Visible Light-Driven H₂ Production over Highly Dispersed Ruthenia on Rutile TiO₂ Nanorods

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ABSTRACT

The immobilization of miniscule quantities of RuO$_2$ ($\sim 0.1\%$) onto one-dimensional (1D) TiO$_2$ nanorods (NRs) allows H$_2$ evolution from water under the irradiation of visible light. Rod-like rutile TiO$_2$ structures, exposing preferentially (110) surfaces, are shown to be critical for the deposition of RuO$_2$ to enable photocatalytic activity in the visible region. This performance is rationalized based on fundamental experimental studies and theoretical calculations, demonstrating that RuO$_2$(110) grown as 1D nanowires on rutile TiO$_2$(110), which occurs only at extremely low loads of RuO$_2$, leads to the formation of a hetero-interface that efficiently adsorbs visible light.

KEYWORDS

Titanium; Ruthenium; H$_2$ production; Water splitting; Heterojunction.
INTRODUCTION

Hydrogen obtained from carbon-free sources is an attractive alternative clean fuel that could potentially offer solutions to global warming through the reduction of CO$_2$ emissions. The splitting of water into H$_2$ and O$_2$ utilizing solar energy is regarded as one of the most promising and sustainable technologies to produce hydrogen.$^{1-3}$ Although titanium dioxide (TiO$_2$) is the most common semiconductor oxide photocatalyst,$^{3-6}$ its practical application is limited because TiO$_2$ absorbs only a small fraction of solar light and the photogenerated electrons/holes recombine rapidly.$^{4,5}$ Anchoring or coupling metal or metal oxide nanoparticles (NPs) onto TiO$_2$ has been used to either enhance its solar-conversion efficiency by retarding the charge carrier recombination or extending its response toward the visible light region stemming from band level alignment.$^{6,7}$ Precious metals possessing much larger work function than TiO$_2$, such as Pt, Pd, Ru and Au, have been considered as the best candidates to suppress the charge carrier recombination and facilitate the charge transfer owing to the formation of Schottky barriers at the heterogeneous nanoscale junction and the localized surface plasmon resonance.$^{3,6,7}$ However, such a method of metallization is uneconomical if it demands large amounts of precious metals.

Since RuO$_2$ belongs to the class of $d$-band metallic conducting transition metal oxides, its electrical resistivity is two-fold higher than that of metallic ruthenium.$^8$ The intraband transitions and localized surface plasmon resonance of RuO$_2$ also play a vital role in its optical response and photoactivity.$^9$ Among several polymorphs of TiO$_2$, rutile is the thermodynamically most stable phase, but the moderate-temperature post treatment usually required to achieve highly crystalline rutile phase, results in large particle sizes and nonporosity.$^6,5$ Coupling rutile TiO$_2$ with RuO$_2$ has been widely studied in numerous catalytic reactions due to their lattice matching and strong metal-support interaction.$^{12-17}$ Seki$^{14}$ claimed that RuO$_2$/rutile-TiO$_2$ catalyst exhibited high catalytic activity and thermal stability.
toward HCl oxidation to Cl₂ due to highly dispersed, ultrafine RuO₂ crystallites, approximately a single unit-cell thickness, that cover the surface of TiO₂ primary particle with strong interaction between RuO₂ and TiO₂. Xiang et al.¹⁵ demonstrated that the redistribution or spreading of RuO₂ occurred from a spherical shape (~ sub 2 nm) to epitaxial island layers along the TiO₂ surfaces during the chlorination reaction, forming a unique heterostructure at the interface. Lin et al.¹⁷ elucidated that among several oxide supports including anatase TiO₂, rutile TiO₂, rutile SnO₂, Al₂O₃ and SiO₂, rutile TiO₂ was the most appropriate support to enhance the catalytic activity of N₂O reduction. Similarly, Jiao et al.¹⁶ employed thermal treatment to transform RuO₂ nanoclusters (ca. 2 nm) into an epitaxial layer on the surface of both anatase and rutile TiO₂, relying on the interfacial atom arrangement match between these two oxides that led to more significant exposure of RuO₂ (110) facets and thus, promoting photocatalytic CO oxidation. Several key strategies are important including: choosing an appropriate support for highly dispersing metallic Ru or RuO₂ NPs to achieve optimal photocatalytic performance; improve the stability as well as decrease the amount of costly precursor being utilized but most notably, aim to preserve all specific properties of each component.

In spite of its promising catalytic features, very little attention has been paid so far concerning the explanation of the photocatalytic properties of the RuO₂/rutile-TiO₂ system. Most reported studies employed RuO₂ as a cocatalyst to facilitate the gas production under UV irradiation.³,⁶,¹⁸-²¹ Recently, a first attempt toward H₂ production from water under UV excitation over RuO₂/anatase-TiO₂ nanocomposites was conducted, where an upward band bending at the RuO₂-anatase-TiO₂ interface has been proposed to explain the good performance of H₂ evolution.²¹ In addition, density functional calculations performed on RuO₂/TiO₂(110) heterostructures for photocatalysis application found that the interface between RuO₂ and rutile TiO₂ strongly affects the atomic and electronic properties of both oxides due to a strong
charge accumulation at the interface.\textsuperscript{22} Upward band bending at the interface could be observed when introducing oxygen vacancies at the interface and subsequently, the electron accumulation at the interface creates a strong internal electric field, leading to efficient separation of photoinduced electron-hole pairs during a photocatalytic process.\textsuperscript{22} According to their calculation, the adsorption energy is lowered by 0.34 eV and the distance between H and bridging oxygen is shortened by 0.18 Å on RuO\textsubscript{2}/TiO\textsubscript{2}(110) in comparison with that on TiO\textsubscript{2}(110) surface, therefore facilitating the splitting of water.

No attempt has been made to investigate the metal-support interaction between rutile RuO\textsubscript{2} and rutile TiO\textsubscript{2} support as well as to explain their photocatalytic properties in targeting H\textsubscript{2} production. We have synthesized a RuO\textsubscript{2}/TiO\textsubscript{2} heterostructure by immobilizing minute quantities of RuO\textsubscript{2} onto 1D TiO\textsubscript{2} nanorods (NRs). Complementary characterization techniques have been applied to gain insight into the promotion effect of the heterostructure on the visible-light-responsive activity combined with DFT calculations of RuO\textsubscript{2} on rutile TiO\textsubscript{2}(110).

**EXPERIMENTAL**

**Synthesis of RuO\textsubscript{2}/TiO\textsubscript{2} heterostructures**

All the chemicals were purchased from Aldrich and used without purification. Typically, a mixture of 7 mL of titanium n-butoxide and 7 mL of hydrochloric acid (35 wt\%) was hydrothermally treated for 11 h at 105 °C. The white precipitate was carefully collected and washed several times with deionized water, thrice by aqueous 0.1 M NH\textsubscript{4}OH solution, and finally with deionized water to entirely remove chlorine contaminants. After drying at 80 °C overnight, the blank TiO\textsubscript{2} rods (denoted as ‘TiO\textsubscript{2}’) were obtained after calcined the \textit{as-syn} TiO\textsubscript{2} rods in air at 200 °C for 2h.

Subsequently, 0.2 g of \textit{as-syn} TiO\textsubscript{2} was re-dispersed in 20 mL of deionized water at 90 °C for 30 min. The impregnation of RuO\textsubscript{2} was carried out by drop-wise addition of an
appropriate concentration of 5 mL aqueous RuCl$_3$.xH$_2$O solution at 90 °C. The fine powder after evaporation was sequentially washed with deionized water, aqueous 0.1 M NH$_4$OH solution, and deionized water to entirely remove chlorine contaminants, and collected by high-speed centrifugation (20000 rpm). The powder was dried at 80 °C overnight and then calcined in air at 200 °C for 2h, denoted as ‘xRuTi’ where x = 0.01, 0.1, 0.25, and 0.5 wt% of RuO$_2$. For comparison, bulk rutile TiO$_2$ particle was prepared by annealed commercial TiO$_2$ P25 (Degussa) at 800 °C for 4 h and named as ‘TiO$_2$ p’.

**Characterizations**

Synchrotron X-ray powder diffraction (SXPD) patterns were collected at beamline 17-BM-B ($\lambda = 0.72768$ Å) of the Advanced Photon Source at Argonne National Laboratory. 5 mg of powder were loaded into a 0.9-mm-ID kapton capillary and two-dimensional diffraction patterns were collected by a Perkin Elmer amorphous silicon detector. The data acquisition was integrated by QXRD while the crystalline phase identification, composition and lattice parameters were subsequently analyzed by Rietveld refinement using TOPAS 4.1 program.

High-resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) images were recorded on Tecnai G$^2$ F20 S-TWIN transmission electron microscope equipped with a field emission electron source. It was operated at 200 kV while the point-to-point resolution and the resolution between lines were 0.24 and 0.10 nm, respectively. The powder samples were deposited from alcohol suspensions onto holey-carbon Cu grids. Brunauer-Emmett-Teller (BET) specific surface areas were determined by N$_2$ adsorption/desorption at 77 K using an Altimira AMI-300ip instrument. The powders were degassed at 150 °C to remove all surface-adsorbed contaminants prior to measurements.

High-resolution X-ray photoemission spectra (XPS) of Ti 2p, O 1s, Ru 3d and Ru 3p were recorded on a laboratory-based monochromated Al K$\alpha$ source with a hemispherical analyzer. The core-level and ultraviolet photoelectron spectra (UPS) were measured with a constant
pass energy of 23.5 eV, which corresponds to an instrumental resolution of 0.51 eV obtained from analyzing both the Au $4f_{7/2}$ and Fermi edge of Au foil.

Further characterization of the materials was also conducted using several techniques available at the Center for Functional Nanomaterials (CFN) at BNL. Raman spectroscopy was performed on a WiTec Alpha combination microscope at room temperature with 633 nm laser as an excitation source. UV-Vis diffuse reflectance (DRS) measurements were collected at room temperature by PerkinElmer Lambda 950 spectrometer equipped with an integrating sphere assembly.

Visible-light-driven H$_2$ production measurements

The photocatalytic hydrogen evolution was conducted in a closed gas circulation and evacuation system. Powder catalyst were suspended in aqueous methanol solution (20 vol%) in a sealed quartz cell. After evacuation and Ar purging several times, the reactor was side-irradiated by a 150 W Xenon arc lamp equipped with a CuSO$_4$ filter and 400 nm long pass filter (400 nm < $\lambda$ < 625 nm) under magnetic stirring. The reaction temperature was maintained at 293 K by continuous water circulation. The evolved gases were determined by gas chromatography (GC Agilent 6890N) equipped with FID and TCD detectors using Ar as the carrier gas. Detailed experiment and calculation of apparent quantum efficiency is described in Supporting Information.

Computational methods

We built our theoretical model based on the previously published STM images of RuO$_x$ supported on TiO$_2$(110) surface.$^{23}$ The nanostructured ruthenia on titania was modelled as follows: (i) TiO$_2$(110) surface consisted of four O-Ti-O three-layers, keeping the two of the bottom fixed at the optimized bulk positions, allowing a vacuum region of 15 Å between repeated slabs; (ii) in order to achieve an isolated wire-like RuO$_2$(110) nanostructure a (3x1) and (3x6) surface models of the titania support were used for optics calculation and density of
states respectively; (iii) a full-relaxed three atomic layer width (O-Ru-O) wire was coupled to the titania support according to Yang et al.’s report\textsuperscript{23}. We performed periodic DFT calculations using the Perdew-Wang 91 (PW91) functional\textsuperscript{24} for the exchange-correlation potential. The effect of the core electrons on the valence states was represented with the projector-augmented wave (PAW) approach,\textsuperscript{25} as implemented in the Vienna ab-initio simulation package (VASP 5.3),\textsuperscript{26,27} with the valence states defined for each atom as Ti(3s,3p,3d,4s), Ru(4s,4p,4d,5s) and O(2s,2p) electrons, while the remaining electrons were kept frozen as core states. The valence electronic states are expanded in a basis of plane waves with a cutoff of 400 eV for the kinetic energy. In order to account for eventual reduction of the titania support (occupation of the Ti 3d states) a Hubbard-like U term was used, (GGA+U), according to the Dudarev et al.’s implementation,\textsuperscript{28} which makes use of an effective parameter $U_{\text{eff}}$. We took a value $U_{\text{eff}} = 4.5$ eV satisfactorily used in our previous work dealing with supported cerium oxide particles on titania.\textsuperscript{29} Calculations were performed at the $\Gamma$ point of the Brillouin zone for the (3x6) surface model and with a 1x4x1 k-points grid for the (3x1) model.

**RESULTS AND DISCUSSION**

**Visible-light-responsive H$_2$ production over RuO$_2$/TiO$_2$ heterostructures**

Figure 1 shows the visible light-driven hydrogen production performance of xRuTi heterostructured photocatalysts as a function of RuO$_2$ content. The time profiles in Figure 1A demonstrates the stable, constant amounts of H$_2$ produced over all the rod-like RuO$_2$/TiO$_2$ heterostructured photocatalysts under the irradiation of visible light (400 nm $< \lambda < 625$ nm). Bulk rutile TiO$_2$ particle (TiO$_2$-p sample) is completely inactive for H$_2$ production with visible light irradiation, while TiO$_2$ nanorods present a moderate activity, producing 33 $\mu$mol of H$_2$ gas per gram catalyst per hour. This observation is consistent with recent report that sub-10 nm rutile NPs exhibited a significant improvement in photocatalytic activity for
visible-light-driven water splitting compared to the bulk oxide.\textsuperscript{30} It is worth noting that the deposition of RuO\textsubscript{2} onto TiO\textsubscript{2} rods significantly enhances the H\textsubscript{2} evolution efficiency regardless of RuO\textsubscript{2} loading amount. As seen in Figure 1B, the activity trend follows a volcano shape where the mass-normalized rate of H\textsubscript{2} production over all xRuTi heterostructure materials is significantly higher than that over TiO\textsubscript{2} NRs with an optimal RuO\textsubscript{2} content of 0.1 wt\% (425 \mu mol g\textsuperscript{-1} h\textsuperscript{-1}). The photocatalytic performance under full UV-visible irradiation (310-625 nm) followed the same trend, as shown in Figure S1 (Supporting Information). The activities normalized to specific surface areas and apparent quantum efficiencies are summarized in Table 1. The apparent quantum efficiencies over supported RuO\textsubscript{2} are 4- to 12-times larger than that with TiO\textsubscript{2} NRs alone. It is observed that increasing RuO\textsubscript{2} loading amount to 0.25 and 0.5 wt\% gradually decreases the H\textsubscript{2} evolved rate regardless of light excitation source. This remarkable result is compared to the case of Pt, which is extensively used as a co-catalyst on TiO\textsubscript{2}. As shown in Figure S2 (Supporting Information), upon the UV irradiation, the H\textsubscript{2} evolution activity over our Ru-based heterostructured photocatalyst is comparable to the platinized TiO\textsubscript{2} NRs prepared by \textit{in situ} photodeposition method. However, Pt does not give activity at all in the visible light region. A few studies have reported visible-light-driven photocatalytic activity over RuO\textsubscript{2}/TiO\textsubscript{2} nanocomposites.\textsuperscript{31,32} Ismail \textit{et al.}\textsuperscript{31} reported that the visible-light photoactivity enhancement toward methanol oxidation was ascribed to the incorporation of a small amount of Ru\textsuperscript{4+} into the anatase lattice and the formation of some structural defects on the surface, facilitating the interfacial charge transfer of electrons/holes, whereas the addition of RuO\textsubscript{2} suppressed the UV-photonic efficiency of TiO\textsubscript{2}. 
Figure 1. (A) Time profiles and (B) mass-normalized $\text{H}_2$ evolution rates over bulk TiO$_2$ particles, TiO$_2$ NRs and xRuTi heterostructures under Vis light illumination (400 – 625 nm).

Table 1. Surface areas, band gap energy, $\text{H}_2$ production rates and apparent quantum efficiencies over blank TiO$_2$ NRs and xRuTi heterostructures.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface area / m$^2$ g$^{-1}$</th>
<th>Band gap / eV$^a$</th>
<th>$\text{H}_2$ production rate, r</th>
<th>AQE / %$^d$</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$r_M^b$, $r_S^c$, $r_M'^b$, $r_S'^c$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>310-625 nm</td>
<td>400-625 nm</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>68</td>
<td>3.06</td>
<td>385 6 33 0.5</td>
<td>0.02 0.003</td>
</tr>
<tr>
<td>0.01RuTi</td>
<td>95</td>
<td>3.02</td>
<td>2001 21 270 2.8</td>
<td>0.12 0.024</td>
</tr>
<tr>
<td>0.1RuTi</td>
<td>90</td>
<td>2.99</td>
<td>3308 37 425 4.7</td>
<td>0.19 0.037</td>
</tr>
<tr>
<td>0.25RuTi</td>
<td>88</td>
<td>2.96</td>
<td>2714 31 160 1.8</td>
<td>0.16 0.014</td>
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<tr>
<td>0.5RuTi</td>
<td>81</td>
<td>2.93</td>
<td>2208 27 148 1.8</td>
<td>0.13 0.013</td>
</tr>
</tbody>
</table>

$^a$ Estimated from Tauc’s plot of UV-Vis-DRS spectra.

$^b$ $r_M$, $r_M'$ - Rates normalized to mass of photocatalyst, $\mu$mol g$^{-1}$ h$^{-1}$, under UV-Vis and visible light irradiations, respectively.

$^c$ $r_S$, $r_S'$ - Rates normalized to BET surface area, $\mu$mol m$^2$ h$^{-1}$, under UV-Vis and visible light irradiations, respectively.

$^d$ AQE - Apparent quantum efficiencies under UV-Vis and visible light irradiations, respectively.
We show here that 0.1 wt% of RuO₂ is the optimal loading amount onto TiO₂ NRs to reach the best photocatalytic performance for evolution of H₂, and also in the case of using TiO₂ particles as a substrate as displayed in Figure S3 (Supporting Information). Excess RuO₂ loading (> 0.1 wt%) may detrimentally occupy the catalytically active sites on the surface of the photocatalyst, which can lead to a reduction of surface area as shown in Table 1. Furthermore, it may reduce the light penetration, retarding the activation of TiO₂ and the generation of photoinduced charge carriers and therefore diminishing the H₂ production. In a similar demonstration, Amama et al.³³ found that depositing beyond 0.4 wt% RuO₂ on TiO₂-glass fiber cotton significantly decreased the conversion of trichloroethylene oxidation. Similarly, the photonic efficiency for the methanol oxidation to HCHO reached a maximum at 0.5 wt% RuO₂-TiO₂ nanocomposite under visible light irradiation and further increasing up to 10 wt% gradually decreased the efficiency.³¹ Much lower optimal contents, 0.05, 0.1, and 0.02 wt% of epitaxial RuO₂ layers, were obtained for P25, commercial anatase and commercial rutile TiO₂, respectively, in the RuO₂/TiO₂/Pt ternary photocatalyst for CO oxidation.¹⁶ Lin et al.³⁴ also observed that loading less than 0.05 wt% RuO₂ on TiO₂ gave much higher activity toward the photocatalytic oxidation of sulfur-containing organic compounds and dyes. Sakata et al.¹⁹ claimed that so small an amount of RuO₂, approximately 0.03 monolayer, on bulk TiO₂ surface (particle size of 0.2-0.4 μm, surface area of 10 m² g⁻¹) is sufficient to produce good photocatalytic activity of H₂ evolution. Excess amount can function as recombination centers because the distance between particles becomes shorter than the distance in which the image force to both electrons and holes is effective.¹⁹ However, different conclusions have been reported by several groups, where 1 ~ 5 wt% of RuO₂ has been suggested to provide the best performance.²¹,³⁵ It can be concluded that optimizing the spatial distribution of RuO₂ loading on rutile TiO₂ support strongly depends on the synthesis method, support nature and experimental conditions. It is critical to develop
a synthesis method that allows the isolation of small amounts of RuO_2 on TiO_2. In the present work, miniscule quantity of RuO_2 gave the optimum photocatalytic H_2 production activity over both UV and visible light illuminations.

**Structure-photoactivity correlation over RuO_2/TiO_2 heterostructures**

The crystallographic structure of TiO_2 NRs and xRuTi heterostructures obtained by X-ray diffraction are shown in Figure 2A. It is observed that the SXPD patterns were unchanged before and after RuO_2 addition onto TiO_2 NRs. Series of well-defined (110), (101), (111) and (211) diffraction peaks at 2θ = 12.9, 16.8, 19.1 and 24.9° were observed for all samples, indicating the dominance of tetragonal rutile phase (space group P4_2/mnm). The phase composition and cell parameters obtained from Rietveld refinement (Figure S4, Supporting Information) are summarized in Table 2. A small fraction of anatase (space group I4_1/amd) is observed as a single peak at 11.9°, occupying 7 ~ 11 wt%. No diffraction features related to the formation of RuO_2 particles are observed, possibly due to the high dispersion of ultrafine, small RuO_2 NPs, and/or the epitaxial growth of very thin RuO_2 nanowire along the TiO_2 (110) direction as observed from the deposition of RuO_2 on TiO_2(110) single crystals.\(^{23,36}\)

The formation of a new \(\lambda\)-Ti_3O_5 phase (1.4 ~ 2.8 wt%) was clearly observed in all xRuTi heterostructure samples. Based on complementary studies described below, we determined that the appearance of this phase was related to our synthesis method used for the deposition of RuO_2 on TiO_2. This phenomenon has not been observed previously on neither RuO_2/anatase-TiO_2, RuO_2/rutile-TiO_2 nor Ru-doped TiO_2 systems.\(^{12-15,21,31-33,35}\)
Figure 2. (A) SXPD patterns and (B) Raman spectra of TiO$_2$ NRs and xRuTi series.

The Raman spectra for different Ru loadings are displayed in Figure 2B, where two intense features of tetragonal rutile TiO$_2$ (space group $D_{4h}^{14}$) at 448 and 615 cm$^{-1}$ were assigned to $E_g$ (planar O-O vibration) and $A_{1g}$ (Ti-O stretch) modes, respectively, accompanied with an anomalously broad band at 243 cm$^{-1}$ corresponding to the multiple phonon scattering process.$^{37,38}$ No characteristic modes of anatase with $D_{4h}^{19}$ space group was found at 145 cm$^{-1}$ ($E_g$), 198 cm$^{-1}$ ($E_g$), 398 cm$^{-1}$ ($B_{1g}$), 518 cm$^{-1}$ ($A_{1g}$) and 640 cm$^{-1}$ ($B_{1g}$).$^{37}$ Four Raman-active modes of RuO$_2$ corresponding to $B_{2g}$ (165 cm$^{-1}$), $E_g$ (528 cm$^{-1}$), $A_{1g}$ (646 cm$^{-1}$), and $B_{2g}$ (716 cm$^{-1}$)$^{35}$ were not observed for all xRuTi heterostructured materials. More importantly, increasing RuO$_2$ content up to 0.1, 0.25 and 0.5 wt% resulted in the substantial red-shift and broadening of both $E_g$ to 445, 414 and 409 cm$^{-1}$, and $A_{1g}$ to 611, 607 and 602 cm$^{-1}$, respectively. It has been established that the Raman line shape, intensity and position are strongly impacted by the phonon confinement effect, lattice strain, defects, crystallite shape and size.$^{38-40}$ Herein, such red shifts of $A_{1g}$ might be attributed to the lattice distortion of TiO$_2$ meanwhile the shifts in $E_g$ obviously indicate the alteration in oxygen stoichiometry or the higher concentration of oxygen vacancy defects in 0.25RuTi and 0.5RuTi compared to others. The Schottky heterojunction at the interface between RuO$_2$ and TiO$_2$ increases the
population of oxygen vacancies, leading to significant charge transfer from TiO$_2$ to RuO$_2$ and facilitation of the photoreaction.$^{41}$ Such oxygen vacancies are preferential adsorption sites for methanol and water dissociation on TiO$_2$(110) surface.$^{22,42,43}$ Owing to identical surface termination, this deduction should also be applicable for RuO$_2$/TiO$_2$ heterostructures and Wei et al.$^{22}$ found that the oxygen vacancy led to more electrons on the two Ru sites surrounding the oxygen vacancy, making these sites more active for catalytic reactions.$^{22,44}$ However, excess quantity of such defects is detrimental to the photoactivity since they become the recombination centers and intensively trapped valence-band holes, reducing the charge density and retarding the separation of charge carriers, and hence, diminishing the photoactivity.

Table 2. Rietveld refinement from SXPD.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Rutile phase</th>
<th>Anatase phase</th>
<th>$\lambda$-Ti$_3$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$W_R$ / %$^a$</td>
<td>$a$ / Å</td>
<td>$c$ / Å</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>91.3</td>
<td>4.607(3)</td>
<td>2.959(9)</td>
</tr>
<tr>
<td>0.01RuTi</td>
<td>91.2</td>
<td>4.604(9)</td>
<td>2.958(1)</td>
</tr>
<tr>
<td>0.1RuTi</td>
<td>89.8</td>
<td>4.608(5)</td>
<td>2.959(4)</td>
</tr>
<tr>
<td>0.25RuTi</td>
<td>91.7</td>
<td>4.605(3)</td>
<td>2.958(9)</td>
</tr>
<tr>
<td>0.5RuTi</td>
<td>86.8</td>
<td>4.605(1)</td>
<td>2.958(9)</td>
</tr>
</tbody>
</table>

$^a$ $W_R$, $W_A$, $W_\lambda$ – Weight percentage of rutile, anatase and $\lambda$-Ti$_3$O$_5$, respectively.

$^b$ $D_R$, $D_A$, $D_\lambda$ - Crystallite size of rutile, anatase and $\lambda$-Ti$_3$O$_5$, respectively.

The possible role of $\lambda$-Ti$_3$O$_5$ in the photocatalytic enhancement of TiO$_2$ based catalysts is still controversial. A phase transition between different polymorphs of Ti$_3$O$_5$, i.e. $\gamma$- to $\beta$-phase, $\lambda$- to $\beta$-phase, $\alpha$- to $\beta$-phase, $\gamma$- to $\delta$-phase, easily happens under thermal treatment or
light irradiation.\textsuperscript{45,46} \(\lambda\)-Ti\textsubscript{3}O\textsubscript{5} exhibited a reversible light-induced metal-to-semiconductor phase transition between black metallic \(\lambda\)-Ti\textsubscript{3}O\textsubscript{5} to brown semiconducting \(\beta\)-Ti\textsubscript{3}O\textsubscript{5} at room temperature.\textsuperscript{45} To understand the effect of the appearance of this new phase, a TiO\textsubscript{2} sample was prepared by using identical impregnation method without addition of the ruthenium precursor. SXPD pattern in Figure S5 (Supporting Information) show the existence of \(\lambda\)-Ti\textsubscript{3}O\textsubscript{5} phase along with anatase and rutile TiO\textsubscript{2}. Hence, we can exclude the formation of \(\lambda\)-Ti\textsubscript{3}O\textsubscript{5} due to the incorporation of RuO\textsubscript{2} and that it was formed as a result of preparation conditions. The H\textsubscript{2} evolution activity over treated TiO\textsubscript{2} was measured under the irradiation of UV-visible light (Figure S5C). It is apparent that the emerging \(\lambda\)-Ti\textsubscript{3}O\textsubscript{5} is detrimental to water splitting reaction while RuO\textsubscript{2} addition dramatically promotes the H\textsubscript{2} production.

Changes in the electronic configuration of TiO\textsubscript{2} NRs upon RuO\textsubscript{2} deposition via the formation of surface defects and changes in the chemical environment were probed by X-ray photoelectron spectroscopy. The Ti 2p + Ru 3d, C 1s + Ru 3d and O 1s core level XPS spectra of bare TiO\textsubscript{2} NRs and representative 0.1RuTi heterostructure, the best photocatalyst, are illustrated in Figure 3. The complete removal of chlorine by rinsing and subsequent annealing was confirmed by the absence of Cl 2p\textsubscript{3/2} and Cl 2p\textsubscript{1/2} peaks (not shown here). The doublet Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} located at 458.7 and 464.4 eV, respectively, is characteristic of the Ti\textsuperscript{4+} state in bare TiO\textsubscript{2} NRs (Figure 3A). The addition of 0.1 wt\% RuO\textsubscript{2} to TiO\textsubscript{2} induced electronic perturbations via a substantial shift of Ti 2p doublet towards lower binding energy (\(\Delta_{BE} = 0.5\) eV). Such a blue shift could be associated with the upward band bending at the interface of the RuO\textsubscript{2}-TiO\textsubscript{2} heterojunction\textsuperscript{21,22} and the formation of lower oxidation state of titanium species, \textit{i.e.} Ti\textsuperscript{3+}. The surface core-level shifts reflect the excess charge at the surface layer of metal atoms due to the reduced coordination.\textsuperscript{42} A downward shift of \(\Delta_{BE} = 0.4\) eV was also detected in the O 1s spectra (Figure 3B) which are consistent with Raman results.
discussed above. The unparallel shift of both Ti 2p and O 1s confirms the interfacial reaction between RuO$_2$ and TiO$_2$, forming Ti-O-Ru bonds.$^{35}$ The presence of ruthenium was clearly confirmed by a broad band representative of Ru 3d$_{5/2}$ peak located at 279 - 282 eV as reported in C 1s + Ru 3d core level spectra in Figure 3C whereas the 3d$_{3/2}$ doublet was superimposed by C 1s feature from carbonaceous impurities and carbonate species. The broad and weak spectrum in the inset indicates the formation of mixtures of Ru$^0$ and oxidized Ru$^{n+}$ species ($n = 2 \sim 4$).$^{8,10,16,21,35}$ Due to the intrinsic submetallic property of RuO$_2$, $^{8-11,21,31,33-35}$ these highly dispersed ruthenium species behave as quasi metallic contact materials to enhance both the conductivity and transfer of photoinduced holes from TiO$_2$ valence band, further facilitating the charge separation, so that the electrons freely migrate from the conduction band of TiO$_2$, reducing the protons and/or water to generate gaseous H$_2$. 
Figure 3. High resolution core-level XPS spectra of TiO$_2$ and 0.1RuTi: Ti 2p + Ru 3p, O 1s, and C 1s + Ru 3d.
The local geometry of the prepared materials was further studied by electron microscopy. SEM images in Figure S6A and B (Supporting Information) shows that our pure TiO$_2$ NRs were uniform nanorods aggregated in three-dimensional (3D) microsphere-like morphology. High-resolution TEM micrograph depicted in Figure S6C (Supporting Information) reveals that the highly crystalline rods had a rather constant diameter of about 5-10 nm and the length can be larger than several hundred nm. The well-resolved lattice fringe at 3.25 Å reveals that the highly crystalline NRs were grown along the [110] direction. After depositing 0.1 wt% RuO$_2$ onto the TiO$_2$ nanorods, the $d$-spacing of 3.25 Å corresponding to the preferred exposure of {110}-type planes of highly single-crystalline rutile structure was maintained (consistent with the FFT pattern in the inset) and the surface of TiO$_2$ rods becomes more heterogeneous (Figure 4A). It is very difficult to recognize and identify the lattice fringes of RuO$_2$ by HR-TEM mode stemming from lattice matching between rutile-like RuO$_2$ and rutile TiO$_2$, ultrafine particles and small loading amounts. Herein, the high angle annular dark field (HAADF) STEM image in Figure 4B indicates that the surface of the rod is rougher than TiO$_2$ NRs only (Figure S6D, Supporting Information) and in some specific regions, 1 ~ 2 nm nanodots (even smaller) were sparsely decorated onto primary TiO$_2$ NRs. The small nanoparticles are most likely a small fraction of sintered RuO$_2$. The EDX spectrum in the inset confirmed the presence of Ti, O and Ru signals. However, the microstructure of the rod surface before and after loading RuO$_2$ in Figure S7 (Supporting Information) obviously indicates an increase in surface roughness as well as the breakage into smaller fraction of rods. The structural analysis in Figure S8 (Supporting Information) visually revealed an obvious difference in the lattice fringes of TiO$_2$ NRs before and after loading RuO$_2$. Combining several factors, the heteroepitaxial growth of rutile RuO$_2$ along rutile TiO$_2$ NRs is proposed to occur because the lattice constants are almost identical. However, if the thickness of epitaxial layers or wires is too thin, approximately few atomic or sub-nanometer level, they
may not be observed microscopically. Similar behavior was studied by our group and other
groups.\textsuperscript{12,13,23,36} We have observed in previous fundamental studies\textsuperscript{23,36} the growth of 1D wire-like rows of RuO\textsubscript{x} extending along the <001> direction of TiO\textsubscript{2}(110) single crystals in which each RuO\textsubscript{2} wire with an apparent width of few angstrom covered three rows of TiO\textsubscript{2}(110) rows. Elevating temperature under UHV pressure resulted in the disappearance of RuO\textsubscript{x} wires and the formation of Ru nanoparticles. The RuO\textsubscript{2}/TiO\textsubscript{2}(110) surfaces were much more reactive towards CO oxidation, ethanol photo-oxidation and water dissociation than TiO\textsubscript{2}(110) or RuO\textsubscript{2}(110) due to the enhanced charge separation at the RuO\textsubscript{2}-TiO\textsubscript{2} interface.\textsuperscript{23,36,47}

The distribution of RuO\textsubscript{2} on TiO\textsubscript{2} NRs is obviously different from that over bulk TiO\textsubscript{2} particles where the presence of abundant round-shaped RuO\textsubscript{2} nanoparticles with an average diameter of 2-3 nm was extensively found in Figure 4C. One can clearly see a well-resolved fringe spacing of 3.25 Å that is indexed to (110) crystallographic plane of rutile TiO\textsubscript{2} and the inset FFT pattern indicates the single-crystalline nature of the support. At high coverage of RuO\textsubscript{2} nanoclusters whose d-spacing of 2.6 Å corresponds to (101) plane on the surface of bulk-like crystalline titania (Figure 4D), it resulted in much lower performance towards light-activated H\textsubscript{2} production over bulk supported catalysts.
Figure 4. (A, B) HR-TEM and HAADF-STEM micrograph of 0.1 wt% RuO$_2$ onto TiO$_2$ NRs, respectively; (C, D) HR-TEM images of 0.1% RuO$_2$ loaded on bulk TiO$_2$ particles. The insets of A and D are corresponding FFT patterns and the inset of B is EDX spectrum.

We carried out DFT studies to understand the electronic band structure of the heterojunction nanocomposites which strongly affects the photocatalytic water splitting performance. In Figure 5A, we show the density of states (DOS) of the full-relaxed (3x6) surface model for the system RuO$_2$ nanowire (RuO$_2^{\text{nw}}$) supported on TiO$_2$(110) that we have
reported previously. The large band below 2 eV is mainly related to O 2p levels from both oxides. The states just below Fermi level consists primarily of Ru 4d states, with small contribution from the O 2p states of the oxygen atoms of RuO₂. Therefore, the states observed in the UPS spectra just below the Fermi level are related to the supported RuO₂, mainly from metallic ruthenium states. The states above the Fermi level consists firstly of Ru 4d levels and above 0.2-0.3 eV the 3d states of titanium appear strongly. Therefore d-d transitions between 4d states of the supported ruthenia along with 3d states of titania support may take place in the heterostructure with an abrupt interface. The total DOS is consistent with the experimental ultraviolet photoelectron spectroscopy valence band (UPS-VB) spectra shown in Figure 5B. The UPS-VB spectra of TiO₂ NRs and 0.1RuO₂/TiO₂ heterostructure were measured in which two features centered at 4.8 eV and 6.6 eV are associated with the typical O 2p-Ti 3d structure of TiO₂. The position of the valence band maximum (VBM) for TiO₂ NRs locates at 1.87 eV (estimated by linear extrapolation), which is characteristic of a VB DOS of rutile TiO₂. It should be noted that the RuO₂ deposition induces a blue-shift to 1.75 eV of VB edge maximum energy and a tailing feature toward the vacuum level at ~-0.6 eV confirms the submetallic character of RuO₂. Such energy shifts in VBM and XPS core levels demonstrate the band gap narrowing, band bending, and the formation of strong built-in electric field at the heterojunction at the interface that was previously reported by DFT calculation, resulting in efficient separation of charge carriers during the photocatalytic process.
Figure 5. (A) Total and partial density of states (DOS) on O, Ru and Ti atoms of RuO$_2$/TiO$_2$(110) system (the Fermi level $E_F$ is set to energy zero); (B) experimental UPS-VB spectra of TiO$_2$ NRs and 0.1RuO$_2$/TiO$_2$ heterostructure; (C) UV-Vis diffused absorption spectra of TiO$_2$ and xRuTi series; and (D) representative band diagram of TiO$_2$ and RuO$_2$/TiO$_2$ heterostructure. The inset of (C) is the Tauc’s plot for direct band gap determination.

Figure 5C shows the UV-Vis diffused absorption spectra of TiO$_2$ NRs and xRuTi heterostructures with various RuO$_2$ contents. The absorption onset of bare TiO$_2$ NRs located at ca. 410 nm due to O 2$p$-Ti 3$d$ transitions. The edges were slightly red-shifted toward the longer wavelength region with increasing RuO$_2$ loading amounts, indicating the narrowing of the band gap. Consequently, the band gaps ($E_g$) determined by Tauc’s plot in the inset are
summarized in Table 1. A gradual reduction of the band gap from 3.06 eV to 2.93 eV is observed with further increasing RuO$_2$ contents up to 0.5 wt%. It is interesting to note that strong, broad absorption bands and long tails across the whole visible regime was observed in all oxide heterostructures which might be associated with several factors, *i.e.* the transition between Ti 3$d$ and Ru 4$d$, band transition of RuO$_2$ itself, defect level states, and/or the localized surface plasmon resonance mediated absorption of RuO$_2$ nanodots.\textsuperscript{10,11} Two types of band-edge transition of RuO$_2$ have been reported: *(i)* O 2$p$- Ru 4$d$ interband transition, resulting in an optical absorption at shorter wavelength range (up to 2.1 eV, ~ 580 nm); and *(ii)* $d$-$d$ intraband transition between partially filled and unfilled Ru 4$d$ orbitals or free carrier absorptions, giving an electronic band at 1.5-1.9 eV (~ 800 – 650 nm).\textsuperscript{10,48} And the proximity of surface plasmon and interband transition energies results in a damping of surface plasmon by interband electron excitations, thus reducing the surface plasmon local field.\textsuperscript{49} In the present study, it might be conclusive that the effect of Ru 4$d$-Ti 3$d$ transition (or hybridized state) and O 2$p$-Ru 4$d$ interband transition of RuO$_2$ is more pronounced than the $d$-$d$ intraband transition of RuO$_2$, exhibiting significant enhancement in visible light absorption, therefore enabling RuO$_2$/TiO$_2$ heterostructure to efficiently produce H$_2$ as compared to blank TiO$_2$. Especially, an increase in visible absorption is coincident with a decrease in UV region; and the O 2$p$-Ti 3$d$ direct transition in range of 200-400 nm for 0.1RuTi sample was distinct from others, possibly stemming from the stronger local electronic distortion in TiO$_2$ by RuO$_2$ and faster interfacial charge transfer from TiO$_2$ to RuO$_2$. Both band gap narrowing and enhanced absorption features in visible regime notably confirm that all rod-like RuO$_2$/TiO$_2$ heterostructures are highly efficient visible-light-responsive photocatalysts.

On the contrary, very poor visible-light absorption behavior was observed when loading 0.1 wt% RuO$_2$ onto bulk TiO$_2$ particles as indicated in Figure S9 (Supporting Information). It is interesting to note that the an absorption tail towards visible light region up to 480 nm were
observed on rutile TiO$_2$ NRs which did not happen with bulk rutile TiO$_2$. Recently, Li et al.$^{30}$ reported similar visible light absorption over sub-10nm rutile TiO$_2$ NPs compared to bulk-like or larger-grain-size rutile TiO$_2$. A slightly increased absorbance in the range of 700-1000 nm is more visible than that ranging from 400 to 550 nm, accounting for the dominance of partially filled and unfilled Ru 4$d$ electronic bands ($d$-$d$ intraband transition). That contributes to extremely lower UV activity and almost no visible-light-responsive activity (not shown here) of bulk TiO$_2$ and 0.1RuTi$_p$ material. The photoluminescence spectroscopy (Figure S10, Supporting Information) was additionally performed to understand the efficiency of charge carrier trapping, migration, transfer and separation. PL peak intensity of xRuTi heterostructure relatively decreases with increasing RuO$_2$ amounts, implying the suppression of electron-hole recombination rate that favors the higher photocatalytic activity. It can be seen that although the loading beyond 0.1 % exhibits lower recombination rate, worse H$_2$ production performance was obtained possibly due to the dominance of light shielding effect and abundance of oxygen vacancy defects as mentioned above that remarkably inhibit the performance.

Gathering the experimental data of $E_g$ and VBM of 0.1RuTi nanocomposite, a possible band level alignment diagram at the interface is schematically shown in Figure 5D. The formation of a heterojunction at the RuO$_2$-TiO$_2$ interface, band gap narrowing, and upward band bending at the interface effectively promote the separation of photoinduced electrons and holes, leading to an increase in photocatalytic H$_2$ evolution.
Scheme 1. Schematic illustration of proposed upward band bending-involved charge transfer pathway of RuO$_2$/TiO$_2$ heterojunction nanocomposite to produce H$_2$ under visible light irradiation.

Scheme 1 illustrates the proposed charge transfer pathway over RuO$_2$/TiO$_2$ heterostructures to produce H$_2$. By this way, it favors the dynamic transfer of electrons and holes from TiO$_2$ to RuO$_2$ via an intimate contact due to higher work function of RuO$_2$, subsequently reacting with protons, water and methanol. The photoinduced holes from VB of TiO$_2$ NRs are irreversibly scavenged by methanol to produce various oxidation intermediates and products such as \( ^{\bullet} \)OH radical, \( ^{\bullet} \)CH$_2$OH, HCHO, HCOOH and CO$_2$. Meanwhile, the photogenerated electrons simultaneously reduce the protons and water to generate H$_2$ gas. These reactions proceed competitively with the recombination of electron-hole pairs. Herein, RuO$_2$ efficiently stabilizes the holes and creates the heterojunction or a Schottky barrier at the heterointerface between RuO$_2$ and TiO$_2$, hindering the charge carrier recombination and consequently, enhancing the H$_2$ evolution. Because Ru is more electronegative than Ti (2.2 vs. 1.54), the strong accumulation of electron density at the interface creates a strong internal
electric field between the interface and its adjacent TiO$_2$ layer.\textsuperscript{22} The distribution of electric field is inhomogeneous, directly relating to the gradient of the space charge or band bending potential.\textsuperscript{11} Thereby, the photoinduced electron-hole pairs adjacent to the interface are separated more efficiently than those generated on pure TiO$_2$ surfaces. The transport, transfer and separation of charge carriers are promoted in the presence of RuO$_2$ and the photocatalytic H$_2$ production activity is prominently enhanced. The unique nanoparticle-nanorod geometry also contributes to the excellent efficiency due to the favorable vectorial electron transport within the 1D TiO$_2$ structure. Additionally, the trapping centers involving Ti$^{3+}$ sites as the electron scavengers and the oxygen vacancies as hole trapping centers are crucial in enhancing the photo-oxidation of methanol and consequently, hydrogen production. It is conclusive that the optimized RuO$_2$ concentration is a crucial factor in accounting for the photocatalytic properties \textit{via} properly manipulating geometry, levels of defects and interfacial electronic alignment.

**CONCLUSION**

We have successfully developed heterojunction nanocomposites by loading miniscule quantities of RuO$_2$ onto 1D rutile TiO$_2$ NRs and these materials exhibited superior visible-light-driven H$_2$ generation activity. Our study proved that the unique geometry, abundance of surface defects, band gap narrowing, visible photoresponse and favorable upward band bending at the heterointerface significantly facilitate the charge transfer and separation of photogenerated electron-hole pairs. 0.1 wt\% of RuO$_2$ was the optimal loading amount to achieve the highest H$_2$ evolved rate. The comparison with bulk-like support and Pt counterpart obviously demonstrates that the rod-like heterostructures is extremely crucial to visible-light-responsive activity. In perspective, this study provides a simple, scalable and cost-effective approach to produce efficient heterogeneous photocatalysts for solar hydrogen production from water.
ASSOCIATED CONTENT

Supporting Information. Includes description of SEM and PL techniques, detailed experiment of H2 production; supporting figures (Figure S1 to S10) of time profiles and H2 production rate of Ru and Pt-based heterostructures under either UV or visible light irradiation, Rietveld refinement, SEM/HR-TEM/HAADF-STEM images, UV-Vis-DRS and Tauc’s plot and PL spectra.

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Notes

The authors declare no competing financial interest.

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H$_2$O
H$^+$

Bulk TiO$_2$
TiO$_2$ nanorods

0.01% 0.1% 0.25% 0.5%