the specific signal information for active oxyhydrogen intermediates became more and more obvious with adding H$_2$O and continuous illumination in in situ reaction tank. In detail, the signals for the chemically adsorbed H$_2$O–, H$_2$O···HO–*, *–OH···H–, low-frequency *–OH, flexural-vibration *–OH, and *–O could be observed. According to the dynamical transfer behavior for e$^-$ and h$^+$ and band structure of Ni$_2$P/CeO$_2$, the photocatalytic reaction model for H$_2$O splitting over Ni$_2$P/CeO$_2$ was completed.
Hence, $e^{-}$ from the conduction band (CB) of CeO$_{2}$ directly transported to the anchored Ni$_{2}$P, and meanwhile h$^{+}$ stayed and retained on the valence band (VB) of CeO$_{2}$. Within LEF effect, $e^{-}$ and h$^{+}$ gathered on Ni$_{2}$P and CeO$_{2}$, accordingly. The suitable $\varepsilon_d$ of both Ni and Ce on corresponding redox active sites (Ni$_{2}$P and CeO$_{2}$) ultimately enhanced the chemical adsorption for active H$^{\ast}$ and oxyhydrogen intermediates, and then $e^{-}$ and h$^{+}$ reacted with these active intermediates. Thus, H$_{2}O$ was chemically adsorbed and subsequently dissociated into $\ast$–H on Ni$_{2}$P and $\ast$–OH on Ni$_{2}$P/CeO$_{2}$ preferentially (Processes (i)–(iii) of Fig. 5c). Simultaneously, H$_{2}$O molecule reacted with the formed $\ast$–OH on CeO$_{2}$ and $\ast$–H on Ni$_{2}$P into $\ast$–OH–HO–$\ast$ under the reduction of $e^{-}$, and H$_{2}$ released by dehydrogenation and H$^{\ast}$ coupling (Steps (iv) and (v) of Fig. 5c); concurrently, h$^{\ast}$ on CeO$_{2}$ oxidized $\ast$–OH–HO–$\ast$ into O$_{2}$ and the remained dissociated H$^{\ast}$ was caught and instantly reduced into H$_{2}$ on Ni$_{2}$P (Steps (vi)–(viii) of Fig. 5c).

CONCLUSIONS

In brief, localized Ni$_{2}$P/CeO$_{2}$ heterojunctions with tunning $\varepsilon_d$ induced by ligand effect were prepared for boosting dynamical transfer behavior of $e^{-}$ and h$^{+}$ and simultaneously lowering their redox reaction barrier with H$_{2}O$, confirmed with in situ DRIFTS and hall effect characterizations. The results present that: (1) $e^{-}$ and h$^{+}$ tended to be transported separately to Ni$_{2}$P and CeO$_{2}$ within the Ni$_{2}$P/CeO$_{2}$ heterojunction with LEF action in kinetics; (2) chemical adsorption of active oxyhydrogen species (e.g., $\ast$H, $\ast$OH, and $\ast$O) had been smoothly resolved on the localized Ni$_{2}$P/CeO$_{2}$ heterojunction by synergistically regulating d-band centers; (3) dehydrogenation and coupling for the active oxyhydrogen species had been successively completed and evolved into H$_{2}$ and O$_{2}$, respectively, with a STH of 1.13% under AM 1.5 G at 25°C. The results suggest an in-depth insight into charge carrier transfer kinetics and reaction dynamics by tuning $\varepsilon_d$ synchronously, endowing inspiration for designing and developing advanced photocatalysts with high STH values.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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