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Inverse opal anatase/rutile TiO₂ multi-heterojunctions enable efficient photoelectrochemical water splitting†

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TiO₂ has garnered significant attention in the field of photoelectrochemical (PEC) water splitting due to its non-toxicity, cost-effectiveness, and exceptional photochemical stability. However, its practical efficiency in H₂ production is greatly hindered by inherent limitations such as low electron mobility, a short carrier diffusion length, and a wide optical band gap. Herein, we present a strategy of combining a crystal phase heterojunction and crystal facet heterojunction to enhance electron-hole separation efficiency in TiO₂. The crystal facet heterojunction of rutile TiO₂ extends the photogenerated electron lifetime by exploiting discontinuous band gaps and accelerates space charge separation. Moreover, the band alignment between rutile and anatase TiO₂ is favorable for electron transfer from rutile to anatase through a phase heterojunction. Consequently, the inverse opal anatase/rutile TiO₂ nanorod (IO-TiO₂/NRs-TiO₂) photoanode affords an excellent hydrogen production rate (682 μmol h⁻¹ g⁻¹), which is 1.6 times higher than that of an inverse opal anatase/rutile TiO₂ single heterojunction and 3 times higher than that of inverse opal anatase. This work provides valuable insights into the rational design of photoanodes with a 3D hierarchical structure.

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Introduction

Sunlight-driven photoelectrochemical (PEC) hydrogen generation represents a promising strategy for addressing the energy crisis and environmental pollution challenges.¹ However, the low conversion efficiency of solar energy to hydrogen and the slow light absorption, charge separation and reaction kinetics hinder the widespread application of PEC water splitting.^{2,3} Therefore, exploring and designing photocatalysts to effectively promote photoinduced charge separation and transfer is a critical scientific issue that needs to be addressed urgently.⁴

Since the pioneering work of Fuji Shima and Honda, who first reported PEC water splitting using TiO₂ as a working electrode, extensive investigations have been conducted on TiO₂ for PEC or photocatalytic water splitting due to its non-toxicity,

low cost, high photochemical stability, and resistance to photo corrosion.^{5,6} However, the practical solar-to-hydrogen efficiency of TiO₂ is significantly limited by its low electron mobility (1 cm² V⁻¹ s⁻¹), short minority carrier diffusion length (10–100 nm), and wide optical band gap (3.2 eV for anatase).⁷ Rutile TiO₂ theoretically possesses greater potential as a photoanode due to its higher thermostability, more efficient charge separation, and smaller bandgap compared to anatase TiO₂. However, rutile TiO₂ often exhibits lower PEC performance than anatase TiO₂ due to the increased recombination rate of electron-hole pairs.^{8,9} Moreover, anatase TiO₂ is an indirect bandgap semiconductor, indicating that photoinduced electrons can be readily separated from holes, thereby enhancing the electron lifetime.¹⁰

Rational design of the material structure is a crucial strategy for suppressing charge recombination and enhancing light absorption.¹¹ Among these strategies, the construction of host-guest heterojunction electrodes using different dimensional nanostructures has been demonstrated to effectively facilitate charge transport and suppress electron-hole pair recombination, resulting in superior performance in PEC applications.^{12,13} In such nanostructures, the host semiconductor with a large surface area and high chemical stability acts as a scaffold for the growth of guest conductive materials. This facilitates efficient collection of electrons generated within the guest materials, thereby reducing bulk charge recombination.^{12,14} For instance, 3D hierarchical structures or arrays such as FTO/FTO-

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nanocrystal/TiO₂,¹⁴ IOs/CdS NRs/CdSe clusters,¹² SnO₂/TiO₂/BiVO₄ arrays,¹³ and TiO₂/WO₃/BiVO₄ arrays,¹⁵ have been reported to enhance the light harvesting and charge transport performance due to the synergistic effects of these component nanostructures. Although TiO₂ is very attractive due to its relatively negative flat band potential and good chemical stability, the intrinsically low mobility of TiO₂ still considerably limits the overall PEC performance of TiO₂-based heterojunction photoanodes.¹³ Notably, tuning heterojunction nanostructures is also a promising strategy to suppress charge recombination in PEC water splitting, such as heterojunctions,¹⁶ phase junctions,¹⁷ facet junctions,¹⁸ and Schottky junctions.¹⁹

Inspired by the concept of junction-structure design, we propose an effective strategy to enhance charge separation and transfer efficiency of TiO₂ by incorporating anatase/rutile heterojunctions with rutile facet heterojunctions. Specifically, inverse opal anatase (IO-TiO₂) is used as a skeleton for the growth of rutile TiO₂ nanorods (NRs), and then the rutile facet heterojunction is further formed by using NRs as a substrate (NRs-TiO₂). In this hierarchical photoanode (IO-TiO₂/NRs-TiO₂), highly oriented IO-TiO₂ plays the role of a conductive skeleton to collect electrons and its face-centered cubic periodic void structure can facilitate the infiltration of the electrolyte solution and promote light scattering. Secondly, the crystal phase heterojunction material shows higher PEC activity than each individual phase due to the disorder of the TiO₂ lattice at the phase junction. The facet junction in rutile TiO₂ can prolong the lifetime of photoinduced electrons by bandgap discontinuity, accelerating spatial charge separation. Consequently, the 3D IO-TiO₂/NRs-TiO₂ photoanode shows excellent hydrogen production efficiency for water splitting, which is 1.6 and 3.0 times higher than that of IO-TiO₂/NRs and IO-TiO₂, respectively. The 3D multi-level structure constructed in this work provides new insights into the rational design of host-guest heterojunction electrodes for highly efficient PEC reactions.

Results and discussion

The impact of the crystal phase heterojunction and crystal plane heterojunction on the charge separation and transfer efficiency of the IO-TiO₂/NRs-TiO₂ photoanode was confirmed through DFT calculations. The results from band structure calculations demonstrate an optimal interlaced arrangement between different crystal faces of anatase and rutile, facilitating REDOX reactions and charge transfer (Fig. 1a).²⁰ The partial density of states (PDOS) of anatase and rutile TiO₂ reveals that the band gap value for anatase is measured to be 3.16 eV, whereas the band gap value for rutile is slightly reduced to 2.87 eV (Fig. 1b). Consequently, it can be anticipated that the construction of crystal phase heterojunctions will diminish the charge transfer energy of anatase, thereby facilitating electron transitions from the valence band to the conduction band and engendering new hole-electron pairs.²¹ Moreover, the work function is a crucial parameter for investigating electron transfer in heterogeneous structures, which can be estimated by calculating the energy difference between the vacuum and the Fermi level of the materials.^{22,23} As shown in Fig. 1c-f, the work functions of

anatase (101), rutile (110), rutile (111), and rutile (101) surfaces are determined to be 7.95, 7.89, 7.57, and 7.26 eV, respectively. Upon coupling the anatase/rutile phase heterojunction with the rutile surface heterojunction, driven by a potential difference, electrons will initially transfer from rutile (111)/(101) to rutile (110) through the surface heterointerface and subsequently from rutile (110) to anatase (101) across the heterogeneous interface until they reach equilibrium at identical energy levels.²¹ In summary, the superior electronic structure and band alignment at the multi-heterojunction interface can promote electron participation in the catalytic process, thereby enhancing the charge separation and transfer efficiency of TiO₂.

The entire preparation process of the IO-TiO₂/NRs-TiO₂ photoanode is illustrated in Fig. 2a. First, the treated FTO conducting glass is coated with polystyrene spheres (Fig. 2b and S1a†), followed by the formation of highly ordered IO-TiO₂ with a pore size of approximately 230 nm through self-assembly of a TBT precursor and subsequent calcination at 450 °C (Fig. 2c and S1b†). Subsequently, NRs (~110 nm in length) are grown on the surface of IO-TiO₂ *via* a hydrothermal reaction (Fig. 2d and S1c†). Finally, rutile TiO₂ nanosheets (with lengths ranging from 2–7 nm) are grown on the provided template by the hydrothermal method, resulting in the formation of a 3D multi-heterojunction photoanode denoted as IO-TiO₂/NRs-TiO₂ (Fig. 2e and S1d†). Varying amounts of both TBT (TiO₂ nanorod precursor) and TiCl₃ (TiO₂ nanosheet precursor) exert notable influences on the structure and morphology of NRs as well as on the coated rutile TiO₂ nanosheets (Fig. S2†). Among them, the IO-TiO₂/NRs-TiO₂ photoanode with TBT-0.15 mL and TiCl₃-0.25 mL exhibits optimal morphology and nanostructures, and was chosen as the target sample. Notably, TEM (Fig. 2f and S3†) and HRTEM images confirm the presence of a crystal phase and crystal plane heterojunction, including anatase/rutile heterostructures (Fig. 2g) and rutile (111)/(101) heterostructures, respectively (Fig. 2h).^{10,24,25} The presence of anatase and rutile phases in the sample was confirmed by selective area electron diffraction (Fig. S4†). Furthermore, the elemental distribution exhibits suitable ratios of Ti, O, and C elements in IO-TiO₂/NRs-TiO₂ with a highly uniform distribution (Fig. 2i and S5†).

Scanning transmission electron microscope (STEM) images of NRs-TiO₂ within IO-TiO₂/NRs-TiO₂ also provide additional evidence for the uniform distribution of Ti, O, and C elements as well as the formation of crystal heterojunctions (Fig. S6†). The cross-section morphology of IO-TiO₂/NRs-TiO₂ further confirms its 3D hierarchical structure (Fig. S7†). Moreover, the structure of the IO-TiO₂/NRs-TiO₂ sample was further investigated using atomic force microscopy. The current peak indicated by the dotted line corresponds to the height change curve (Fig. S8†), and it can be observed that these current peaks are predominantly located near the junctions of crystal phases and crystal facet heterojunctions. Within the pure IO-TiO₂ range corresponding to the height change curve, all current values are consistently lower and tend to remain flat, thereby revealing successful preparation of a multi-heterojunction system that significantly enhances carrier mobility.

The crystal structures of FTO, IO-TiO₂, IO-TiO₂/NRs, and IO-TiO₂/NRs-TiO₂ were investigated using X-ray diffraction (XRD).



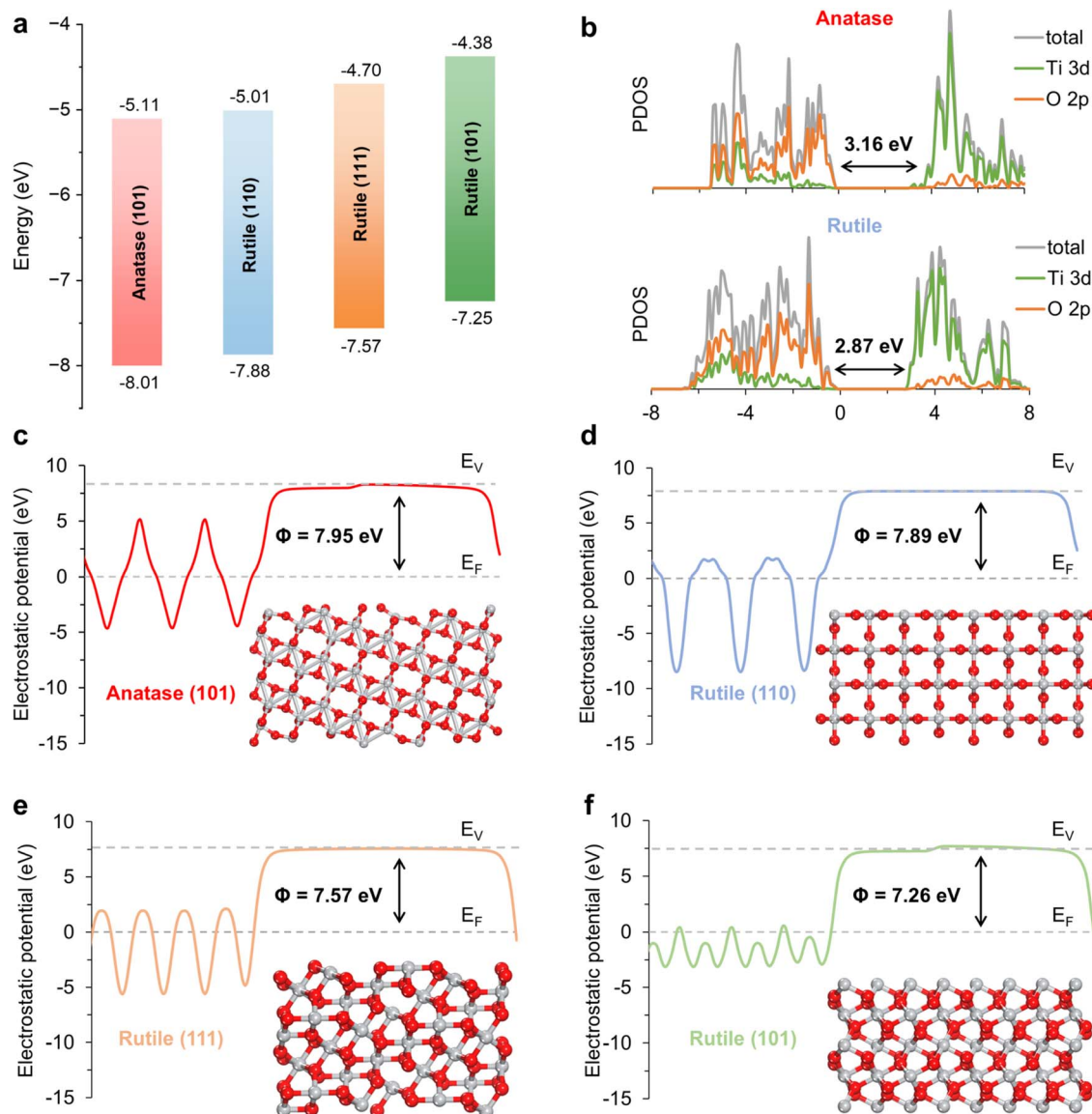


Fig. 1 (a) The band structures and migration of the charges and holes in anatase (101), rutile (110), rutile (111), and rutile (101) surfaces. (b) The partial density of states (PDOS) of anatase and rutile TiO₂ unit cells using the HSE 06 functional. The zero of the energy corresponds to the Fermi level. Electrostatic potential of (c) anatase (101), (d) rutile (110), (e) rutile (111), and (f) rutile (101) surfaces.

IO-TiO₂ exhibits distinct peaks at 25.3° and 48.0° as shown in Fig. 3a, corresponding to the characteristic peaks of anatase TiO₂. After growing NRs on the IO-TiO₂ surface, IO-TiO₂/NRs not only retains their anatase phase but also exhibits rutile characteristic diffraction peaks at 27.4° (110), 36.1° (101), and 62.7° (002). These results provide evidence for the successful formation of an anatase/rutile-phase junction between IO-TiO₂ and NRs. After further coating of TiO₂ nanosheets on NRs, an enhanced rutile phase is observed in IO-TiO₂/NRs-TiO₂. The composition of the prepared photoanode was further investigated using Raman spectroscopy. As displayed in Fig. 3b, while IO-TiO₂ only exhibits characteristic Raman peaks of anatase (402, 515, and 630 cm⁻¹), IO-TiO₂/NRs not only displays similar Raman peaks of anatase but also demonstrates weak Raman peaks corresponding to the rutile phase (232, 446, and

608 cm⁻¹), suggesting the construction of a phase heterojunction between IO-TiO₂ and NRs.²⁶ In contrast, IO-TiO₂/NRs-TiO₂ exhibits comparable Raman peaks for anatase and stronger peaks for the rutile phase, providing strong evidence for the formation of a facet heterojunction between NRs and the coated TiO₂ nanosheets.

The element composition and corresponding chemical environment of IO-TiO₂, IO-TiO₂/NRs, and IO-TiO₂/NRs-TiO₂ were determined by X-ray photoelectron spectroscopy (XPS) analysis. The presence of Ti, C, and O elements in IO-TiO₂/NRs-TiO₂ was confirmed by the XPS full spectrum (Fig. S9†). The Ti 2p peaks at 463.6–464.1 eV and 457.9–458.4 eV correspond to Ti 2p_{3/2} and Ti 2p_{1/2} respectively, which confirmed that Ti in the sample is in the +4 valence state (Fig. S10a†).²⁷ Two oxygen chemical states were observed: lattice oxygen with a binding



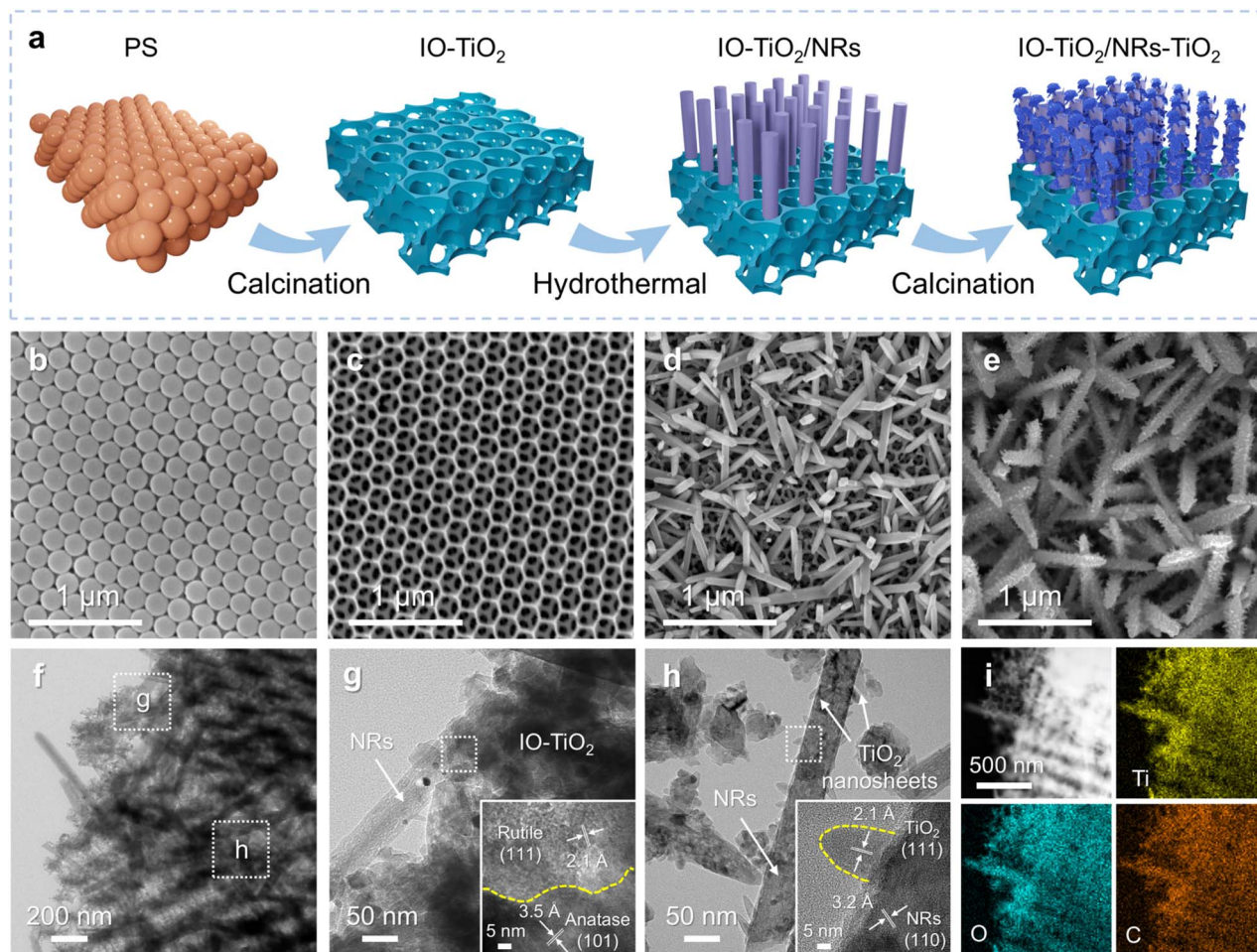


Fig. 2 (a) Schematic diagrams for IO-TiO₂/NRs-TiO₂. SEM images of (b) PS spheres, (c) IO-TiO₂, (d) IO-TiO₂/NRs, and (e) IO-TiO₂/NRs-TiO₂. TEM images of (f) IO-TiO₂/NRs-TiO₂, (g) the anatase/rutile heterojunction, and (h) the rutile crystal surface heterojunction. (i) EDS element mapping of IO-TiO₂/NRs-TiO₂.

energy range of 529.1–530.0 eV and hydroxyl oxygen with a BE range of 531.2–532.0 eV (Fig. S10b†).^{28,29} Compared to IO-TiO₂, the Ti 2p peaks of IO-TiO₂/NRs exhibit a slight positive shift, indicating the successful integration of IO-TiO₂ and NRs. Upon coating with TiO₂ nanosheets, a further redshift in IO-TiO₂/NRs-TiO₂ suggests the formation of a facet heterojunction between NRs and the coated TiO₂ nanosheets. Meanwhile, the corresponding binding energy of O 1s shifts towards a more negative position, suggesting electron transfer to Ti atoms and hole transfer to O atoms after heterojunction formation.

The peak shifts of the three samples were investigated using *in situ* XPS measurement, revealing the impact of heterojunctions on the efficiency and transfer of photogenerated electrons.³⁰ Under light irradiation, the binding energies of Ti 2p_{3/2} and Ti 2p_{1/2} significantly shifted towards higher positions (Fig. 3c), while the O 1s peaks exhibited a shift towards lower values (Fig. 3d), indicating predominant transfer of separated electrons to O atoms and holes to Ti atoms.³¹ Notably, IO-TiO₂ exhibits minimal shifts in the Ti 2p_{3/2} (~0.9 eV) and Ti-OH (~0.16 eV) peaks after light irradiation due to the high recombination rate of photoexcited charge pairs, while IO-TiO₂/NRs demonstrates significantly enhanced shifts in the Ti 2p_{3/2} (~1.1

eV) and Ti-OH (~0.4 eV) peaks owing to efficient photo-generated charge separation facilitated by the anatase/rutile heterojunction. IO-TiO₂/NRs-TiO₂ displays the most pronounced shifts in the Ti 2p_{3/2} (~1.5 eV) and Ti-OH (~1.0 eV) peaks, which may be mainly attributed to the formation of multiple heterojunctions. In addition, a notable reduction in the peak Ti-OH intensity of IO-TiO₂/NRs-TiO₂ under irradiation was observed. This decrease can be attributed to the excitation of electrons from the valence band to the conduction band upon exposure of IO-TiO₂/NRs-TiO₂ to visible light, leading to the formation of electron-hole pairs. These charge carriers facilitate the dissociation of H₂O on the IO-TiO₂/NRs-TiO₂ surface. As the irradiation time increases, more Ti-OH groups engage in the photocatalytic reaction, consequently reducing the intensity of the corresponding peak. Based on these results, it can be concluded that multiple heterojunctions indeed promote more efficient charge separation and transfer.

We further investigated the light absorption of the samples. The results demonstrate that the IO-TiO₂/NRs-TiO₂ photocatalyst (TBT-0.15 mL and TiCl₃-0.25 mL) exhibits superior light adsorption compared to other samples, as evidenced by its morphology and nanostructures (Fig. S11†). Moreover, IO-TiO₂,



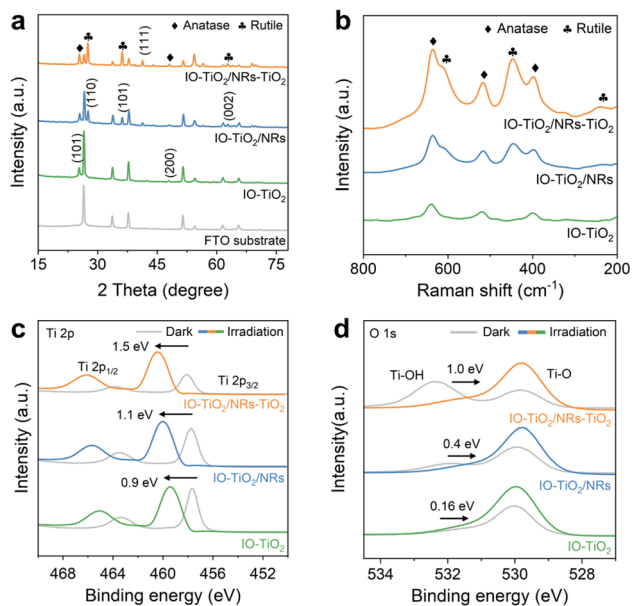


Fig. 3 (a) XRD patterns of FTO, IO-TiO₂, IO-TiO₂/NRs, and IO-TiO₂/NRs-TiO₂. (b) Raman spectra of IO-TiO₂, IO-TiO₂/NRs and IO-TiO₂/NRs-TiO₂. (c) XPS spectra of IO-TiO₂, IO-TiO₂/NRs and IO-TiO₂/NRs-TiO₂ in dark and irradiated states: (c) Ti 2p and (d) O 1s.

IO-TiO₂/NRs, and IO-TiO₂/NRs-TiO₂ exhibit strong UV absorption (Fig. S12[†]). Notably, IO-TiO₂/NRs-TiO₂ demonstrates the highest visible light absorption among them due to two key factors: (1) the inverse opal structure enhances light absorption through multiple scattering events. (2) The presence of multi-heterojunctions (phase and facet heterojunctions) facilitates efficient charge separation and leads to a redshift in the absorption edge.³²

To elucidate the role of a multi-heterojunction structure in the IO-TiO₂/NRs-TiO₂ photoanode, we prepared three comparative samples (IO-TiO₂/TiO₂, FTO-NRs, and NRs-TiO₂) as reference materials. The scanning electron microscopy (SEM) image reveals the presence of numerous TiO₂ nanosheets on the surface of IO-TiO₂ (Fig. S13a[†]), while distinct nanostructures are observed for FTO-TiO₂ and NRs-TiO₂ (Fig. S13b and c[†]). Additionally, both IO-TiO₂/TiO₂ and NRs-TiO₂ exhibit positive shifts in their Ti 2p peaks compared to FTO-NRs (Fig. S14a[†]), with a similar shift observed for the binding energy of hydroxyl oxygen in IO-TiO₂/TiO₂, FTO-NRs and NRs-TiO₂ (Fig. S14b[†]). These findings confirm the successful synthesis of IO-TiO₂/TiO₂, FTO-NRs and NRs-TiO₂ catalysts. The linear sweep voltammetry (LSV) measurements were conducted on various photoanodes prepared using the as-synthesized catalysts under sunlight illumination. All samples exhibited negligible current densities in the absence of light (Fig. 4a). Under light irradiation, IO-TiO₂, IO-TiO₂/TiO₂, and FTO-NRs exhibited photocurrent densities of 0.14, 0.23, and 0.35 mA cm⁻² at 1.23 V vs. RHE, respectively (Fig. S15[†]). After constructing a facet heterojunction and phase heterojunction, the photocurrent density increases to 0.43 and 0.71 mA cm⁻², respectively, at the same potential. These results demonstrate that both types of heterojunctions significantly enhance the PEC performance. More

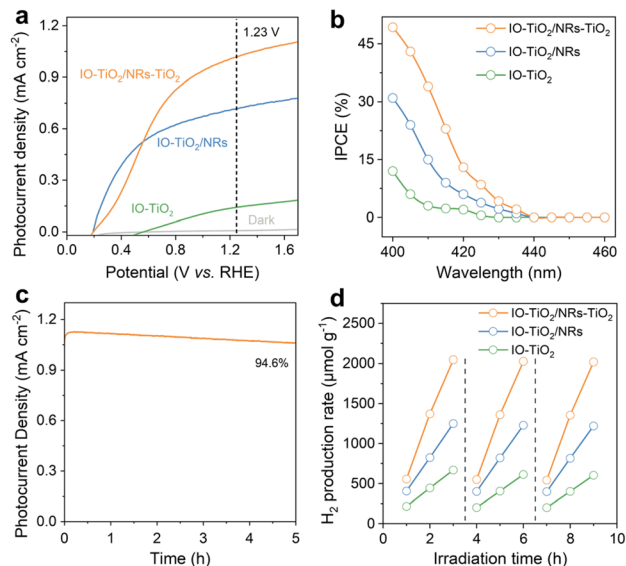


Fig. 4 (a) Linear sweep voltammetry (LSV) curves and (b) incident photon to current conversion efficiency (IPCE) of IO-TiO₂, IO-TiO₂/NRs and IO-TiO₂/NRs-TiO₂. (c) Long-term photocurrent-time curves of IO-TiO₂/NRs-TiO₂. (d) The cycling photocatalytic H₂-evolution test of IO-TiO₂, IO-TiO₂/NRs and IO-TiO₂/NRs-TiO₂.

importantly, IO-TiO₂/NRs-TiO₂ notably exhibits the highest photocurrent density (1.01 mA cm⁻²), which is 2.3 and 1.4 times higher than that of NRs-TiO₂ and IO-TiO₂/NRs, respectively, demonstrating comparable values to those reported by other research groups (Table S1[†]). In addition, compared to the original IO-TiO₂, the onset potential of IO-TiO₂/NRs and IO-TiO₂/NRs-TiO₂ exhibited a cathodic shift of approximately 334 mV, with a steeper curve slope observed after the peak. This suggests that the heterojunction-modified catalyst possesses higher catalytic activity and faster kinetics. Although the photocurrent of IO-TiO₂/NRs increases more rapidly in the range of 0.2 to 0.5 V vs. RHE, it tends to saturate as the potential continues to increase. In contrast, the photocurrent of IO-TiO₂/NRs-TiO₂ continues to increase rapidly up to 0.8 V vs. RHE, indicating superior catalytic kinetics. These results indicate the enhanced light-harvesting efficiency attributed to the presence of multiple heterojunctions.

The efficiency of a photoanode in producing hydrogen from solar energy in a semi-electrolytic cell can be quantified using the applied bias photon-to-current efficiency (ABPE). As illustrated in Fig. S16a,† IO-TiO₂/NRs-TiO₂ exhibits a peak ABPE value of 0.387% at 0.68 V vs. RHE, which is higher than that of IO-TiO₂ (0.351%) and bare TiO₂ (0.026%). This observed enhancement in ABPE confirms that rutile TiO₂ facilitates charge transfer by accepting holes, thereby significantly improving the water splitting efficiency of the photoanode. Furthermore, compared to IO-TiO₂ and bare TiO₂, IO-TiO₂/NRs-TiO₂ demonstrates superior charge separation efficiency at 1.23 V vs. RHE, indicating that multi-heterojunction TiO₂ can effectively achieve spatial separation of photogenerated carriers (Fig. S16b[†]). The incident photon to current conversion efficiency (IPCE) of the photoanode was measured at 1.23 V vs. RHE



using a single wavelength filter, power meter, and light source. Fig. 4b illustrates that IO-TiO₂ exhibits the lowest IPCE. However, upon introducing a heterojunction, an enhanced IPCE is achieved in the wavelength range of 400–430 nm for IO-TiO₂/NRs (anatase/rutile-phase heterojunction), while IO-TiO₂/NRs-TiO₂ demonstrates the maximum IPCE value due to its multi-heterojunction structure which facilitates efficient charge separation and transfer.³³ Furthermore, as shown in Fig. 4c, IO-TiO₂/NRs-TiO₂ demonstrates excellent photostability, and maintains 94.6% of the initial photocurrent at 1.23 V vs. RHE for 5 h. Moreover, no significant changes in the morphology and the crystal structure of the IO-TiO₂/NRs-TiO₂ photoanode were found after long-term stability tests, characterized by SEM (Fig. S17a†) and XRD (Fig. S17b†). The hydrogen evolution measurements were conducted to assess the water splitting activity of IO-TiO₂, IO-TiO₂/NRs, and IO-TiO₂/NRs-TiO₂. As displayed in Fig. 4d, under the influence of 10% triethanolamine (v/v) as a sacrificial reagent, the kinetics of H₂ production exhibits an almost linear increase with irradiation time. IO-TiO₂ demonstrates a relatively low rate of H₂ production due to its high recombination rate of photoinduced charge pairs. Conversely, IO-TiO₂/NRs displays an enhanced rate of H₂ production attributed to the presence of an anatase/rutile-phase heterojunction facilitating charge separation. Notably, among all tested photoanodes, IO-TiO₂/NRs-TiO₂ showcases superior performance in terms of hydrogen production with a yield reaching approximately 2046 μmol g⁻¹ after 3 h, which is about 1.6 and 3 times higher than that achieved by IO-TiO₂/NRs and IO-TiO₂, respectively. Notably, IO-TiO₂/NRs-TiO₂ without any metal doping exhibits a hydrogen production rate comparable to that of other studies on rutile or anatase TiO₂ with Pt loading (Table S2†), indicating that the construction of multiple heterojunctions promotes efficient separation of photogenerated charges.¹⁰ Furthermore, no significant decrease in activity is observed for IO-TiO₂/NRs-TiO₂ after 9 times of continuous testing, suggesting that the 3D multi-heterojunction structure remains highly stable for H₂ evolution.

To demonstrate the capability of a multi-heterojunction in facilitating charge-carrier separation, a series of photoluminescence (PL) measurements were conducted. In comparison to IO-TiO₂, a noticeable reduction in emission intensity is observed for IO-TiO₂/NRs (Fig. 5a), indicating that the anatase/rutile-phase heterojunction effectively mitigates recombination of photogenerated electron–hole pairs. Importantly, the significant decrease in emission intensity for IO-TiO₂/NRs-TiO₂ compared to IO-TiO₂/NRs highlights efficient charge separation facilitated by multiple heterojunctions, promoting electron separation and conduction band shifting, thereby enhancing luminescence annihilation. Furthermore, time-resolved photoluminescence (TRPL) measurements were employed to investigate the lifetimes of electron–hole pairs. The average lifetimes (τ_{ave}) for IO-TiO₂, IO-TiO₂/NRs, and IO-TiO₂/NRs-TiO₂ are approximately 1.26 ns, 1.83 ns, and 5.13 ns respectively (Fig. 5b and Table S3†). Notably, the τ_{ave} of charge carriers in IO-TiO₂/NRs-TiO₂ exhibits a remarkable increase by a factor of 4.07 compared to that in IO-TiO₂ and a significant enhancement by a factor of 2.80 compared to that in IO-TiO₂/NRs.

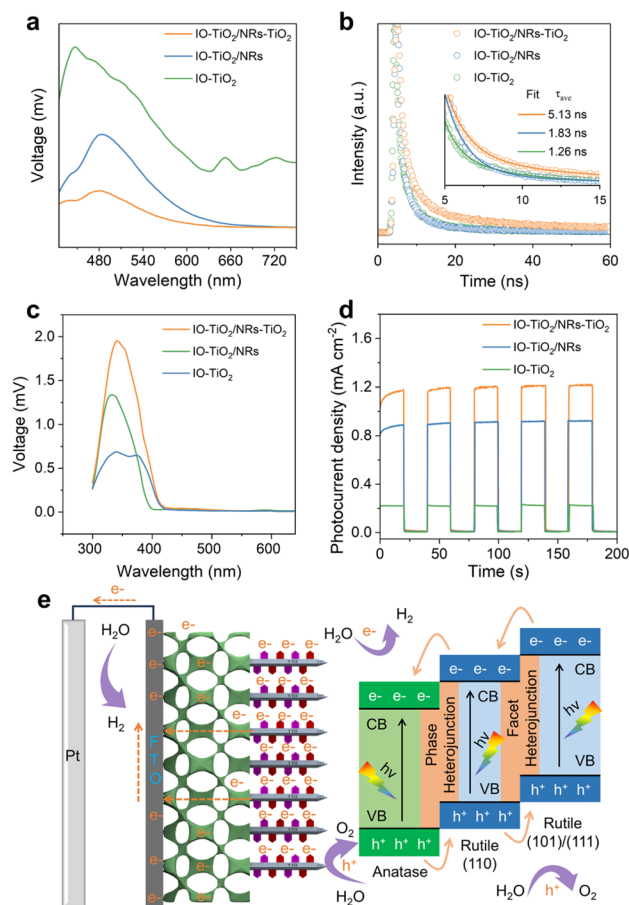


Fig. 5 (a) PL spectra, (b) TRPL spectra, (c) SPV spectra, and (d) photocurrent response of IO-TiO₂, IO-TiO₂/NRs and IO-TiO₂/NRs-TiO₂. (e) Schematic diagram of the band alignment and charge transfer in an IO-TiO₂/NRs-TiO₂ heterojunction, and the light scattering and electron transport in the IO-TiO₂/NRs-TiO₂ photoanode for water splitting.

Transient-state surface photovoltage (TS-SPV) measurements were further used to investigate the dynamic properties of photoexcited charge separation.³⁴ As shown in Fig. 5c, IO-TiO₂/NRs-TiO₂ exhibits the most pronounced response peak compared to IO-TiO₂ and IO-TiO₂/NRs, once again confirming the efficient separation of photogenerated charges. Moreover, Fig. 5d presents that the photocurrent stabilized at approximately 1.1 mA cm⁻² upon light illumination, indicating the rapid transfer of photo-generated electrons from NRs/TiO₂ to IO-TiO₂. Furthermore, when the light is turned off, the photocurrent decays rapidly to a negligible dark current, indicating the rapid transport of photo-generated electrons from the IO-TiO₂ backbone to the FTO substrate. In addition, the EIS fitting results reveal that the charge transfer resistances of IO-TiO₂, IO-TiO₂/NRs, and IO-TiO₂/NRs-TiO₂ are 342.6 Ω, 111.5 Ω, and 62.2 Ω, respectively (Fig. S18†). These findings indicate that both crystal phase heterojunctions and facet heterojunctions significantly enhance charge transfer efficiency. All these results confirm that a multi-heterojunction can indeed improve the interfacial charge transfer and reduce interfacial reaction resistance, thus greatly



promoting the charge spatial separation and prolonging the lifetime of the excited electrons.³⁵

Based on the simulation and experimental results, we propose a mechanistic explanation for the augmented efficiency of charge separation and transfer through the construction of multiple heterojunctions (Fig. 5e). Under light illumination, IO-TiO₂/NRs-TiO₂ can significantly enhance light collection through multiple scattering between radially oriented nanorods, the coated rutile TiO₂ nanosheets and inverse opal, effectively absorbing photons and generating lots of electron-hole pairs. At the TiO₂/electrolyte interface, band bending occurs due to the initial difference in electrochemical potential, which drives holes in TiO₂ to move into the TiO₂/electrolyte interface, thereby oxidizing water to O₂. Meanwhile, the photogenerated electrons generated in the rutile crystal face of the coated TiO₂ nanosheets are transferred to IO-TiO₂ along the NRs, which are then collected by the FTO substrate and subsequently transported to the Pt cathode, reducing water to H₂.¹⁰ Notably, the formation of a type II facet heterojunction of NRs-TiO₂ can promote the charge separation process in rutile TiO₂. And the conduction band of IO-TiO₂ is slightly lower, and the band alignment between rutile TiO₂ and anatase TiO₂ is favourable for electron transfer from rutile to anatase through a phase heterojunction. Therefore, the presence of an anatase/rutile-phase heterojunction and rutile facet heterojunction in the IO-TiO₂/NRs-TiO₂ samples would greatly facilitate the charge separation and transfer process, thereby enhancing the PEC performance.

Conclusions

In summary, the strategy of combining a crystal phase heterojunction with a crystal faceted heterojunction is proposed for the first time to enhance TiO₂ charge transfer efficiency as well as PEC activity. Specifically, the IO-TiO₂/NRs-TiO₂ photoanode with a 3D hierarchical structure has been prepared by hydrothermal and calcination methods. Firstly, IO-TiO₂ with a periodic void structure favors light absorption. Secondly, the disordered lattice at the anatase/rutile phase junction improves the PEC activity. In addition, the crystal heterojunction of rutile prolongs the photoelectron lifetime through the discontinuous band gap and accelerates the space charge separation. Impressively, the IO-TiO₂/NRs-TiO₂ photoanode exhibits a current density of 1.12 mA cm⁻² at 1.23 V vs. RHE and a hydrogen production efficiency of 682 μmol h⁻¹ g⁻¹ under simulated light conditions, which is far superior to that of IO-TiO₂ and the single heterojunction of IO-TiO₂/NRs. This work provides a new idea for constructing photoanodes with excellent electron-hole separation performance.

Data availability

All data can be found in the main article or the ESI.†

Author contributions

S. C. and Z. L. designed the research; C. H., J. C., and Y. X. conducted the research; B. X., C. H., J. C., and Y. X. analyzed the data; B. X., C. H., S. C., and Z. L. wrote the paper.

Conflicts of interest

There are no conflicts to declare.

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