Enhanced photocatalytic hydrogen production by loading histidine on TiO$_2$

Xiaojing Han$^{1,2}$, Hongrui Ma, Chuanyi Wang and Yingxuan Li

1 School of Environmental Science and Engineering, Shaanxi University of Science and Technology, Xi’an 710021, People’s Republic of China
2 Department of Chemistry and Chemical Engineering, Lvliang University, Lvliang 033000, People’s Republic of China

E-mail: wangchuanyi@sust.edu.cn and liyinxuan@sust.edu.cn

Keywords: photocatalysis, titanium dioxide, histidine co-catalysis, water-splitting

Abstract

Although TiO$_2$ exhibits excellent photocatalytic properties, its application has been limited owing to rapid $e^-/h^+$ recombination. Therefore, TiO$_2$ has failed to reach the desired effect in terms of efficient photocatalytic hydrogen production. In this study, a range of titanium dioxide catalysts loaded with histidine (His) were prepared by an easy dipping method, viz. by treating TiO$_2$ in His aqueous solutions with different concentrations at ambient temperature. Photocatalytic hydrogen evolution by splitting water was performed on His-modified TiO$_2$ under 300-W Xe irradiation. His-loaded TiO$_2$ catalysts exhibited improved photocatalytic performance compared with pristine TiO$_2$; TiO$_2$ treated in $1 \times 10^{-3}$ mol·L$^{-1}$ His showed the highest photocatalytic H$_2$ evolution activity (4.77 $\mu$mol g$^{-1}$ h$^{-1}$ gm$^{-2}$), which was 3.77 times higher than that of pure TiO$_2$. Infrared and XPS analysis showed that His was successfully combined to the TiO$_2$ surface by hydrogen bonding, constructing a fast channel for interfacial charge transfer. In the photocatalytic process, the photogenerated holes could migrate from the valence band of TiO$_2$ to the highest occupied molecular orbital of His, which reduced the recombination rate of photogenerated $e^-/h^+$ pairs, consequently, improved H$_2$ production efficiency. Importantly, the composite catalyst exhibited no decline in photocatalytic activity over 30 h of operation. This research provides an alternative approach for creating high-efficiency photocatalysts for H$_2$ production.

1. Introduction

Photocatalytic hydrogen evolution (PHE) via water-splitting is considered an environment-friendly technique for obtaining clean energy [1]. Especially, PHE using semiconductors as the catalyst and solar energy as the light source offers a green approach for the economical and non-polluting production of hydrogen [2]. Among various semiconductors, titanium dioxide (TiO$_2$) remains popular and has many potential applications in photocatalysis due to its stable physicochemical properties and special photooxidation capability. However, the application of TiO$_2$ (P25) has also been restricted because of the low H$_2$ evolution performance which results from high $e^-/h^+$ recombination efficiency under light irradiation [3]. Furthermore, it is well known that the titania polymorphs can directly affect the photocatalytic properties of TiO$_2$. For example, the mixture of rutile and anatase exhibits well activity for PHE due to the preferential transfer of photogenerated electrons from anatase to rutile [4]. Therefore, commercial TiO$_2$ (P25) containing rutile (~20%) and anatase (~80%) is selected as the base material for producing highly active TiO$_2$-based photocatalysts for PHE in the present study.

To improve the PHE activity, concerted efforts have been made to improve the photocatalytic activities of TiO$_2$ photocatalysts, including incorporation of co-catalysts [5], doping [6], and building heterojunctions [7]. Among these methods, loading co-catalysts has been attracted extensive attentions due to their unique properties in accelerating transfer of photogenerated charge carriers for improved PHE activity. In previous reports, inorganic co-catalysts including noble-metal (such as Pt [5] and Pd [8], metal oxides (primarily...
based on quantum dots) [9], and earth-abundant alternatives (such as NiOx, CoOx, and so on) are usually adopted for photogenerated charge transport.

In addition to the inorganic materials, loading organic co-catalysts has been an emerging research area for improving the PHE performance of TiO2 [10, 11]. In this type of catalyst, the loaded organic groups can provide trapping sites for the photoinduced holes or electrons and reduce the recombination rate of photogenerated electron-hole pairs [12]. For instance, organics with amino group (–NH2) can act as strong Lewis base and hole-stabilizers to enhance photocatalytic water-splitting for H2 evolution [13, 14]. However, to our knowledge, only a few effective organic co-catalysts for PHE have been reported. Therefore, seeking novel co-catalysts based on organics with is highly desirable for energy conversion.

Based on the above analysis, histidine (His) with one –NH2 group may be a potential co-catalyst in accelerating hole transfer kinetics of photocatalytic process. Although pure TiO2 treated with His has been applied to the photocatalytic reduction of heavy metal [13, 15], His in this reaction was only used to enhance the capacity of TiO2 for adsorbing heavy metals. Herein, we show an easy dipping method to synthesize a series of photocatalysts, by employing His as an organic co-catalyst, to enhance the activity of H2 production of TiO2 nanoparticles. His was attached to the surface of TiO2 via the hydrogen bonding between the oxygen in TiO2 and the nitrogen in His. The functionalized TiO2 nanoparticles retain good dispersibility in water. The fabricated composites exhibited a high PHE efficiency (4.77 µmol g−1 h−1 gm−2), which was 3.77 times higher than that of TiO2. Our findings in this study are expected to provide a new method for the development of organic co-catalysts of PHE via water-splitting.

2. Experimental section

2.1. Synthesis of catalysts

Chemicals and reagents: Degussa TiO2 (P25, Evonik Germany), methanol, and His were obtained from commercial sources without any purification. His (content ≥99%) was purchased from Shanghai Lanji Technology Development Co., Ltd., China. Methanol (CH3OH, content ≥99.5%) was provided by Tianjin Kemiu Chemical Reagent Co., Ltd. Deionized water used throughout the experiment was prepared by an ultrapure water device (EPED-S2-90DF).

Synthesis of catalysts: The titanium dioxide loaded with His (TiO2–His) samples were synthesized via a simple dipping method. Different concentrations of 1 × 10−1, 1 × 10−2, 1 × 10−3 and 1 × 10−4 mol · L−1 were produced by dissolving the required weight of His in 100 ml deionized water, followed by dispersal of 200 mg of TiO2 powder in the 100 ml. This His aqueous solution was then sonicated for 10 min and the mixture was reacted for 2 h in the dark at ambient temperature. Finally, the product was centrifuged and carefully rinsed with deionized water three times and then freeze dried. The prepared samples were named TiO2–His-1, TiO2–His-2, TiO2–His-3, and TiO2–His-4, corresponding to samples treated with His concentrations of 1 × 10−1, 1 × 10−2, 1 × 10−3 and 1 × 10−4 mol · L−1, respectively.

2.2. Characterization of catalysts

The crystalline structure of the samples was recorded by x-ray diffraction (XRD) using a Bruker D8 advance powder diffractometer for scattering angles from 20° to 80° employing a Cu Kα radiation source (0.1542 nm, 40 mA, 40 kV). The morphology and lattice structure of the samples were observed by transmission electron microscope (TEM) on a FEI Tecnai F20 instrument operated at 200 kV. Sample powders were dispersed in absolute ethanol and sonicated for 10 min and then dropped onto a copper mesh, and the solvent evaporated prior to installation in the TEM. The particle size was measured on Malvern Zetasizer Nano ZS90 (Malvern, UK). The measuring temperature was fixed at 25.0 ± 0.1 °C and the volume was controlled between 1.0 and 1.5 ml. The UV–visible diffuse reflectance spectra were obtained using a Shimadzu UV-2600 spectrometer with an integrating sphere and BaSO4 as the absorbance standard. The obtained ultraviolet–visible absorption curve was fitted with Tauc plot procedure and then obtained the corresponding band gap (Eg) value by extrapolation. The formula of this fitting equation is as follows: \( \alpha h\nu = A(h\nu − E_g)^n \), where \( \alpha \), \( h\nu \), and \( A \) are absorption coefficient, Planck’s constant, the frequency of the light and a constant, respectively. For direct semiconductor, \( n \) equals 1, whereas for indirect semiconductor \( n \) is equals to 4. Fourier transform infrared (FTIR) spectra of the samples were recorded on Thermo Scientific Nicolet iS5 using the KBr pellet support, scanning from 4000 to 400 cm−1 at room temperature. Surface chemical information of the samples was obtained with an AXIS SUPRA x-ray photoelectron spectrometer (XPS) using a monochromatic Al Kα source (1486.6 eV). The spectra of all detected elements were calibrated by the referencing C1s peak at 284.6 eV. All peaks were analysed by XPS Peak Fit software. The electron paramagnetic resonance (EPR) measurements were taken on a Bruker EMX spectrometer equipped with a quartz capillary column. The EPR spectrum of solid materials were recorded at room temperature and the date processing of the spectra was performed using g-value conversion in the software. The steady-state photoluminescence (PL) spectra were
acquired with a fluorescence spectrometer (Edinburgh Instruments) at room temperature, which equipped with a 300-nm laser as the excitation source. The time-resolved fluorescence emission spectrum was conducted with Horiba Jobin Yvon Data Station by time-correlated single-photon counting.

Photoelectrochemical tests were conducted on a CHI600E electrochemical workstation. The photoelectrochemical cell was equipped with a quartz glass window as the light source channel. All tests were carried out by using a standard three-electrode configuration, in which the samples constituted the working electrodes, Pt wire was the counter electrode, and a normal calomel electrode (saturating KCl) was the reference electrode. The working electrodes were prepared by uniformly coating the catalyst colloids on fluorine-doped tin oxide (FTO) conductive glass (area: $1.0 \times 1.0 \text{cm}^2$) and then dried at $60^\circ\text{C}$ for 1 h. The photocurrent was recorded in 0.5 mol L$^{-1}$ Na$_2$SO$_4$ solution using a 300-W xenon lamp as light source.

2.3. Photocatalytic reaction

Photocatalytic H$_2$ production was evaluated on a Labsolar-AG system (Beijing Perfectlight Technology). In each measurement, the catalyst (20 mg) was suspended in a water/methanol solution (100 ml) with a volume ratio of 4:1. The solution was then moved to the reaction apparatus after 10 min ultrasonic treatment at ambient temperature. The photochemical reaction apparatus was evacuated for 15 min to remove air and dissolved oxygen. During photocatalysis process, a xenon lamp without any optical filter was employed as the light source and a magnetic stirring (500 rpm) was used to ensure uniform dispersal. The volume of H$_2$ produced was determined using online gas chromatography (Agilent 7890B, TCD detector, and Ar as the carrier).

3. Results and discussion

3.1. Photocatalysts characterization

Figure 1 depicts the XRD patterns of pure TiO$_2$ and the as-synthesized photocatalysts. Identical diffraction peaks for TiO$_2$ and synthesized photocatalysts were obtained (figure 1), which demonstrated that His-modification did not affect the original crystalline phase composition of anatase and rutile (the typical component of P25) structures [16, 17]. As seen from the TEM images (figures 2(a) and (d)), the pure particle size of TiO$_2$ and TiO$_2$-His-3 is between 20 nm and 50 nm. To further determine the size distribution, the nanoparticle size distribution histograms of TiO$_2$ and TiO$_2$-His-3 are shown in figures 2(c) and (f), respectively. It can be seen that TiO$_2$ is decorated by His shows similar particle size with pristine TiO$_2$, which is consistent with the result of TEM. Namely, the introduction of His has no effect on the particle size of TiO$_2$. The lattice fringes of the TiO$_2$ and TiO$_2$-His-3 nanoparticles were estimated from representative high-magnification transmission electron microscopy (HRTEM) images in figures 2(b) and (e). The marked lattice fringes of the two crystalline polymorphs were 0.35 nm and 0.32 nm, corresponding to the (101) crystal facets of anatase and (110) crystal facet of rutile phase, respectively (figure 2(b)) [18]. Comparing figure 2(b) with figure 2(e), demonstrated that the introduction of His did not change the morphological structure of TiO$_2$.

Figure 3 shows the UV–vis diffuse reflectance spectra for the pristine TiO$_2$ nanoparticles and His-modified TiO$_2$ nanoparticles. The typical absorption band in the UV region for TiO$_2$ is corresponding to the charge transfer of O$^{2-} \rightarrow \text{Ti}^{4+}$, that is, inner electron transition of TiO$_2$ nanoparticles from the valence
Figure 2. The typical TEM and HRTEM images of TiO$_2$ nanoparticles (a, b) and TiO$_2$-His-3 (d, e); the particle size distributions of TiO$_2$ (c) and TiO$_2$-His-3 (f).

Figure 3. UV–vis diffuse reflectance spectra of the as-prepared samples. The inset shows the Tauc plot of $(\alpha h\nu)^{1/2}$ as a function of photon energy for different materials.

The adsorption edge for the modified TiO$_2$ is attributed to the conjugated structure between the $\pi$-conjugated structure of His and TiO$_2$, consistent with previous reports [13]. In addition, the Tauc equation was used to evaluate the band gap ($E_g$) of the samples [19, 20]. The inset in figure 3 shows the plot of $(\alpha h\nu)^{1/2}$ as a function of photo energy ($h\nu$) for catalysts. The band gaps are calculated to be 3.10, 2.96, 2.97, 2.96 and 2.98 eV, respectively for TiO$_2$, TiO$_2$-His-1, TiO$_2$-His-2, TiO$_2$-His-3 and TiO$_2$-His-4, respectively. In compared with TiO$_2$ (3.10 eV), the band gap of the His-modified catalysts exhibited no obvious changes, indicating that the amount of His on the surface of TiO$_2$ had little affect the band gap of the samples [21].

Because TiO$_2$-His-3 exhibited the highest activity for photocatalytic H$_2$ production (figure 6(a)), TiO$_2$-His-3 was selected as for studying the interaction between His and TiO$_2$. The FTIR spectra of TiO$_2$ and TiO$_2$-His-3 recorded in the range of 4000–400 cm$^{-1}$ are shown in figure 4(a). The absorption peaks at 1400 and 1639 cm$^{-1}$ for TiO$_2$ and TiO$_2$-His-3 were ascribed to the bending vibration of C=O and O–H, respectively, which were caused by the adsorbed CO$_2$ and water [22, 23]. In addition, three absorption peaks, located at 1065 and 3185 cm$^{-1}$, were clearly observed in the spectrum of TiO$_2$-His-3, which were attributed to C–O bending vibration and C–N asymmetric stretching vibration in His, respectively [24]. At the same time, slightly weaker absorption peaks around 2920 and 2854 cm$^{-1}$ correlate with the C–H stretching vibration of the methylene group in His [25]. The presence of characteristic peaks of His on the FTIR spectrum of TiO$_2$-His-3 indicates that His was successfully combined on the surface of TiO$_2$. Furthermore, the TiO$_2$-His-3 exhibited an obvious new peak at 3426 cm$^{-1}$ that can be assigned to O–H stretching vibrations [24]. The strong peak of O–H stretching vibrations may be caused by the N–H–O hydrogen bond formed by the N atom of the amino group and imidazole ring interacting with an oxygen atom on TiO$_2$ [26]. Analysis of the FTIR spectra demonstrates that His was effectively anchored to the surface of TiO$_2$ via hydrogen bonding, consistent with previous reports [27]. Furthermore, the H-bond formed on the His-TiO$_2$...
Figure 4. (a) FTIR spectra of TiO$_2$ and TiO$_2$-His-3 catalysts; (b) XPS spectra of TiO$_2$ and TiO$_2$-His-3 catalysts; (c) Ti 2p and (d) O 1s spectra of TiO$_2$ and TiO$_2$-His-3 catalysts.

Figure 5. EPR spectra of TiO$_2$ and TiO$_2$-His-3 samples.

interface is conducive to the transfer of photogenerated charges [28]. Therefore, it is reasonable to speculate that enhanced photocatalytic activity of TiO$_2$ can be achieved by His loading.

To further explore the details of the interactions between His and the TiO$_2$ nanoparticle, high-resolution XPS spectra for TiO$_2$ and TiO$_2$–His–3 were examined (figures 4(b)–(d)). It is noteworthy that the peak of N atoms did not appear in TiO$_2$–His–3 (figure 4(b)), mainly due to the low content of His. Two peaks located at 458.1 (Ti 2p3/2) and 464.0 (Ti 2p1/2) eV were assigned to the Ti$^{4+}$ in the lattice of TiO$_2$ (figure 4(c)) [29–32]. After the introduction of His, the XPS curve of Ti for TiO$_2$–His–3 was similar to that of the un-treated TiO$_2$, indicating that the state of Ti in TiO$_2$–His–3 nanoparticles was not affected by the adsorption of His. The high-resolution O 1s spectra of TiO$_2$ and TiO$_2$–His–3 were deconvoluted into three individual peaks, located at binding energies of 529.5, 531.7, and 533.1 eV (figure 4(d)), which are attributed to the lattice O in TiO$_2$, absorbed oxygen, the O atom of hydroxyl species or adsorbed H$_2$O, respectively [33, 34]. After His treatment, the relative magnitude of the lattice O signal (at 529.5 eV) decreased significantly from 35.09% to 11.70%, which is due to the interaction between lattice oxygen in TiO$_2$ and nitrogen in His [35]. This phenomenon demonstrates that His was mainly adsorbed on the O atoms of TiO$_2$ via hydrogen bonding, not on the Ti atoms, consistent with the infrared analysis results.

The EPR is used to detect unpaired electron [36]. No EPR signal is observed for pure TiO$_2$ (figure 5), indicating no unpaired electrons in TiO$_2$ which is consistent with the previous reports [37]. In contrast, a strong symmetric EPR signal (g = 2.003) for TiO$_2$–His–3 catalyst is observed. This can be explained that there are more delocalized π electrons at the interface between the His layers and TiO$_2$ nanoparticles [38]. Because of the existence of conjugated π electrons in His imidazole ring, so the EPR spectrogram of His has a strong signal [39]. When TiO$_2$ is modified by His, more delocalized π electrons exist in TiO$_2$–His–3, therefore, there will appear an obvious EPR signal.
3.2. Photocatalytic activity

The normalized H₂ evolution of all samples, in the presence of sacrificial reagent (methanol) and under xenon lamp irradiation, are shown in figure 6. The error bars of as-prepared photocatalysts (figure 6(a)) is obtained after three parallel experiments. The normalized H₂ evolution rate of TiO₂-His-3 was the largest of all samples (4.77 µmol · g⁻¹ · h⁻¹ · g⁻¹) and this was 3.77 times higher than that of pure TiO₂. To investigate the stability, TiO₂-His-3 was repeatedly employed to run the H₂ reduction reaction for three cycles (figure 6(b)). After three photocatalytic runs, photocatalytic efficiency did not exhibit any evident decay after repeated runs, thereby revealing the high stability of the TiO₂-His-3 photocatalyst. To study the effect of the optical absorption properties on the activities of the samples, the PHE of the TiO₂ and TiO₂-His-3 catalysts from an aqueous solution containing CH₃OH were examined under visible-light irradiation (λ > 400 nm), and negligible H₂ production was detected. Therefore, an effect of the red shift of absorption edges (figure 3) on photocatalytic H₂ production of the samples was not apparent.

In order to further explore the influence of organic-modified TiO₂ on PHE efficiency, the H₂ evolution rates of relevant photocatalysts are summarized in table 1. The PHE rates of organic functionalized TiO₂ increase significantly, which is 1.5–2.6 times higher than that of TiO₂ in the literatures. In this study, the H₂ evolution rate is enhanced by a factor of 4.52, which is higher than the level of results reported in the literatures.

3.3. Photocatalytic mechanism

To elucidate the mechanism behind the enhancement of activity photocurrent transient responses were measured using several on-off cycles under chopped irradiation (figure 7(a)). The transient photocurrents, formed by the separation of the photogenerated e⁻/h⁺ pairs reflect the recombination rate of photoinduced charge [44]. The TiO₂-His-3 catalyst exhibited a higher photocurrent response than that of the TiO₂ sample (figure 7(a)), indicating a lower electron-hole recombination rate. This verified that His served as a valid co-catalyst that could accelerate the separation of photogenerated e⁻/h⁺ pairs and improve the performance of PHE [45]. The steady-state PL spectra of the two samples under an excitation wavelength of 300 nm are shown in figure 7(b). Compared with TiO₂, the PL intensity of TiO₂-His-3 was greatly decreased, indicating that the radiative e⁻/h⁺ recombination in TiO₂-His-3 was suppressed [46, 47]. The significant PL cutbacks of TiO₂-His-3 come from interfacial charge transfer between TiO₂ and His, consistent with the results of the
photocurrent test. Based on these results, it is confirmed that the improved hydrogen production efficiency of TiO$_2$-His-3 (figure 6) is resulted from the enhanced separation of the photoinduced charges after loading His.

Based on the above discussion, a possible reaction mechanism for photocatalytic H$_2$ production on TiO$_2$-His-3 is schematically illustrated in figure 9. To further determine the direction of the charge transfer in TiO$_2$-His-3 under irradiation by light, the relative energy level of His and TiO$_2$ were compared. According to the VB spectra (figure 8) and the band gap value, we determined that the VB position and $E_g$ value of TiO$_2$ were 2.6 eV and 3.1 eV versus SHE, respectively. The CB potential of a semiconductor ($E_{CB}$) can be calculated according the empirical equation: $E_{CB} = E_{VB} - E_g$ [48]. The calculated CB energy level for TiO$_2$ is $-0.5$ eV versus SHE. According to previous literature for density functional theory calculations, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy of His in water are $-6.57$ and $-0.43$ eV, respectively [49]. The photogenerated electrons and holes were excited in TiO$_2$ under UV-light irradiation (figure 9). Without His, the generated charge pairs of pristine TiO$_2$ are easily recombined, leading to low PHE activity. Because the LUMO level of His ($-6.57$ eV) was much more negative than the CB of TiO$_2$ ($-0.5$ eV), the photoexcited electrons would preferably transfer to the CB of the TiO$_2$ to reduce H$_2$O. The energy level of HOMO in His ($-0.43$ eV) is between the CB and VB of TiO$_2$ (figure 9). Furthermore, the hydrogen bond formed by His and the exposed O atoms in the surface of TiO$_2$ can make the conjugated $\pi$ electrons in His more delocalized at the interface between His and TiO$_2$, which is beneficial for transferring holes [47]. As a result, the intimate contact can offer a channel for interfacial charge transfer between His and TiO$_2$. Therefore, the photogenerated holes in TiO$_2$ may be directly transferred from the VB of TiO$_2$ to the HOMO of His and react with CH$_3$OH. This hole transfer at the interface is beneficial for the separation of the photoinduced charge carriers. Thus, an enhanced photocatalytic activity in PHE was acquired on TiO$_2$-His-3. A similar photocatalytic reaction mechanism has been reported previously in polyaniline-modified TiO$_2$ photocatalysts [10].

Significantly, TiO$_2$-His-3 had higher H$_2$ production activity than TiO$_2$-His-1, TiO$_2$-His-2 and TiO$_2$-His-4 catalysts (figure 6(a)). This phenomenon may be understood by considering the effect of the amount of His loaded on TiO$_2$, that is, the unique His-TiO$_2$ interface formed by tuning the amount of His on the surface can facilitate the transfer of photogenerated holes. For TiO$_2$-His-3, the superior performance...
of H$_2$ generation was largely ascribed to the boundary effect and high compatibility between TiO$_2$ and His [50]. Too much or too small histidine will affect the compatibility of the interface. If the quantity of histidine on the surface of TiO$_2$ is too small, insufficient numbers of hydrogen bonds are formed between His and TiO$_2$, that is, there are too few hydrogen bonds to form a complete His-TiO$_2$ interface and this affects the hole transfer rate. Therefore, the H$_2$ production activity of TiO$_2$-His-4 is much lower than that of TiO$_2$-His-3. However, for TiO$_2$-His-1 and TiO$_2$-His-2, too much histidine will induce self-assembly of the histidine molecules that have already bound to TiO$_2$, which will result in the initial His-TiO$_2$ interface to be subsequently covered. This result is consistent with the result of previous studies, that is, the photocatalytic activity decreases as the thickness of the surface layer composite increases [51]. As a result, the PHE activities of TiO$_2$-His-1 and TiO$_2$-His-2 decreased in compared with TiO$_2$-His-3.

4. Conclusions

In summary, a green and easy strategy was developed to synthesise a range of His-modified TiO$_2$ catalysts for photocatalytic H$_2$ evolution via water-splitting. This simple approach resulted in the formation of hydrogen bonds between lattice O in TiO$_2$ and the hydroxy group in His, thus, His have close interaction with TiO$_2$ nanoparticles. Among the obtained catalysts, the TiO$_2$-His-3 sample exhibited the highest H$_2$ production rate (4.77 μmol·g$^{-1}$·h$^{-1}$·gm$^{-2}$), corresponding to 4.77-folds larger than that of the pristine TiO$_2$. The improved photocatalytic performance of TiO$_2$-His-3 was attributed to the unique His-TiO$_2$ interface between His and TiO$_2$ through hydrogen bonding, which was conducive to the transfer of photogenerated holes from the VB of TiO$_2$ to the HOMO of His. Moreover, the TiO$_2$-His-3 photocatalyst kept constant PHE activity within three cycle tests of total 30 h, demonstrating the high stability of the photocatalyst. The simple charge modification approach by using organic His as co-catalyst could be applied to other photocatalytic systems and various high-performance photocatalysts for energy conversion may be designed.

Acknowledgments

The authors would like to express their sincere appreciation to the National Natural Science Foundation of China (21972082).

ORCID iDs

Chuanyi Wang  https://orcid.org/0000-0002-7146-115X
Yingxuan Li  https://orcid.org/0000-0002-9139-4177

References

[1] Liu Y, Zhang Z Y, Fang Y R, Liu B K, Huang J D, Miao F J and Bao Y N 2019 Appl. Catal. B 252 164–73
[2] Chen X B, Shen S H, Guo L J and Mao S S 2010 Chem. Rev. 110 6503–70
[3] Zhang H J, Chen G H and Bahnemann D W 2009 J. Mater. Chem. 19 5089–121
[4] Afanasiev P 2020 Appl. Catal. A 598 117548
[5] Li X G, Bi W T, Zhang L, Tao S, Chu W S, Zhang Q, Luo Y, Wu C Z and Xie Y 2016 Adv. Mater. 28 2427–31
