Surface engineering to reduce the interfacial resistance for enhanced photocatalytic water oxidation

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Abstract

Interfacial resistance of the charge carriers across TiO_2 to co-catalysts is one of the main limiting factors for realizing high photocatalytic efficiency of water oxidation. Herein, an amorphous TiO_x layer is introduced on the surface of crystalline TiO_2 catalyst to form the core-shell structure (am@TiO_2) via a oxidation corrosion method. Owing to the surface disordered Ti-O layer, the obtained am@TiO_2 exposes abundant $-\text{OH}$ groups for the homogeneous loading of nano-sized IrO_x , while the charge carriers interfacial migration is substantially enhanced. The as-prepared $\text{IrO}_x\text{-am@TiO}_2$ exhibits the photocatalytic water oxidation performance with a O_2 evolution rate of $143.6 \mu\text{mol/g}\cdot\text{h}$, which is approximately 14 times higher than that of the bare am@TiO_2 . Moreover, an apparent quantum yield (AQY) of 18.99% is obtained under LED-405 illumination. This work provides a direction for improving the photocatalytic performance and helps to gain fundamental understanding on the water oxidation steps.

Keywords: TiO_2 , water oxidation, hole-transfer, photocatalysis, IrO_x , co-catalyst

1. Introduction

Overall water splitting via photocatalysis to hydrogen (H_2) generation has been considered to be one of the potential technologies for addressing the current energy and greenhouse effect related issues.^[1-4] However, its oxidation is the rate-determining step and limits the final efficiency.^[5-8] Loading co-catalysts, such as IrO_x , RuO_x , and MnO_x , onto photocatalysts has been proven to be an effective strategy to improve the water oxidation efficiency,^[9-11] but the efficiency is still lower than the theoretical values of the semiconductors. The interface barrier between photocatalyst and co-catalyst is the main cause for reducing the ratio of separated holes reaching the surface.^[12]

There are three accepted steps for powder semiconductor photocatalysis involved in electron-hole pairs: generation in catalyst under illumination, separation from bulk to surface and reaction at the reduction or oxidation sites.^[13-14] It should be noted that not all the separated carriers migrate to the surface reaction sites successfully and the part of carriers consumption reduces the photocatalytic efficiency.^[15] That is, how to ensure all the separated electron-hole pairs moving to the surface and participating in the particular reaction is a determinate factor for improving the photocatalytic efficiency.^[16] For the loading co-catalyst based photocatalytic water splitting system, one of the available strategies to further improve the solar-to chemical energy efficiency is increasing the ratio of separated carriers taking part in surface reaction, but this has been rarely studied.^[17]

The most effective strategy for furthest achieving the highest utilization rate of photogenerated carriers is establishing the carrier-transfer channel by using a metal,^[18-20] graphene^[21-22] or compound materials^[23] to form a sandwiched system with photocatalyst-carrier transfer-reaction sites. For example, electron-transfer channel based on Au metal was introduced between TiO_2 and CdS to form an anisotropic CdS–Au– TiO_2 junction, which exhibited the enhanced photocatalytic activity owing to the fast vectorial electron transfer.^[18]

Although the electron-transfer has been well studied, less attention has been paid to the hole-transfer based system, which is very useful for the oxidation reaction.

It is well known that TiO_2 has been used in photocatalysis largely due to its suitable valance-band position for oxidizing water to O_2 with the low efficiency.^[16,24-25] The IrO_x -based samples have been regarded as the practical water oxidation catalysts with the fast kinetics and outstanding stability in O_2 generation from water splitting.^[5] To ensure a high-efficiency and stable water oxidation system, herein, we take advantages of using both TiO_2 and IrO_x to achieve the fast hole transfer and utilization by introducing a hole-transfer bridge, which consists of amorphous TiO_2 (am: TiO_2) layer and metallic Ir. The am: TiO_2 is first introduced on TiO_2 surface using developed method based on carbon nitride (CN) corrosion. Then the obtained TiO_2 sample (am@ TiO_2) is employed to load IrO_x via photo-deposition^[26-27] and chemical reduction methods to form the four-layer of TiO_2 -am: TiO_2 -Ir- IrO_2 nano-junction system (IrO_x -am@ TiO_2). Owing to the homojunction of TiO_2 to am: TiO_2 , and the fast carrier transportation character of am: TiO_2 layer, the interfacial resistance for the hole transfer is greatly reduced and thus the sample of IrO_x -am@ TiO_2 exhibited the highest photocatalytic water oxidation performance with the O_2 generation rate of $143.6 \mu\text{mol/g}\cdot\text{h}$ under the illumination of AM 1.5.

2. Results and Discussion

2.1 Photocatalyst synthesis and characterization

Figure 1. (a) Schematic illustration of the synthesis of am@TiO₂ via two-step process. (b) TEM image of CN-TiO₂ sample, scale bar, 100 nm. (c) XRD patterns of the TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂ samples. (d) HRTEM image of am@TiO₂ sample, scale bar, 5 nm and (e) the corresponding magnified TEM, scale bar, 1 nm. (f) The concentration distribution based on the STEM measurement of oxygen element of the sample of am@TiO₂. Scale bar, 100 nm.

The am@TiO₂ was synthesized by mixing anatase TiO₂ and urea (mass ratio, 1:4), followed by two-step calcination process as shown in **Figure 1a**. The mixtures were treated at 550 °C in N₂ atmosphere to obtain the compound of g-C₃N₄ and TiO₂ (CN-TiO₂), which was confirmed by Fourier-transform infrared spectroscopy (FTIR) spectra (**Figure S1a**). **Figure 1b** shows the transmission electron microscope (TEM) image of CN-TiO₂ with the obvious CN layer. The sample of CN-TiO₂ was further annealed at 550 °C in air for 2h to obtain the am@TiO₂, which showed no g-C₃N₄ signals in the FTIR result (**Figure S1a**). Moreover, X-ray photoelectron spectroscopy (XPS) further confirmed that the CN was removed thoroughly (**Figure S2**). X-ray powder diffraction (XRD) patterns show the similar patterns of CN-TiO₂ and am@TiO₂ (**Figure S1b**), suggesting that the thickness of the surface amorphous layer was less.

The reference sample of TiO₂ (TiO₂-ref) was synthesized under the same experimental condition in the absence of urea. XRD patterns of the am@TiO₂ and TiO₂-ref in **Figure 1c** displayed the same peaks, suggesting the thin amorphous TiO₂ layer, and the high resolution TEM (HRTEM) image further confirmed its *ca.* 5 nm thickness (**Figure 1d-e**). Moreover, their TEM images (**Figure 1d** and **Figure S3**) showed the similar particle size with the different surface state of with and without amorphous layer, confirming the CN component was the determinant factor for the formation of am@TiO₂ sample.

The element oxygen concentration distribution based on the O-K ray intensity obtained from scanning transmission electron Microscope (STEM) was further measured to confirm the surface state of am@TiO₂. As shown in **Figure 1f**, more oxygen percentage of surface region than bulk part can be clearly observed, suggesting that there are abundant surface adsorbed –OH or H₂O species. It should be noted that the thickness of the amorphous layer can be tuned by CN content as shown in **Figure S4-S5**. The defect (bulk and surface) information on TiO₂, TiO₂-ref and am@TiO₂ was further studied by positron annihilation technique. The three-exponential fitted results show that the three samples exhibit the near life values with the percentages listed in **Table S1**, suggesting that no defect sites such as oxygen, titanium and line vacancies were introduced by the surface amorphous layer.

The CN corrosion mechanism for am@TiO₂ formation from CN-TiO₂ sample was studied by a Quasi *in situ* XPS measurement. CN-TiO₂ was treated to obtain five samples under 500 °C for different durations of 15, 30, 45, 60 and 90 min. As shown in **Figure S6a**, there are obvious Ti³⁺ signals at the binding energy values of *ca.* 457.4 and 463.2 eV^[28-30] for the first 60 minutes, with the sample treated after 30 min showing the highest intensity. For the signal of O 1s XPS results (**Figure S6b**), the samples exhibit the increased signal intensity of adsorbed –OH and H₂O at *ca.* 532.3 and 533.8 eV^[29], indicating that the treatment induced more surface oxygen vacancy sites, and this is consistent with the STEM result in **Figure 1f**. The Ti⁴⁺ ions of surface Ti-O layers receive the electrons from N³⁻ ions oxidation, and then

form the Ti^{3+} sites with the nearby oxygen vacancies, which will adsorb water to produce the adsorbed $-\text{OH}$, and then the surface disordered Ti-O layers forms.

$\text{IrO}_x\text{-am@TiO}_2$ was synthesized via a two-step process, i.e. first photo-deposition and then chemical treatment by H_2/Ar at 200°C . XRD pattern of the $\text{IrO}_x\text{-am@TiO}_2$ suggests that the phase structure of the am@TiO_2 unchanged after IrO_x loading (**Figure 1c**), and no obvious IrO_x -based XRD peaks, confirming the low loaded content. Raman spectra of samples of $\text{TiO}_2\text{-ref}$, am@TiO_2 and $\text{IrO}_x\text{-am@TiO}_2$ show the main peaks loaded at 395 , 515 and 635 cm^{-1} (**Figure S7a**), which are assigned to the typical E_g , A_{1g} and B_{1g} of Raman vibration modes.^[29] The relative intensity of B_{1g}/E_g of am@TiO_2 sample is decreased compared with $\text{TiO}_2\text{-ref}$ sample. It has been reported that the E_g and B_{1g} can be attributed to the symmetric stretching and bending vibration patterns of O-Ti-O.^[29] The changes of B_{1g}/E_g suggest that the coordinate form of surface O-Ti-O bonds has been disorganized by the non-defective sites. FTIR results in **Figure S7b** show the similar curves. However, the sample of am@TiO_2 or $\text{IrO}_x\text{-am@TiO}_2$ exhibits a stronger intensity for the peaks at 1600 and 3400 cm^{-1} assigned to adsorbed $-\text{OH}$ groups^[5] in comparison to the $\text{TiO}_2\text{-ref}$, further confirming the more surface disordered Ti-O arrangement for am@TiO_2 -based samples. It should be mentioned that $\text{IrO}_x\text{-am@TiO}_2$ exhibits a similar $-\text{OH}$ group intensity to that of bare am@TiO_2 , suggesting that the loading of IrO_x nanoparticles does not change the surface $-\text{OH}$ sites on the am@TiO_2 surface. Moreover, the surface areas were measured by N_2 adsorption and desorption as shown in **Figure S8**, in which the three samples exhibited the BET surface areas of 10.7 , 10.7 and $10.6\text{ m}^2/\text{g}$, respectively. No obvious difference was detected, implying that the difference of $-\text{OH}$ amount of the samples came from the surface properties.

Figure 2a and **Figure S8** show the TEM image of $\text{IrO}_x\text{-am@TiO}_2$, the homogeneous nano-sized (ca. 1.5 nm) dark dots are evenly distributed on the TiO_2 surface. However, the reference sample of $\text{IrO}_x\text{-TiO}_2\text{-ref}$ shows the obvious aggregated particles of loaded IrO_x (**Figure S9**), suggesting that the surface am:TiO_2 layer help the homo-dispersion of IrO_x

particles. The HRTEM image in **Figure 2b** shows that the IrO_x is loaded on amorphous layer. The yellow magnified region shows the clear interplanar spacing value of 0.22 nm attributed to the tetragonal IrO_2 (200) (**Figure 2c**), however, the bulk region of this IrO_x particle contacted with am@ TiO_2 seems disparate and belongs to metallic Ir, the Ir- IrO_2 core-shell structure is formed by the H_2 reduction and air oxidation. The high-angle annular dark field (HAADF) STEM image further confirms the uniform size (ca. 3 nm) of bright dots on the support (**Figure 2d**), and the corresponding element mapping suggests that the detected dots are Ir-based samples. The line mapping shows the weak Ir elemental signal, confirming the low content of loaded IrO_x (**Figure 2e-f**). Moreover, a particle size of around 3 nm of the loaded IrO_x can be obtained (**Figure S10**). The elemental mapping on the reference sample of $\text{IrO}_x\text{-TiO}_2\text{-ref}$ was also carried out (**Figure S11**). The relative large particle size (ca. 10 nm) of IrO_x with the agglomeration can also be found.

Figure 2. TEM analysis of the $\text{IrO}_x\text{-am@TiO}_2$ sample. (a) TEM image, (b) HRTEM image, and (c) the corresponding magnified region with the clear lattice fringes, scale bar, 2.5 nm.

(d) HAADF-STEM image and the elemental mapping. (e) STEM result with the line mapping, scale bar, 10 nm, and (f) the corresponding elemental line mapping results.

The optical characteristics of the TiO_2 -ref, am@TiO_2 and $\text{IrO}_x\text{-am@TiO}_2$ were studied via using UV-Vis-NIR absorption spectroscopy and room-temperature photoluminescence (PL) spectroscopy. As shown in **Figure S12a**, all three samples showed the same absorption cut-off edge of *ca.* 388 nm, which is a typical optical property of anatase TiO_2 .^[28-30] However, for the am@TiO_2 -based samples, the obvious tail absorption can be detected and the loading of IrO_x nanoparticles can further increase the absorption, suggesting that the surface amorphous TiO_2 layer and loaded IrO_x are helpful for the utilization of incident photons. The band gaps of the TiO_2 -ref, am@TiO_2 and $\text{IrO}_x\text{-am@TiO}_2$ were measured to be 3.20, 3.15 and 3.07 eV (**Figure S12b**), respectively. The PL spectra was measured at the excitation wavelength of 295 nm. As shown in **Figure S12c**, all three samples showed the obvious signals in the range of 350 to 500 nm and the sample of TiO_2 -ref gave the highest intensity, followed by am@TiO_2 and $\text{IrO}_x\text{-am@TiO}_2$, suggesting that the amorphous layer and IrO_x loading can boost the separation of photogenerated carriers.

Figure 3. XPS analysis of the TiO_2 -ref, am@TiO_2 and $\text{IrO}_x\text{-am@TiO}_2$. (a) Ti 2p, (b) O 1s and (c) Ir 4f.

Figure 3a shows the Ti 2p XPS spectrum of the samples of TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂, two main peaks at 458.7 and 464.4 eV, which can be assigned to the Ti⁴⁺ 2p_{3/2} and 2p_{1/2},^[28-30] respectively, can be found. The fitted peak locations of the three samples are 458.7, 458.55 and 458.6 eV with the values of full width at half maximum (FWHM) of 1.038, 1.028 and 1.034 eV (**Figure S13**), suggesting that there are no Ti³⁺ species in the studied samples. This result is also consistent with the above analysis about the material preparation mechanism in Figure S6. **Figure 3b** shows the corresponding O 1s XPS spectra with the three peaks located at 529.9, 531.9 and 533.5 eV, which are assigned to Ti-O, adsorbed -OH groups and water molecules,^[29] respectively. However, the sample of TiO₂-ref shows almost no adsorbed water signal (**Figure S14**). The increased -OH group signals are consistent with FTIR results (**Figure S7b**) and suggest that amorphous TiO₂ layer and IrO_x can facilitate the water adsorption. The Ir 4f XPS spectrum of IrO_x-am@TiO₂ shows two main characteristic peaks centered at 60.3 and 63.5 eV (**Figure 3c**), which are assigned to the Ir⁰ 4f_{7/2} and 4f_{5/2},^[31-32] respectively. Moreover, there are two weak peaks at 61.9 and 65.1 eV assigned to the Ir⁴⁺ 4f_{7/2} and 4f_{5/2},^[31-32] respectively. The result of Ir valence state of surface IrO_x particles consisting of 4+ and 0, is in agreement with HRTEM analysis (**Figure 2c**). The relative content of IrO₂ to metallic Ir was calculated to be 23.9% based on the peak area integral. It has been reported that the surface IrO₂-based materials can be changed into Ir hydroxyls, which are proven to be useful for the generation of OER intermediates.^[32] Thus, the Ir⁰ species receive charge carriers from the amorphous TiO₂ and then transfer them to the IrO_x for OER steps.

2.2 Photocatalytic water oxidation performance

Figure 4. Photocatalytic water oxidation performance of $\text{IrO}_x\text{-am@TiO}_2$ sample. (a) O_2 generation values of $\text{TiO}_2\text{-ref.}$, am@TiO_2 and $\text{IrO}_x\text{-am@TiO}_2$ samples measured under the illumination of AM 1.5 and (b) the corresponding O_2 generation. (c) O_2 generation values of $\text{IrO}_x\text{-am@TiO}_2$ sample under three LED lamp illuminations: LED-365, LED-405 and LED-425. (d) The stability measurement of $\text{IrO}_x\text{-am@TiO}_2$ under visible-light conditions of LED-405 and LED-425. (e) O 1s and (f) Ir 4f XPS spectra of $\text{IrO}_x\text{-am@TiO}_2$ before and after reaction. All the O_2 evolution experiments were carried out in AgNO_3 (0.01g/mL) solution.

The photocatalytic water oxidation performance of $\text{IrO}_x\text{-am@TiO}_2$ was conducted to verify the advantage of hole-transfer bridge for transfer of holes. The online gas chromatography (GC) signals show that the O_2 is indeed generated under the illumination of simulated sunlight (AM 1.5) (**Figure S15**). The O_2 generation rates of the $\text{TiO}_2\text{-ref.}$, am@TiO_2 and $\text{IrO}_x\text{-am@TiO}_2$ are illustrated in **Figure 4a** and **Figure S16**, in which the sample of $\text{IrO}_x\text{-am@TiO}_2$ giving the best activity. Typically, the O_2 evolution rates were 10.3, 22.4 and 143.6 $\mu\text{mol/g}\cdot\text{h}$ for the $\text{TiO}_2\text{-ref.}$, am@TiO_2 and $\text{IrO}_x\text{-am@TiO}_2$, respectively (**Figure 4b**). It should be noted that the latter two samples gave around 2.16 and 13.9 times higher than $\text{TiO}_2\text{-ref.}$, confirming

that the amorphous TiO₂ layer and IrO_x loading are effective in separating the photogenerated carriers and promoting the surface water oxidation processes. Moreover, the IrO_x loading content plays a vital role for the final optimal O₂ evolution (**Figure S17a**). The 1.5% IrO_x-am@TiO₂ sample showed the highest performance. We also synthesized the two reference samples of IrO_x-TiO₂-ref and IrO_x-am@TiO₂-1, which were synthesized via the same preparation process with IrO_x-am@TiO₂ but using TiO₂-ref as supporter and in N₂ atmosphere, respectively. The corresponding photocatalytic water oxidation performance can be found in **Figure S19**. Clearly, the activity of IrO_x-am@TiO₂-1 or IrO_x-TiO₂-ref is lower than the sample of IrO_x-am@TiO₂, suggesting that the surface amorphous TiO₂ layer can be helpful for the separation and migration of photogenerated carriers. Moreover, the sample of IrO_x-am@TiO₂-1 exhibits a better activity than IrO_x-TiO₂-ref, further confirming that the surface amorphous TiO₂ layer is helpful for the carrier interface migration across TiO₂ to IrO_x.

Next, the photocatalytic performance of the IrO_x-am@TiO₂ was measured under the monochromatic incident illumination to investigate the apparent quantum/conversion yield (AQY). As shown in **Figure 4c**, the linear increase in the O₂ generation as a function of reaction times can be observed under the illumination of the three monochromatic lamps of LED-365, 405 and 425, suggesting that the IrO_x-am@TiO₂ is activated not only under UV condition of LED-365, but also the visible-light of LED-405 or LED-425. The O₂ evolution rates were 70.3, 38.56 and 16.66 μmol/g*h for the LED-365, 405 and 425, respectively. The AQY can be calculated according to the following equation: $AQY = (4 * O_2 \text{ molecules}) / (\text{number of incident photons}) * 100\%$. As shown in **Figure S17b**, the calculated AQY values were 38.4%, 18.9% and 7.82% under the illumination of LED-365, 405 and 425, respectively. Please note that the surface disordered Ti-O layers and the loading of Ir-IrO₂ nanoparticles are responsible for the visible-light absorption [33-34].

However, for the TiO₂-ref and am@TiO₂, the former shows almost no activity under LED-405 and LED-425 while the latter exhibits considerable O₂ evolution under the illumination of

above two lamps (**Figure S18**). This is consistent with the above UV-vis absorption results (**Figure S12a**), further suggesting that the surface amorphous TiO_2 layer and loaded IrO_x nanoparticles can assist to the effective utilization of visible-light photons.

The stability of the $\text{IrO}_x\text{-am@TiO}_2$ under the visible-light condition (LED-405 and 425) was studied. Almost no change in the activity was detected over four cycles of measurements (**Figure S19** and **Figure 4d**). The chemical valence states after the stability test were further measured to confirm unchanged surface state. As shown in **Figure 4e**, the O 1s XPS spectra exhibits the same peak location before and after the long-time measurement, suggesting the stable chemical environment. However, the proportions of surface OH group and adsorbed water were 20.9% and 15.3% before the stability test based on the area integral, while these values increased to 24.2% and 17.2% after the reaction, respectively (Table S2). Considering the fact that no peak position is shifted, these increased surface OH groups and H_2O molecules can be attributed to the weakly adsorbed components during the testing. Moreover, the Ir 4f XPS spectra before and after the reaction suggest no shift in the peak positions (**Figure 4f**). The relative ratio of IrO_2 to metallic Ir based on the area integral after the stability test is calculated to be 23.79%, close to the previous value (**Figure 3c**), suggesting that the surface IrO_2 layer is very chemical stable during OER processes, and also acts as a protective layer for the inner metal. Thus, it can be preliminary concluded that the photogenerated holes firstly transferred across the amorphous TiO_2 layer to metal Ir, and then reach to the surface IrO_2 for finishing following multi-step OER steps without changing the surface IrO_2 chemical state.

2.3 Catalytic mechanism investigation

Figure 5. Electrochemical properties of the samples. (a) Polarization curves of the $\text{TiO}_2\text{-ref.}$, am@TiO_2 and IrOx-am@TiO_2 ; and (b) the corresponding Tafel plots and (c) the overpotential values at the current density values of 5 and 10 mA/cm^2 . (d) Photocurrent responses of the three recorded under the illumination of AM 1.5, and (e) the corresponding current density values measured under the two bias voltages of 0.4 V and 0.8 V. (f) Transient responses of photocurrents of the three samples measured under the illumination of LED-405 lamp. All the measurements were carried out in 0.5 M Na_2SO_4 solution.

The inherent characteristics of photocatalytic process is the interfacial and surface reactions. The photogenerated charge carriers migrate to the surface reaction sites and then take part in the corresponding reactions.^[35-36] The electrocatalytic performances of the $\text{TiO}_2\text{-ref.}$, am@TiO_2 and IrOx-am@TiO_2 were further investigated to gain insight into the internal kinetics of the enhanced photocatalytic water oxidation. The polarization curves were first studied in a neutral solution (**Figure 5a**). All three samples showed considerable current responses in the voltage ranges of 1.3 to 1.8 V (vs. RHE), suggesting that these TiO_2 -based samples can

achieve the electrolysis of water. It should be noted that the IrO_x-am@TiO₂ exhibits the first current response, followed by am@TiO₂ and then TiO₂-ref, confirming that the introduction of surface amorphous TiO₂ layer and IrO_x loading can boost the water splitting.

The corresponding Tafel plots, which are useful for exploring the reaction kinetics during the electrocatalytic process, are shown in **Figure 5b**. The calculated Tafel slopes for the TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂ were 342, 325 and 203 mV/dec, respectively. The overpotential (η , mV) is the other vital parameter for investigating the difficult degree of the water oxidation. The TiO₂-ref sample shows the largest overpotential value at the current densities (j) of 5 or 10 mA/cm² (**Figure 5c**), promisingly, both am@TiO₂ and IrO_x-am@TiO₂ exhibit clear decreases in the overpotential values. Particularly, the measured η values of the TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂ were 410, 308 and 250 mV, respectively to achieve 10 mA/cm² current densities. The smallest η and the fastest reaction kinetics of the IrO_x-am@TiO₂ co-determine the excellent water splitting performance.

The photoelectric properties were also studied to confirm the excellent performance of photogenerated carrier migration and surface reaction under the illumination of simulated sunlight. All three samples (TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂) exhibited considerable photocurrent responses at the potential range of 0 to 1.6 V (vs. RHE) (**Figure 5d**), in particular, the IrO_x-am@TiO₂ obtained the highest current value as compared to the am@TiO₂ and TiO₂-ref, suggesting that the amorphous TiO₂ layer and IrO_x loading could timely extract photogenerated holes for the surface reaction. The current values of three samples (TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂) had been compared under the bias voltage values of 0.4 and 0.8 V (**Figure 5e**) with the sample of IrO_x-am@TiO₂ achieving the highest current density value.

Furthermore, the applied bias photon-current efficiency (ABPE) can be obtained based on the following equation:

$$ABPE = [j \times (1.23 - V_{app})] / P_{light} \quad (1)$$

where j is the photocurrent density (mA/cm^2); V_{app} is the applied bias (vs. RHE), and P_{light} is the incident light intensity ($100 \text{ mW}/\text{cm}^2$). It can be clearly seen that $\text{IrO}_x\text{-am@TiO}_2$ obtained the highest ABPE value of 0.53% at the bias voltage of 0.3 V, followed by 0.22% at 0.41 V for the am@TiO_2 and 0.12% at 0.52 V for the $\text{TiO}_2\text{-ref}$ sample (**Figure S20a**). This further confirms that the introduction of surface TiO_2 and IrO_x can facilitate fast and high photon-current conversion.

The transient response of the photo-to-current was further carried out as it is very important for explaining the separation ability of photogenerated carriers. As shown in **Figure 5f**, all samples showed the typical current-time (I-t) signals when illuminated using a LED-405 lamp (and LED-425 condition in **Figure S20b**). No significant response delay was detected, suggesting the typical semiconductor property of the TiO_2 -based samples. However, for the $\text{TiO}_2\text{-ref}$ and am@TiO_2 , some current recovery delay can be detected (**Figure S21**). This suggests that the charge carriers are generated under illumination, and the current values are originated from the surface chemical reaction. However, for the $\text{TiO}_2\text{-ref}$ or am@TiO_2 , the surface reaction is not completed owing to the surface reaction dynamics.

The density functional theory (DFT) calculations were further carried out to obtain more information about the carriers migration of am@TiO_2 -based samples. The charge density difference shows that the interface region of crystal and amorphous TiO_2 is the electron collection center (**Figure 6a**), and thus the surface reaction sites i.e. catalyst-solution interface exhibit the electron deficiency, which can promote the water or -OH groups adsorption. The projected density of states (PDOS) of the above model were next conducted to study the promotion of carrier separation. As shown in **Figure 6b**, an obvious defect energy level in the bandgap of the PDOS of amorphous TiO_2 can be observed, confirming the presence of many defect sites, which will provide more free carriers. According to the merit of electron accumulation in crystal and amorphous TiO_2 interface, the am@TiO_2 layer will be in such a

condition of polarization, that is, it works as the hole transfer bridge and then can promote the photocatalytic oxidation performance.

Figure 6. Interface study on the samples. (a) Charge density difference and (b) the corresponding PDOS spectra of am@TiO₂ sample. (c) EIS spectra of the TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂. (d) Photocatalytic water oxidation mechanism: (1) reference IrO_x-TiO₂ sample and (2) IrO_x-am@TiO₂ sample.

The surface reaction refers to carrier migration resistance can be studied via electrochemical impedance spectroscopy (EIS) under dark and illumination conditions. The samples of TiO₂-ref., am@TiO₂ and IrO_x-am@TiO₂ show the typical semicircles with the reduced radiuses (**Figure 6c** and **Figure S22**), suggesting that the surface amorphous TiO₂ layer and IrO_x loading can reduce the resistance of the carrier interface migration. The fitted results based on the circuit diagram (**Figure S23**) can be found in **Table S3**. The parameters of R1 and R2 are known as the carrier resistance across the electrode-to-catalyst and catalyst-to-solution interfaces,^[23] respectively. Clearly, some slight changes in the R1 values can be observed, while the reduction of R2 values appears when comparing the TiO₂-ref and IrO_x-am@TiO₂.

Notably, the R2 value of the TiO₂-ref was measured to be 360 ohm/cm², which is almost 6 times higher than that of the am@TiO₂, further confirming that the adsorbed water or -OH group can lower the energy barrier of the carriers migration.

The mechanism of our photocatalytic water oxidation can be summarized as follows: TiO₂ nanoparticles generate electron-hole pairs upon illumination; and the holes are transferred to the IrO_x sites across amorphous TiO₂ layer, which acts as a hole-transfer bridge. In the absence of this bridge, the interface resistance between TiO₂ and IrO_x is high and thus the carrier migration rate is slow (**Figure 6d-1**). However, in the case of IrO_x-am@TiO₂, the TiO₂ layer weakens the Schottky barrier and the photogenerated holes are rapidly travelled across the TiO₂ layer to Ir and then IrO_x for completing the water oxidation (**Figure 6d-2**).

3. Conclusions

In this work, a four layer i.e. TiO₂-am:TiO₂-Ir-IrO₂ material with a hole-transfer bridge is designed using a facile two-step synthesis method. With the support of am:TiO₂-Ir, the photogenerated holes of TiO₂ are transferred to the water oxidation sites of IrO₂ promptly, and induce a photocatalytic O₂ generation rate of 143.6 μmol/g*h under the illumination of AM 1.5. Moreover, the sample of IrO_x-am@TiO₂ exhibits an AQY value of 18.99% LED-405 illumination. DFT calculations confirm that the surface am:TiO₂ layer possesses many defect sites, which promote the migration of free electrons to the interface of amorphous and crystal phases. This work introduces a promising strategy to boost carrier transfer via building a hole-transfer bridge and help us for designing more efficient photocatalysts.

Supporting Information

Supporting Information is available from the author. Experimental part. FTIR spectra, XRD, and N 1s XPS spectra of TiO₂, CN-TiO₂ and am@TiO₂ samples. TEM images of TiO₂ precursor, TiO₂-ref and CN-TiO₂ samples. Positron annihilation results of TiO₂, TiO₂-ref and

am@TiO₂. Quasi *in situ* XPS measurement of CN-TiO₂-based samples. Raman, FTIR, Ti 2p_{3/2}, O 1s XPS curves, ABPE and I-t results of TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂ samples. BET results. TEM images of IrO_x-TiO₂-ref sample. Ir element line mapping result. Element mapping of reference IrO_x-TiO₂-ref sample. The optical characteristics of the TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂. The online GC signals. O₂ generation of the am@TiO₂ and TiO₂-ref samples. O₂ generation rates of the IrO_x-am@TiO₂ with the different IrO_x content loading and the AQY plots. The photocatalytic water oxidation performance of samples of IrO_x-TiO₂-ref, IrO_x-am@TiO₂-1 and IrO_x-am@TiO₂. O₂ generation values of the TiO₂-ref. and am@TiO₂ samples under LED-405 and 425 illumination. The stability test of the IrO_x-am@TiO₂. EIS plots.

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TOC

A hole-transfer bridge consisting of amorphous TiO_2 and metallic Ir is designed for inducing the separation and migration of photogenerated carriers. With the help of surface IrO_2 layer, the transferred holes are used timely for the reaction of water oxidation for O_2 generation with the enhanced solar-to- O_2 conversion efficiency even under visible-light illumination.

Supporting Information

Surface engineering to decrease the interface resistance for enhanced photocatalytic water oxidation

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Experimental Procedures

Materials. Chloroiridic acid (H_2IrCl_6 , AR), ethanol (AR, 99.5%), urea ($\text{CH}_4\text{N}_2\text{O}$, AR) and silver nitrate (AgNO_3 , AR) were purchased from Sinopharm Chemical Reagent Company. Anatase titanium oxide (TiO_2 , 99%) was bought from Beijing Innochem Science & Technology Limited Company. Water was purified through Ulupure ultra-pure water system before utilization. All chemicals were utilized as received without further purification.

Synthesis of am@TiO₂ sample. The calculated urea and TiO_2 (anatase phase) were transferred into one agate mortar for grinding thoroughly. The obtained mixture was added into one grinding miller for further treatment at the speed of 2000 revolutions per minute. Then the uniform product was moved into one tube furnace and treated at the temperature of 550 °C 4h under N_2 atmosphere. The heating rate was 2 °C/min. After finishing the calcination, the yellow product (CN-TiO_2) was collected and grinded for further use. Some amount of CN-TiO_2 was further added into the same tube furnace for treatment ca. 2h under the O_2 atmosphere. The reference TiO_2 ($\text{TiO}_2\text{-ref.}$) was synthesized by following the same above steps without the urea adding.

Synthesis of IrO_x-am@TiO₂. The nano-sized IrO_x particles were loaded onto am@TiO₂ surface by the following steps: the calculated amount of am@TiO₂ was added into H_2IrCl_6 solution and then the mixture was treated by vacuum-pumping. After that, the suspension solution was treated further by the illumination of simulated sunlight ca. 4h. The black suspension was changed into colourless solution. The gray powder was collected by centrifugation and dried. And then the product was moved into the tube furnace for further treatment under the condition of (5%) H_2/Ar and 200 °C 2h. Please note that the loading amount of IrO_x is the theoretical mass ratio of metallic Ir being relative to TiO_2 .

Characterizations. X-ray diffraction (XRD) was measured by Rigaku Smartlab-9kW instrument using Cu K α X-ray ($\lambda = 1.54186 \text{ \AA}$) radiation at a scanning rate of 2 °/min. The morphology and energy-dispersive X-ray spectroscopy (EDS) mapping were characterized by

FEI Tecnai G2 F20 transmission electron microscope (TEM) at an acceleration voltage of 200 kV. The ultraviolet-visible-near infrared (UV-Vis-NIR) spectra in the air against BaSO₄ was carried out on a Perkin-Elmer Lambda 1050 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra DLD spectrometer with Al K α ($h\nu$ = 1486.6 eV) as the excitation source. Raman spectra was recorded on a Via Reflex Raman Spectrophotometer. Room-temperature photoluminescence (PL) and time-resolved fluorescence spectroscopy were recorded on a PerkinElmer LS55 fluorescence spectrophotometer. Fourier transform infrared reflectance (FTIR) was carried out on a Bruker V70 spectrometer. Electrochemical measurements were conducted using a conventional three-electrode cell on a CHI760E (CH Instruments, Inc., Shanghai) electrochemical workstation. For the electrocatalytic measurements, the TiO₂-based electrodes were prepared by following the steps: a 95 wt.% of the TiO₂-based materials (3 mg), a drop of 5 wt.% of polytetrafluoroethylene and a few drops of ethanol were mixed and grinded to be a homogeneous white paste. Then the homogeneous white paste was embedded on ITO with a coating surface area of 1 cm² (1 cm $\times$ 1 cm). The as-prepared electrodes were dried at 60 °C for 12 h.

Photocatalytic water oxidation. Photocatalytic oxygen generation was performed in a vacuum system. Typically, catalyst sample of 100 mg was suspended in 100 mL AgNO₃ (0.01g/mL) solution in the reaction cell. After evacuated for 30 min, the reactor cell was irradiated by the lamps. The gaseous products were analyzed by an on-line gas chromatograph with thermal conductivity detector (Agilent GC-7890B; MS-5A column; Ar carrier; flow rate, 25 mL/min; the column temperature, 100 °C). For the AQY calculation, the detail parameters of used LED lamps were measured by using AVANTES spectrometer (AvaSpec-ULS2048CL), the distance between the light source and reaction solution was kept to be 10 cm, and the light spot radius was *ca.* 1 cm, that is, the irradiation areas were all 3.14 cm². The

light intensity of the three LED lamps was kept the same to be 2.1232 mW/cm². The FWHM values of the LED-365, 405 and 425 were measured to be 10.02, 11.75 and 18.33 nm, respectively.

Computational details. All density functional theory calculations was implemented in the Vienna Ab initio Simulation Package (VASP) with the projected-augmented wave pseudopotential (PAW) [S1-S2]. Then the PBE functional was adopted to describe the electronic exchange-correlation energy with the consideration of the van der Waals correction [S3]. The electronic cut-off energy was set to 500 eV and the k-points were sampled at the Gamma point. The LDA+U method [S4] was chosen to consider the strong localized d electrons for Ti element and the screened effective electron-electron interaction parameter U_{eff} was set to 5.8 eV based on the previous reference [S5].

FigureS1. The structural information of the TiO_2 , CN-TiO_2 and am@TiO_2 samples: (a) FTIR spectra and (b) XRD patterns.

Figure S2. XPS N 1s spectra of the TiO_2 , CN-TiO_2 and am@TiO_2 samples.

Figure S3. TEM images of the (a) TiO_2 precursor, (b) TiO_2 -ref. (c and d) HRTEM of TiO_2 -ref.

Figure S4. TEM images of the CN-TiO₂ with the different CN layer thickness, scale bar, 100 nm. Please note that the two samples were synthesized from the mass ratios of 1:1 and 1:3 of TiO₂ to urea.

Figure S5. TEM and HRTEM images of the am@TiO₂ with different thicknesses of surface amorphous layer. (a)-(d), (b)-(e) and (c)-(f) are the one-to-one correspondence.

It should be noted that the three samples of a-c were synthesized from the calcination of CN-TiO₂ samples, which were obtained from the treatment of mixture of TiO₂ and urea with the mass ratios of 1:1, 1:2 and 1:3.

Table S1. Positron annihilation results of TiO₂, TiO₂-ref and am@TiO₂.

Sample	τ_1 (ns)	I ₁ (%)	τ_2 (ns)	I ₂ (%)	τ_3 (ns)	I ₃ (%)
TiO ₂	0.1749	37.1	0.3528	61.3	2.266	1.609
TiO ₂ -ref	0.1737	41.75	0.3575	56.64	2.366	1.610
am@TiO ₂	0.1764	39.1	0.3726	59.4	2.424	1.563

Figure S6. Quasi *in situ* XPS measurement of CN-TiO₂-based samples, obtained from the calcination of CN-TiO₂ sample at 500 °C with the different time, 15 min, 30 min, 45 min, 60 min and 90 min. (a) Ti 2p XPS and (b) O 1s XPS spectra.

Figure S7. Structure information of the TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂: (a) Raman and (b) FTIR spectra.

Figure S8. The N₂ adsorption and desorption plots and the corresponding BET surface areas of the am@TiO₂, IrO_x-am@TiO₂ and TiO₂-ref samples.

Figure S9. TEM images of IrO_x-am@TiO₂ sample.

Figure S10. (a) TEM and (b) HRTEM image of IrO_x-TiO₂-ref sample.

Figure S11. The corresponding line mapping result of Ir element of IrO_x-am@TiO₂ sample.

Figure S12. Element mapping of reference IrO_x-TiO₂-ref sample without amorphous TiO_x layer.

Figure S13. The optical characteristics of the TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂: (a) UV-Vis-NIR absorption spectra, (b) band gap calculations and (c) room-temperature PL spectra under the excitation wavelength of 295 nm.

Figure S14. Ti $2p_{3/2}$ XPS curves of the TiO_2 -ref, am@TiO_2 and IrO_x - am@TiO_2 . The fitted FWHM and the peak location values are shown. Please note that the FWHM values are obtained from fitting and only for the purpose of offering the qualitative description of the symmetry of Ti $2p_{3/2}$ peak

Figure S15. O $1s$ XPS spectra of the TiO_2 -ref, am@TiO_2 and IrO_x - am@TiO_2 .

Figure S16. The online GC signals of the IrO_x-am@TiO₂ (a) without and (b) with simulated sunlight illumination (AM 1.5).

Figure S17. O₂ generation of the am@TiO₂ and TiO₂-ref samples under the simulated sunlight illumination.

Figure S18. (a) O₂ generation rates measured under the illumination of simulated sunlight of the IrO_x-am@TiO₂ with the different IrO_x content loading. (b) AQY values of 1.5% IrO_x-am@TiO₂ sample measured under the illumination of LED-365, LED-405 and LED-425.

Figure S19. The photocatalytic water oxidation performance of samples of IrO_x-TiO₂-ref, IrO_x-am@TiO₂-1 and IrO_x-am@TiO₂. (a) The real-time oxygen production and (b) the corresponding O₂ generation rate. Please note that the sample of IrO_x-TiO₂-ref was synthesized by using the same way with IrO_x-am@TiO₂ except using the TiO₂-ref. And the reference sample of IrO_x-am@TiO₂-1 was obtained from the similar preparation process with IrO_x-am@TiO₂ but using the N₂.

Figure S20. O_2 generation values of the $\text{TiO}_2\text{-ref.}$ and am@TiO_2 samples under LED-405 and 425 illumination.

Figure S21. The stability test of the $\text{IrO}_x\text{-am@TiO}_2$. Please note that the sample was recycled after the reaction of 2h and treated by stirring in 0.01M HNO_3 ca. 1h to remove the surface loading Ag particles, then added into the reaction solution for the next cycle measurement.

Table S2. Integral area values calculated from the O 1s XPS spectra of the IrO_x-am@TiO₂.

	Before stability	After stability
O-Ti	2.475	2.471
-OH group	0.813	1.023
Adsorbed H ₂ O	0.595	0.725

Figure S22. (a) ABPE curves of the TiO₂-ref, am@TiO₂ and IrO_x-am@TiO₂. (b) The current-time response of these three samples measured under the illumination of LED-425 lamp.

Figure S23. I-t responses of (a) TiO₂-ref and (b) am@TiO₂ samples.

Figure S24. EIS plots of the samples measured in dark condition.

Figure S25. A circuit diagram used for the EIS study.

Table S3. The fitted results of the EIS plots for the $\text{TiO}_2\text{-ref.}$, am@TiO_2 and $\text{IrO}_x\text{-am@TiO}_2$ samples

Sample	Dark		Illumination	
	R1 (ohm/cm ²)	R2 (ohm/cm ²)	R1 (ohm/cm ²)	R2 (ohm/cm ²)
$\text{TiO}_2\text{-ref.}$	1.89	360	1.83	70.38
am@TiO_2	1.79	67.35	1.65	22.79
$\text{IrO}_x\text{-am@TiO}_2$	1.61	34.11	1.73	4.44

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