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Constructing Ru/TiO₂ heteronanostructures toward enhanced photocatalytic water splitting via RuO₂/TiO₂ heterojunction and Ru/TiO₂ Schottky junction

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The metallic Ru and RuO₂ dual co-catalysts modified TiO₂ nanobelts photocatalysts are constructed through a wetness impregnation reduction method with post thermal oxidation.

The samples are characterized carefully and their photocatalytic activities for half reactions of water splitting as well as pure water splitting are evaluated systematically under solar light irradiation. The detailed characterizations and analyses clearly reveal the formation of Schottky junction at Ru-TiO₂ interface and RuO₂/TiO₂ heterojunctions, respectively. The results of photocatalytic tests show that both Ru and RuO₂ can improve the photocatalytic activity for H₂/O₂ evolution and water splitting. Moreover, the photocatalytic activity of TiO₂ NBs can be further enhanced by co-modification of dual Ru and RuO₂ co-catalysts. The RuO₂/TiO₂ heterojunction improves the transfer of photogenerated holes of TiO₂ to the RuO₂, where water can be oxidized by the holes to evolve O₂, and the Ru/TiO₂ Schottky junction promotes the transfer of photogenerated electrons of TiO₂ NBs to the metallic Ru for proton reduction into H₂. These two processes allow for accomplishment of the enhanced overall water splitting. This work provide an important reference for designing highly efficient

photocatalysts for water splitting through loading of dual co-catalysts containing the same element but with different valence.

1. Introduction

Photocatalytic water splitting for hydrogen and oxygen production by using solar irradiation and semiconductor materials has been generally considered as the most promising technology for solar energy conversion and the basis of the future renewable energy resources. In the past forty years, a lot of scientific studies^[1-8] have been carried out to improve the solar light harvesting and quantum efficiency for solar-driven water splitting, which is still the core mission of the scientific community of photocatalysis. The reaction of water splitting into hydrogen and oxygen ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$, $\Delta G_{298} = +237.2 \text{ kJ / mol}$) is composed by two half-reactions involving oxygen evolution reaction (OER) via water oxidation ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$, $E^0 = +1.23 \text{ V vs NHE}$) and hydrogen evolution reaction (HER) via proton reduction ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, $E^0 = 0 \text{ V vs NHE}$).^[2,9] The separation and transport of photoexcited electrons and holes as well as the surface redox reactions on photocatalysts are the key issues for the photocatalytic water splitting towards H_2 and O_2 evolution. To address these issues, researchers have found that the loading of co-catalysts is an effective way to improve the overall reaction efficiency.^[9-12] The co-catalysts can create heterojunctions with the host photocatalyst to enhance charge separation, and meanwhile, serve as the active sites for the redox reactions (HER or OER) on the photocatalyst surface. Nevertheless, the single co-catalyst loading may only cause unilateral migration of the charge carrier, either electrons or holes, which restricts the enhancement effect on the overall photocatalytic activity. Therefore, it is of great importance to achieve dual co-catalyst loading with synergistic effect for improving HER and OER simultaneously in order to attain high efficiency in photocatalytic water splitting.

Generally, the noble metals, such as Pt, Au, and Pd, have been widely used as the effective HER co-catalysts due to the low overpotential.^[10,13,14] The Schottky junctions formed at the metal-semiconductor interfaces can greatly promote the migration of photogenerated electrons from semiconductor to metal, which improves charge separation and enhances hydrogen production via proton reduction on the metal surfaces. Recently, the lower-cost metallic Ru nanoparticles have received attentions as stable catalysts for efficient hydrogen generation in a photocatalytic system.^[15,16] Since ruthenium oxide (RuO₂) has been known as an effective OER catalyst which can accept the photogenerated holes from excited photocatalysts,^[12,17-21] it is of particular interest to introduce RuO₂ and metallic Ru together as dual co-catalysts onto one photocatalyst. By this way, the RuO₂ and Ru would be able to direct the separate migration of photogenerated holes and electrons, and function as active sites for O₂ and H₂ evolution, respectively. Herein, to explore the effectiveness of dual co-catalysts, we deposit Ru/RuO₂ nanoparticles onto anatase TiO₂ nanobelts (NBs) through a wetness impregnation reduction method with post-annealing. The ratio of Ru to RuO₂ is tuned by adjusting the annealing temperature. Synergetic enhancement on photocatalytic O₂ and H₂ evolution was observed when Ru and RuO₂ co-exist on TiO₂ NBs. Our studies demonstrate that the Ru/RuO₂ dual co-catalysts are very promising for solar-driven water splitting towards efficient hydrogen production.

2. Results and discussion

The X-ray diffraction (XRD) patterns of the prepared samples are shown in **Figure 1**, S3 and S4. The host TiO₂ appears as belted morphology (Figure S2) with a crystal structure of anatase phase (Figure S3). After loading Ru species on the TiO₂ NBs surface, the signature diffraction peaks related to ruthenium oxides and metallic ruthenium did not show up due to the low crystalline.

The typical Ru-loaded TiO₂ sample, Ru_{8.0}/TiO₂ NBs as optimized sample, was annealed in air at different temperature for 5 hours to increase the crystallinity and improve the contact

between the Ru co-catalysts and host TiO₂ NBs. In addition, the metallic Ru particles would be partly converted into RuO₂ during the annealing process, in which the ratio of Ru to RuO₂ is regulated by the annealing temperature. Figure 1 shows the XRD patterns of Ru_{8.0}/TiO₂ NBs-T (T refers to the different annealing temperature: 200, 400, 600, and 800). After annealing, the signature peak of rutile RuO₂ appears at 27.98° (XRD pattern of rutile RuO₂ is shown in Figure S5) and the peak intensity increases along with increased annealing temperature.^[26-31] The existence of crystallined RuO₂ is verified by the TEM observations (Figure S8). Note that annealing at 800 °C led to a small peak at 27.37° corresponding to the (110) plane of rutile TiO₂ formed via phase transformation of anatase TiO₂.^[32] We could not observe the diffraction peaks belonging to metallic Ru, which might be due to very low concentration and small particle size.

Nevertheless, the nanoparticles of Ru-based species can be observed under transmission electron microscopy (TEM). As shown in **Figure 2** and S6, the ruthenium co-catalysts nanoparticles with size of about 4-10 nm are uniformly dispersed on the surface of TiO₂ NBs (width of 100-150 nm, Figure S2). The HRTEM image (Figure 2B) displays the typical lattice fringe with d-spacing of ~0.32 nm, corresponding to the (110) plane of rutile RuO₂.^[28,33,34] Some small nanoparticles with a size of ca. 4-6 nm aside the RuO₂ NPs are believed as metallic Ru based on their different contrast, but the corresponding lattice fringes were not observed due to the poor crystallinity. Generally, the size of Ru NPs has great important role in catalytic reactions. In this work, the size of Ru NPs on TiO₂ NBs is about 4-6 nm, which is consistent with the optimal size reported by S. H. Joo et al.^[35] After annealing in air at high temperature, the ruthenium co-catalysts on TiO₂ NBs appeared as sheet-like structures (Figure 2C, S7 and S8), which are still RuO₂ as evidenced by the HRTEM analysis (Figure 2D). These observations suggest that the ruthenium co-catalysts will reconstruct upon thermal treatment and oxidation. The metallic Ru species can be hardly identified in the HRTEM image. However, the existence of metallic Ru can be verified by the XPS analyses.

As shown in **Figure 3A** and Table S1, the XPS peak of Ru_{8.0}/TiO₂ NBs can be fitted into three peaks centered at 285.0, 286.4, and 288.6 eV originated from surface adventitious carbon and physisorbed organic species (same as all samples) and three pairs of Ru 3d_{5/2} and Ru 3d_{3/2} at ca. 279.68 and 283.72 eV for metallic Ru, 280.57 and 284.53 eV for Ru⁴⁺ cations in RuO₂, and 282.11 eV and 286.12 eV for RuO₂ satellite, respectively.^[36,37] This result suggests that metallic Ru and RuO₂ species coexist on TiO₂ NBs surface, which is consistent with the TEM results (Figure 2). The annealing treatment leads to changes of the surface Ru⁰/Ru⁴⁺ ratio, which decreases along with higher annealing temperature (9.4% for Ru_{8.0}/TiO₂ NBs, 4.7% for Ru_{8.0}/TiO₂ NBs-200, 2.1% for Ru_{8.0}/TiO₂ NBs-400, and 0 for Ru_{8.0}/TiO₂ NBs-600 and Ru_{8.0}/TiO₂ NBs-800), as estimated from Figure 3A and S13A. These results suggest that the metallic Ru species on TiO₂ surfaces are gradually oxidized into RuO₂ during the annealing process.

In addition, we found that the Ru 3d binding energy of RuO₂ species on the annealed sample decreases slightly as compared to the sample without annealing. This might be attributed to the increased undercoordinated surface Ru atoms on RuO₂ surface.^[38] The O 1s peak in the high-resolution XPS spectra of parent TiO₂ NBs and Ru_{8.0}/TiO₂ NBs can be fitted into three peaks centered at around 529.9, 531.4, and 532.5 eV ascribed to adsorbed oxygen species and lattice oxygen of TiO₂ NBs (Figure 3B and Table S1). After annealing at high temperature in air atmosphere, a new peak at 528.60 eV, ascribed to the undercoordinated O species atoms at the RuO₂ surface,^[39,40] can be observed for all the annealed samples. It is worth noting that after loading Ru species on surface of TiO₂ NBs, the binding energies of lattice oxygen and Ti 2p of TiO₂ decrease simultaneously as compared to the host TiO₂ NBs (Figure 3B-C and Table S1). This can be ascribed to the attached RuO₂ decreasing the surface electron density of anatase TiO₂ NBs.^[12]

To better understand the photocatalytic water splitting processes over the Ru/RuO₂ co-loaded TiO₂ NBs, we employed these photocatalysts for the tests of two half-reactions, hydrogen

evolution reaction with EDTA as electron donor and oxygen evolution reaction with $\text{Ag}(\text{NO}_3)_3$ as electron acceptor, under solar light irradiation. The optimized amount of Ru-loading is 8.0 wt.% in terms of the activity for H_2 evolution, as evidenced by Figure S15. By fixing Ru content at 8.0 wt.%, the effects of annealing temperature on the photocatalytic activity is shown in **Figure 4A-D**.

After annealing at 200 °C, both H_2 and O_2 evolution rate for $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-200 (23.32 mmol $\text{h}^{-1} \text{g}^{-1}$ and 0.73 mmol $\text{h}^{-1} \text{g}^{-1}$ for H_2 and O_2 evolution, respectively) increased dramatically as compared to unannealed $\text{Ru}_{8.0}/\text{TiO}_2$ NBs (11.96 mmol $\text{h}^{-1} \text{g}^{-1}$ and 0.57 mmol $\text{h}^{-1} \text{g}^{-1}$ for H_2 and O_2 evolution, respectively), suggesting that the thermal treatment is effective for increasing the photocatalytic activity possibly due to improved crystallinity of Ru/ RuO_2 cocatalysts and the more intimate contact between Ru/ RuO_2 and the host TiO_2 NB. Further increasing the annealing temperature to 400 °C led to even higher photocatalytic activities of $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-400 with the gas production rate of 25.34 mmol $\text{h}^{-1} \text{g}^{-1}$ and 1.21 mmol $\text{h}^{-1} \text{g}^{-1}$ for H_2 and O_2 evolution, respectively. However, when the annealing temperature increased to above 600 °C, the photocatalytic activity of the samples gradually decrease. The activity of $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-800 was even lower than that of unannealed $\text{Ru}_{8.0}/\text{TiO}_2$ NBs. This might be due to the complete oxidation of metallic Ru species into RuO_2 as evidenced by the XPS results (Figure S13) and restructure of RuO_2 nanosheets (Figure S8). Our observations suggest that the metallic Ru species on TiO_2 NBs play very important roles in photocatalytic water splitting. To further confirm the synergistic effect of the RuO_2 and metallic Ru on TiO_2 NBs for photocatalytic activity, we have also carried out comparison tests by using RuO_2 NPs modified TiO_2 NBs ($\text{RuO}_2/\text{TiO}_2$ NBs-400) and metallic Ru NPs modified TiO_2 NBs ($\text{Ru}^0_{8.0}/\text{TiO}_2$ NBs) as control samples (characterized by XRD, TEM, XPS, UV-Vis absorption, and the results are shown in Figure S4, S9, S12, and S14 and discussions can be seen in supporting information). As shown in **Figure 5A and B**, the photocatalytic H_2 evolution rates over both control samples were obviously lower than that of $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-400 with Ru^0

and RuO₂ co-loaded. Similar comparison results were also observed for photocatalytic O₂ evolution (Figure 5C and D). Interestingly, comparing to the RuO₂/TiO₂ NBs-400 sample, the Ru⁰_{8.0}/TiO₂ NBs sample exhibited higher H₂ evolution rate whereas lower O₂ evolution rate, suggesting that Ru⁰ and RuO₂ serve as the different active sites for H₂ and O₂ evolution, respectively.

The photocatalytic overall water splitting over the samples were measured in pure water under solar light irradiation. **Figure 6** shows the amount of detected H₂ in the vessel during the water splitting reaction. Among these different Ru-modified TiO₂ NBs, the sample annealed at 400 °C (Ru_{8.0}/TiO₂ NBs-400) still exhibited the highest H₂ evolution rate (40.2 μmol h⁻¹ g⁻¹). The results were consistent with the test data from the aforementioned half-reactions. However, the O₂ evolution was not proceeding as we expected.

For Ru_{8.0}/TiO₂ NBs-400, we observed stoichiometric H₂ and O₂ evolution in the first hour reaction as shown in Figure S16, indicating the remarkable photocatalytic activity for pure water splitting over Ru_{8.0}/TiO₂ NBs-400 photocatalyst. When the light irradiation time was further prolonged, the amount of O₂ in the system decreased whereas H₂ was still evolving, indicating that the evolved O₂ were consumed during the reaction. The O₂ consuming may be caused by a sequence of following reactions:^[41-43]

When metallic Ru catalysts are loaded on TiO₂ NB surface, it would establish Schottky junction^[44-45] between the Ru metal (work function as 4.71 eV) and TiO₂ (work function as 4.2 eV),^[46-49] and allow for transfer of photogenerated electrons from TiO₂ to Ru and consequently promotes separation of photogenerated charge carriers (Figure S17). The

corresponding Schottky barrier height (E_{SB}) is calculated to be 0.66 eV according to the formulation of $E_{SB}=\varphi-\chi$, where φ is work function of Ru and χ is electron affinity of TiO_2 , respectively. This hypothesis is supported by the XPS results showing the binding energy shift of Ti and O towards high energy (Figure S14 and Table S1) as well as the enhanced photocatalytic activities (Figure 5 and 6). Moreover, the metallic Ru particles can serve as the active sites for proton reduction towards H_2 evolution, which is evidenced by the significantly higher photocatalytic H_2 generation rate of $Ru^0_{8.0}/TiO_2$ NBs than that of pure TiO_2 NBs and RuO_2/TiO_2 NBs-400. As for RuO_2 , it is known as a hole trapper driving the transfer of photogenerated holes from TiO_2 ,^[17-21] and can serve as active sites for water oxidation reaction ($2h^++2H_2O\rightarrow O_2+4H^+$) towards O_2 evolution. This explains why the RuO_2/TiO_2 NBs-400 sample showed much higher photocatalytic O_2 evolution rate than the $Ru^0_{8.0}/TiO_2$ NBs. After RuO_2 coupled with TiO_2 semiconductor, (work function of RuO_2 is ca. 5.0 eV, which is higher significantly than that of the anatase TiO_2 with ca. 4.2 eV), a heterojunction can be formed at RuO_2 and TiO_2 interface, as clearly seen TEM images in Figure 2, which can drives the photogenerated holes of TiO_2 NBs across heterojunction to TiO_2 (supported by XPS results in Figure 3). Therefore, in this work, we designed and prepared Ru/ RuO_2 co-loaded TiO_2 NBs through the combination of wetness impregnation reduction method and post annealing. The coexistence of RuO_2 nanosheets and metallic Ru^0 species on TiO_2 NBs, as proved by the analyses of XRD, HRTEM, and XPS, led to the double-junctions of Ru/ TiO_2 / RuO_2 (**Figure 7A**). The photocatalytic test results indicated that the Ru^0 and RuO_2 dual co-catalysts significantly improved photocatalytic activities for H_2/O_2 evolution and overall water splitting as compared to the TiO_2 NB samples loaded with single catalyst of either Ru^0 or RuO_2 . The principle of the enhanced activities is shown in Figure 7B. Upon excitation of TiO_2 with solar light, the built-in electric field (Figure 7C) in the formed double junction region promotes separate transport of photogenerated electrons and holes towards opposite directions (further confirmed by PL results, as shown in Figure S18). The electrons

flow across the Schottky junction to metallic Ru^0 species for proton reduction into H_2 , while the holes transport to RuO_2 sites for water oxidation (**Scheme 1**). Such a synergistic effect by Ru^0 and RuO_2 greatly improves the electron-hole separation and the overall photocatalytic activities. This mechanism may apply to other dual co-catalysts (the same element but with different valence) and other semiconductors (such as ZnO , BiVO_4 , BiOCl , and $\text{g-C}_3\text{N}_4$, *etc.*). S. H. Joo et al.^[35] demonstrated that thin ruthenium oxide layers exist on Ru NPs, which plays an important role in many catalytic reactions. For photocatalytic water splitting, the photogenerated holes transport to RuO_2 layer (contacted with TiO_2) for water oxidation, while the photogenerated electrons transfer to metallic Ru^0 species core. This structure also can promote the transfer and separation for the photogenerated electron-holes pairs.

3. Conclusion

Highly dispersed Ru/ RuO_2 nanoparticles are deposited successfully on anatase TiO_2 NBs by a wetness impregnation reduction method. Then the samples are annealed at high temperature in air to adjust the Ru/ RuO_2 ratio by the thermal oxidation as well as to improve the crystallinity of co-catalysts and contact between the co-catalysts and host photocatalyst. The detailed characterization reveals that the metallic Ru NPs and RuO_2 NSs co-catalysts are supported successfully on TiO_2 NBs, and the Ru/ TiO_2 Schottky junction and $\text{RuO}_2/\text{TiO}_2$ heterojunction are formed at Ru and TiO_2 NBs interface and RuO_2 NSs and TiO_2 NBs interface after annealing at 400 °C, respectively. The activity results show a synergistic enhancement of the dual co-catalysts for solar-derived water splitting over TiO_2 NBs photocatalysts. The $\text{RuO}_2/\text{TiO}_2$ heterojunctions improve the transfer of photogenerated holes of TiO_2 to the RuO_2 , where water can be oxidized by the holes to evolve O_2 , and the Schottky junction promotes the transfer of photogenerated electrons of TiO_2 NBs to the Ru, where H^+ is reduced into H_2 , finally achieving the enhanced overall water splitting into the H_2 and O_2 .

4. Experimental Section

Preparation of Ru/TiO₂ NBs: The experimental procedure for the preparation of the Ru/TiO₂ NBs nanostructures consists of several simple steps, which is presented in Fig. S1. Firstly, anatase TiO₂ NBs were prepared by the previous reported hydrothermal method,^[22-25] see supporting information. Then, 1.0 g of as-prepared anatase TiO₂ NBs were impregnated with RuCl₃ solutions (10 mg Ru/mL), followed by the ultrasonic treatment for 5 min. Adding the desired amount of RuCl₃ to prepare samples with different Ru contents (Ru wt% =0.5, 1.0, 2.0, 4.0 and 8.0), which denotes as Ru_x/TiO₂ NBs (x=0.5, 1.0, 2.0, 4.0 and 8.0). Thereafter, the slurry was dried at 120 °C for 5 h and the obtained solid samples were further treated by NaBH₄ reduction. Final products were washed thoroughly with distilled water to completely remove ions and collected by centrifugation, finally dried at 120 °C. To study the effect of annealing temperature on the composition, structure and photocatalytic activity of samples, the Ru_{8.0}/TiO₂ NBs sample as optimized sample was annealed at 200, 400, 600, and 800 °C for 5 h, respectively, which denotes as Ru_{8.0}/TiO₂ NBs-T (T=200, 400, 600, and 800)..

Preparation of RuO₂/TiO₂ NBs: 0.5 g anatase TiO₂ NBs were dispersed in the solution containing 50 mL ethanol and 50 mL H₂O with constant stirring for 30 min. Then, the desired amount of RuCl₃ (20 mg Ru/mL) was added to above suspension. After stirring for 30 min, NaOH solution (1.0 M) was slowly added to adjust the pH=7.0 and suspension was then stirring for 5 h. Resulting products were collected by centrifugation and then washed thoroughly with distilled water and ethanol for 3 time, respectively.

Preparation of Ru⁰/TiO₂ NBs: 0.5 g anatase TiO₂ NBs were firstly dispersed in 80 mL methanol with constant stirring for 30 h. Subsequently, the desired amount of RuCl₃ solution (10 mg Ru/mL) was slowly added to the mixed solution. The suspension was then stirred for 2 h and sonicated for 20 min successively, and transferred to a Teflon-lined autoclave of 100 mL capacity. The autoclave was maintained at 200 °C for 15 h and then allowed to cool to

room temperature. The products (denotes as $\text{Ru}^{0}_{8.0}/\text{TiO}_2$ NBs) were washed thoroughly with distilled water and finally dried at 60 °C.

Catalyst characterizations: X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The field emission scanning electron microscopy (FESEM) images were taken with a JEOL JSM-6340F scanning electron microscope. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2010 and JEM -2100 transmission electron microscope at an accelerating voltage of 200 kV. XPS spectra were determined on a VG ESCALAB 250 XPS system with a monochromatized Al Ka X-ray source (15 kV, 200 W, pass energy=20 eV). UV-vis absorption spectra were recorded on a Lambda 750 UV/vis/NIR spectrophotometer (Perkin-Elmer, USA). Photoluminescence (PL) spectra were accomplished in solid with Shimadzu RF5301 Spectrofluorophotometer with an excitation wavelength of 300 nm.

Photocatalytic activity testing: The photocatalytic hydrogen evolution, oxygen evolution, and photocatalytic pure water splitting under solar light irradiation were performed in a closed quartz Pyrex reaction vessel. For photocatalytic hydrogen evolution, 10 mg photocatalyst was suspended in 10 ml of water containing 0.1 g of ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) by a magnetic stirrer in Pyrex reaction vessel. The above suspension was degassed 15 min using N_2 to remove air prior to irradiation under a 300 W xenon lamp (MAX-302, Asahi Spectra, USA). The gas product composition was analyzed every 1 h by an Agilent 7890A gas chromatograph (GC) with TCD detector

For the photocatalytic oxygen evolution reaction, typically, 10 mg of the as-prepared sample was dispersed into 10 mL AgNO_3 (0.1 M) solution. The suspension was sonicated for 5 min and then degassed with Ar for 15 min to remove the O_2 in the system prior to irradiation under a 300 W xenon lamp. The produced O_2 at a regular interval (1h) was analyzed by gas chromatograph (Agilent 7890A) with TCD detector.

The photocatalytic pure water splitting was also carried out in quartz reactor at room temperature. Typically, 10 mg of the as-prepared sample was dispersed into 10 mL pure water. The suspension was degassed with Ar for 15 min to remove the O₂ in the system prior to irradiation under a 300 W xenon lamp. The H₂ and O₂ in the reactor at a regular interval (1 h) were analyzed by gas chromatograph (Agilent 7890A) with TCD detector..

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. XRD patterns of $\text{Ru}_{8.0}/\text{TiO}_2$ NBs and $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-T (T=200, 400, 600, and 800) annealed at different temperatures. (A and B represent anatase and rutile phase TiO_2 , respectively)

Figure 2. Characterization of the nanostructure of the composite catalyst. (A and B) TME and HRTEM images of $\text{Ru}_{8.0}/\text{TiO}_2$ NBs, (C and D) TME images and (E and F) HRTEM images of $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-400 annealed at 400 °C in air.

Figure 3. High resolution core XPS spectra of (A) $\text{C}1\text{s}+\text{Ru}3\text{d}$, (B) $\text{O}1\text{s}$, and (C) $\text{Ti}2\text{p}$ of (a) TiO_2 NBs, (b) $\text{Ru}_{8.0}/\text{TiO}_2$ NBs, and (c) $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-400 samples.

Figure 4. Photocatalytic H₂ (A and B) and O₂ (C and D) evolution over Ru_{8.0}/TiO₂ NBs-T (T=200, 400, 600, and 800) annealed at different temperatures under solar light irradiation, respectively.

Figure 5. Photocatalytic H₂ (A and B) and O₂ (C and D) evolution over Ru modified samples with different Ru chemical state under solar light irradiation.

Figure 6. Amount of detected H₂ in the vessel during the photocatalytic water splitting reaction over various Ru modified samples.

(A) Formation of Ru/TiO₂/RuO₂ heteronanostructures

(B) Proposed band structure of Ru/TiO₂/RuO₂

(C) Charge separation

Figure 7. The schematic illustrating of proposed band structure of the Ru/TiO₂/RuO₂ in junctions area. (A) formation of Ru/TiO₂/RuO₂ heteronanostructures, (B) the model of band structure for Ru_{8.0}/TiO₂ NBs-400. (C) Charge separation in the heterojunction and Schottky junction region.

Scheme 1. The proposed mechanism of photocatalytic water splitting for H₂ and O₂ evolution over the Ru modified TiO₂ NBs under solar light irradiation.

The coexistence of RuO_2 and Ru on TiO_2 NBs leads to the double-junctions of $\text{Ru}/\text{TiO}_2/\text{RuO}_2$. Upon excitation of TiO_2 , the built-in electric field in the double-junction region promotes separate transport of photogenerated electrons and holes acrossing the Ru/TiO_2 Schottky junction and $\text{RuO}_2/\text{TiO}_2$ heterojunction to Ru and RuO_2 for proton reduction and water oxidation, respectively, achieving the enhanced photocatalytic activities.

Keyword: TiO_2 nanobelts, co-catalysts, photocatalytic water splitting, heterojunctions, Schottky junctions

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Constructing Ru/TiO_2 heteronanostructures toward enhanced photocatalytic water splitting via $\text{RuO}_2/\text{TiO}_2$ heterojunction and Ru/TiO_2 Schottky junction

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Supporting Information

Constructing Ru/TiO₂ heteronanostructures toward enhanced photocatalytic water splitting via RuO₂/TiO₂ heterojunction and Ru/TiO₂ Schottky junction

*Quan Gu, Ziwei Gao, Sijia Yu, and Can Xue**

S1.1 Materials

Commercial P25 TiO₂ nanoparticles ($\geq 99.5\%$ trace metals basis), ruthenium (III) chloride trihydrate (RuCl₃·3H₂O, 99.98%), sodium borohydride (NaBH₄, granules, 99.99% metals basis), AgNO₃, and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were acquired from Sigam-Aldrich. Methanol was obtained in analytical reagent grade from Fisher Scientific. Ethanol and hydrochloric acid (HCl, 37%) were acquired from EMD Millipore Corporation. Sodium hydroxide (NaOH) was obtained in analytical reagent grade from Sinopharm chemical reagent Co. Ltd. All of these chemicals were used without further purification.

S1.2. Preparation of Ru/TiO₂ NBs

The experimental procedure for the preparation of the Ru/TiO₂ NBs nanostructures consists of several simple steps, which is presented in Figure S1. Firstly, anatase TiO₂ NBs were prepared by the previous reported hydrothermal method.^[1-4] Typically, a certain amount of P25 was dispersed in 80 mL 10 M NaOH solution with constant stirring for 20 min. The mixed solution was placed into a Teflon-lined autoclave of 100 mL capacity. The autoclave was maintained at 200 °C for 24 h and then cooled to room temperature naturally. The obtained product was washed with distilled water for 3 times, and then dispersed in 100 mL 0.1 M HCl aqueous solution (allowing ion exchange from Na⁺ to H⁺ to form H₂Ti₃O₇). H₂Ti₃O₇ NBs (the SEM image is shown in Figure S2A) were washed thoroughly with distilled

water to completely remove ions, and then dried at 60 °C, finally, annealed at 800 °C for 2 h to obtained anatase TiO₂ NBs (SEM image is shown in Figure S2B).

Figure S1 the synthetic route of Ru_{8.0}/TiO₂ NBs-400 composites

Figure S2 FESEM images of (A) H₂Ti₂O₇ NBs and (B) anatase TiO₂ NBs

Figure S3 XRD patterns of Ru_x/TiO₂ NBs (x=0.5, 1.0, 2.0, 4.0 and 8.0) with different Ru amounts.

Figure S4 XRD patterns of Ru_{8.0}⁰/TiO₂ NBs, RuO₂/TiO₂ NBs-400, and Ru_{8.0}/TiO₂ NBs-400. For comparison, two ruthenium-containing TiO₂ samples with a tin content of ca. 8.0 wt.% were prepared by hydrolysis method (the sample denoted as RuO₂/TiO₂ NBs-400) and hydrothermal reduction (the sample denoted as Ru_{8.0}⁰/TiO₂ NBs), respectively. As shown in

Figure S4, the diffraction peaks belonging to rutile RuO_2 appears in the XRD pattern of $\text{RuO}_2/\text{TiO}_2$ NBs-400 and diffraction peak at 43.7° belonging to metallic Ru exists in the XRD pattern of $\text{Ru}^0_{8.0}/\text{TiO}_2$ NBs,^[5,6] suggesting that ruthenium co-catalyst on $\text{RuO}_2/\text{TiO}_2$ NBs-400 and $\text{Ru}^0_{8.0}/\text{TiO}_2$ NBs are mainly rutile RuO_2 and metallic Ru, respectively.

Figure S5 XRD patterns of (a) Ru, (b) Ru/RuO₂, and (c) RuO₂ by hydrothermal method, impregnation method, and hydrolysis method, respectively.

Figure S6 TEM images of (A) Ru_{2.0}/TiO₂ NBs, (B) Ru_{4.0}/TiO₂ NBs, and (C) Ru_{8.0}/TiO₂ NBs.

Figure S7 TEM image (A) and mapping of (B) O, (C) Ti, and (D) Ru elements in the $\text{Ru}_{8.0}/\text{TiO}_2$ -400 NBs.

Figure S8 TEM and HRTEM of (A and B) $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-200, (C and D) $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-600, and (E and F) $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-800.

The samples annealed at 200, 600, and 800 °C in air atmosphere were also characterized by TEM (Figure S8). When the treated temperature is lower ($\text{Ru}_{8.0}/\text{TiO}_2$ -200 sample), partial

Ru/RuO₂ NPs reconstruct due to the thermal treatment and oxidation to form RuO₂ nanosheets (NSs) on TiO₂ NBs, as shown in Figure S8A and B. Some Ru/RuO₂ NPs still can be clearly discernable in Figure S8B. With treated temperature further increased to 600 °C, all ruthenium species was oxidized to RuO₂ NSs (no metallic Ru NPs can be seen in the TEM images of Ru_{8.0}/TiO₂-600 sample), as shown in Figure S8C and D. The TEM image (Figure S8E) of Ru_{8.0}/TiO₂-800 annealed at 800 °C in the air atmosphere indicate that RuO₂ NPs with average diameter of about 10 nm are well-dispersed on TiO₂ NBs. These results indicate that the higher temperature leads to the changes of morphology and exposed facet due to the dissolution of the RuO₂ NSs.

Figure S9 TEM and HRTEM of Ru_{8.0}⁰/TiO₂ NBs and RuO₂/TiO₂ NBs-400.

Figure S9 shows the TEM and HRTEM images of Ru_{8.0}⁰/TiO₂ NBs and RuO₂/TiO₂ NBs-400 samples. TEM images of Ru_{8.0}⁰/TiO₂ NBs (Figure S9A and B) show that the highly dispersed Ru nanoparticles (NPs) with average size of about 6 nm can be seen clearly on the surface of the (101) planes of TiO₂ NBs at the 8.0 wt% loading. HRTEM in Figure 9C exhibits a lattice fringes with d-spacing of 0.23 nm, corresponding to the (100) crystal plane of metallic

ruthenium,^[7] and d space of 0.35 nm, indexed towards the (101) plane of TiO₂ NBs. For RuO₂/TiO₂ NBs-400, the RuO₂ NPs with size of 10-20 nm are dispersed on TiO₂ NBs, as shown in Figure 9D. HRTEM image of RuO₂/TiO₂ NBs-400 (Figure 9E) shows a (110) lattice fringe of rutile RuO₂ with d spacing of about 0.32 nm.^[8,9] These results indicate that the ruthenium co-catalysts on Ru_{8.0}⁰/TiO₂ NBs and RuO₂/TiO₂ NBs-400 are mainly metallic ruthenium and rutile RuO₂ NPs, respectively.

Figure S10 UV-visible absorption spectra of Ru_x/TiO₂ NBs (x=0.5, 1.0, 2.0, 4.0 and 8.0) with different Ru amounts.

Figure S11 UV-visible absorption spectra of TiO_2 NBs, $\text{Ru}_{8.0}/\text{TiO}_2$ NBs, and $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-T (T=200, 400, 600, and 800) annealed at different temperatures.

Figure S12 UV-visible absorption spectra of $\text{Ru}_{8.0}^0/\text{TiO}_2$ NBs, $\text{RuO}_2/\text{TiO}_2$ NBs-400, and $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-400.

The optical properties of parent TiO_2 NBs, Ru_x/TiO_2 NBs ($x=0.5, 1.0, 2.0, 4.0$ and 8.0) with different Ru amount, $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-T (T=200, 400, 600, and 800) annealed at different temperatures, $\text{Ru}_{8.0}^0/\text{TiO}_2$ NBs, and $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-400 samples were characterized by UV-Vis absorption, and the results are shown in Figure S10-12. UV-Vis absorption spectrum of

parent TiO₂ NBs shows a sharp absorption edge around 385 nm, which is typical of anatase titanium oxide. After loading the Ru species on the TiO₂ NBs surface, the spectra of Ru_x/TiO₂ NBs, Ru_{8.0}⁰/TiO₂ NBs, and Ru_{8.0}/TiO₂ NBs-400 samples (Figure S10 and S12) show an enhanced absorption in the visible-light region (400-800 nm) but the shape and optical absorption threshold of the spectra is similar with that of parent TiO₂ NBs. For Ru_x/TiO₂ NBs samples, the absorption intensity in the visible-light region increases gradually with the Ru loading increasing (Figure S10). After annealing Ru_{8.0}/TiO₂ NBs at high temperature in air atmosphere, no clearly alterations can be observed in the UV-Vis adsorption spectrum of Ru_{8.0}/TiO₂ NBs, as shown in Figure S11.

Figure S13 High resolution core XPS spectra of (A) Ru 3d, (B) O 1s, and (C) Ti 2p of Ru_{8.0}/TiO₂ NBs-T (T=200, 400, 600, and 800) annealed at different temperatures. (a) 200, (b) 400, (c) 600, and, (d) 800.

Figure S14 High resolution core XPS spectra of (A) C1s+Ru3d, (B) O 1s, and (C) Ti 2p of (a) $\text{Ru}^0_{8.0}/\text{TiO}_2$ NBs, (b) $\text{RuO}_2/\text{TiO}_2$ NBs-400, and (c) $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-400 samples.

Figure S14 compare the high resolution core XPS spectra of C1s, Ru3d, O 1s, and Ti 2p of $\text{Ru}^0_{8.0}/\text{TiO}_2$ NBs, $\text{RuO}_2/\text{TiO}_2$ NBs-400, and $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-400 samples prepared by different methods. There are only Ru 3d peaks (280.26 and 284.43 eV for Ru 3d 5/2 and Ru 3d 3/2) assigned to RuO_2 can be observed for $\text{RuO}_2/\text{TiO}_2$ NBs-400, suggesting that the Ru species in $\text{RuO}_2/\text{TiO}_2$ NBs-400 photocatalyst is assigned to RuO_2 . For $\text{Ru}^0_{8.0}/\text{TiO}_2$ NBs sample, the Ru 3d XPS represent both Ru 3d peaks for metallic Ru (279.68 and 283.88 eV for Ru 3d 5/2 and Ru 3d 3/2) and RuO_2 (280.56 and 284.63 eV for Ru 3d 5/2 and Ru 3d 3/2), but the metallic Ru is dominant ($\text{Ru}^0/\text{Ru}^{4+}$ is about 1.3, the metallic Ru species is metastable and can be further oxidized), suggesting that the Ru species on the surface of $\text{Ru}^0_{8.0}/\text{TiO}_2$ NBs is mainly metallic Ru. Different from RuO_2 modified samples, the binding energy of lattice oxygen and Ti 2p of $\text{Ru}^0_{8.0}/\text{TiO}_2$ NBs increase simultaneously as compared to the parent TiO_2 NBs, indicating that metallic Ru increases the charge density of TiO_2 NBs.

		Binding Energy of elements (eV)										
Core level		C 1s			Ru 3d			O 1s				Ti 2p
Samples	TiO ₂ NBs	285.00	286.3 9	288.61	-			-	529.92	531.49	532.56	458.72 and 464.52
	Ru _{8.0} /TiO ₂ NBs	285.00	286.3 1	288.70	279.68 and 283.72	280.57 and 284.53	282.11 and 286.12	-	529.86	531.40	532.51	458.62and 464.41
	Ru _{8.0} /TiO ₂ NBs-200	285.00	286.7 1	288.51	279.67 and 289.73	280.41 and 284.48	282.10 and 286.08	538.66	529.84	531.45	532.54	458.70 and 464.50
	Ru _{8.0} /TiO ₂ NBs-400	285.00	286.8 1	288.66	279.64 and 284.69	280.22 and 284.39	282.09 and 286.05	528.63	529.83	531.46	532.52	458.64 and 464.48
	Ru _{8.0} /TiO ₂ NBs-600	285.00	286.5 1	288.49	-	280.17 and 284.22	281.90 and 285.97	528.75	529.90	531.54	532.59	458.66 and 464.50
	Ru _{8.0} /TiO ₂ NBs-800	285.00	286.9 2	288.90	-	280.15 and 284.21	281.80 and 285.93	528.44	529.66	531.44	532.50	458.45 and 464.24
	Ru _{8.0} ⁰ /TiO ₂ NBs	285.00	286.4 7	288.80	279.68 and 283.88	280.56 and 284.63	282.10 and 286.09	-	530.06	531.70	532.77	458.88 and 464.67
	RuO ₂ /TiO ₂ NBs-400	285.00	286.4 6	288.90	-	280.26 and 284.43	281.90 and 286.00	528.67	529.94	531.56	532.67	458.71 and 464.69
Identify		Surface adventitious carbon	Physisorbed organic C species		Ru (0001) surface	RuO ₂		Ru 3d 5/2 satellite of RuO ₂	Undercoordinated O species	Lattice oxygen of TiO ₂	Adsorbed oxygen species	TiO ₂

Table S1 Peak positions of C 1s, Ru 3d, O 1s, and Ti 2p on samples from XPS spectra.

Figure S15 Photocatalytic H_2 production over Ru_x/TiO_2 NBs ($x=0.5, 1.0, 2.0$, and 8.0) with different Ru amounts

Figure S16 Photocatalytic water splitting for H_2 and O_2 evolution over $\text{Ru}_{8.0}/\text{TiO}_2$ NBs-400 under solar light irradiation.

Figure S17 Schematic energy-level diagrams of Ru and TiO₂ before (A) and after contact (B), respectively.

Figure S18 Room-temperature photoluminescence (PL) spectra of the TiO₂ NBs, Ru_{8.0}/TiO₂ NBs, and Ru_{8.0}/TiO₂ NBs-400 samples tested at an excitation wavelength of 300 nm.

It is known that the photoluminescence (PL) property of semiconductor is related to the transfer, separation, and recombination of the photoinduced electrons and holes. Therefore, to clearly understand the improvement of photocatalytic activity over Ru modified sample, the

photoluminescence (PL) spectra of the TiO₂ NBs, Ru_{8,0}/TiO₂ NBs, and Ru_{8,0}/TiO₂ NBs-400 samples were tested at an excitation wavelength of 300 nm. As shown in Figure S18, the parent TiO₂ NBs shows a very strong emission peak around at 380 nm corresponding to the radiative charge recombination. For Ru_{8,0}/TiO₂ NBs and Ru_{8,0}/TiO₂ NBs-400 samples, no PL peak at 380 nm can be observed in Figure S18, suggesting that the radiative charge recombination is effectively inhibited by ruthenium species loading because of the junctions promote the transfer and separation of the photogenerated electrons and holes.

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