Electronic Supplementary Information

Conductive polyaniline-mediated efficient electron transfer in Z-scheme photocatalysts for enhanced overall water splitting

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1. Experimental sections

1.1 Chemicals and materials

$SrCO_3$, $Rh_2O_3 \cdot 5H_2O$, $(NH_4)_2S_2O_8$ (APS), and aniline monomer were purchased from Shanghai Titan Scientific Co. Ltd. Aniline was purified twice under reduced pressure and stored below in a refrigerator prior to use. TiO_2 nanoparticles (P25, 20% rutile and 80% anatase) were purchased from Degussa. $Bi(NO_3)_3 \cdot 5H_2O$ was purchased from Guangzhou Jinhuada Chemical Reagent Co., Ltd. Graphene oxide (GO) was purchased from Ashine Advanced Carbon Materials Co., Ltd. All solutions used throughout the experiments were prepared with ultrapure water (18.2 MΩ).

1.2 Preparation of photocatalysts

1.2.1 Preparation of $Ru/SrTiO_3$:Rh

$SrTiO_3$:Rh(1%) were synthesized according to a reported procedure.[1] The starting materials of $SrCO_3$, TiO_2, and $Rh_2O_3 \cdot 5H_2O$ were mixed in a mortar at the ratio of Sr:Ti:Rh=1.03:0.99:0.01. The mixture was calcined at 1100 ℃ for 10 h in air. Ru cocatalyst (1 wt%) that act as an active site for H_2 evolution was loaded on $SrTiO_3$:Rh by photodeposition from an aqueous methanol solution (methanol/water=1/9) containing $RuCl_3 \cdot 3H_2O$. The obtained $Ru/SrTiO_3$:Rh photocatalyst was collected by filtration, washed with water, and dried at 60 ℃ in a vacuum oven overnight.

1.2.2 Preparation of $BiVO_4$

$BiVO_4$ powder was prepared by a liquid-solid reaction.[1] $Bi(NO_3)_3 \cdot 5H_2O$ (5.33 g) and V_2O_5 (1.00 g) were added into 50 mL of HNO_3 aqueous solution (0.5 M). The suspension was stirred at room temperature for 3 days. The obtained yellow $BiVO_4$ powder was collected by filtration, washed with water, and dried at 60 ^oC in a vacuum oven overnight.

1.2.3 Preparation of $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$

To synthesize the $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$ photocatalysts, $Ru/SrTiO_3$:Rh and $BiVO_4$ particles were first dispersed in 20 mL of 1 M H_2SO_4 solution to form a homogenous suspension with a aid of ultrasonication for 30 min. Afterwards, a calculated amount of aniline monomer was added into above suspension and stirred for 30 min to ensure the adsorption of aniline monomer on both of the photocatalyst particles. After that, a calculated amount of $(NH_4)_2S_2O_8$ (the molar ratio of $(NH_4)_2S_2O_8$ to aniline was kept to be 1) was dissolved into 5 mL of 1 M H_2SO_4 solution and the obtained solution was added dropwise into above mixture to initiate the oxidative polymerization of the aniline. The polymerization reaction was allowed to proceed for 6 h at 0 ℃ in an ice bath. The obtained $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$ photocatalysts were collected by filtration, washed with water, and dried 60 ℃ in a vacuum oven overnight.

$Ru/SrTiO_3$:Rh/PANI and $BiVO_4$/PANI photocatalysts were synthesized by the identical processes for $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$ without the addition of $BiVO_4$ and $SrTiO_3$:Rh, respectively. The $Ru/SrTiO_3$:Rh/$BiVO_4$ mixture was prepared by filtrating a suspension containing dispersed $Ru/SrTiO_3$:Rh and $BiVO_4$ particles. The bare PANI sample without any photocatalyst particles was also prepared using the same experimental procedures.

1.2.4 Preparation of $Ru/SrTiO_3$:Rh/RGO/$BiVO_4$ photocatalyst

The $Ru/SrTiO_3$:Rh/RGO/$BiVO_4$ photocatalyst was prepared according to a reported procedure.[1] 100 mg of $BiVO_4$ and 2 mg of graphene oxide (GO) were first dispersed in 50 mL of 50 vol% CH_3OH aqueous solution with the aid of ultrasonication for 2 h. Then, above suspensions were bubbled with N_2 gas and irradiated with a 300-W Xe lamp with a cut-off filter of 420 nm for 2 h, during which the GO was reduced to

RGO by the photogenerated electrons of $BiVO_4$ to obtain RGO/$BiVO_4$. Finally, RGO/$BiVO_4$ was mixed with Ru/$SrTiO_3$:Rh in water to obtain Ru/$SrTiO_3$:Rh/RGO/$BiVO_4$, which was directly used as a Z-scheme photocatalyst for photocatalytic water splitting study.

1.3 Characterization

X-ray diffraction (XRD) patterns were investigated with a Rigaku Smartlab diffractometer with a nickel filtrated Cu *K*α radiation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a Talos F200x field emission transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on an ESCALAB Xi^+ electron spectrometer (Thermo Scientific) using an Al *K*a X-ray source. Binding energies were referenced to the C 1s peak (set at 284.8 eV) of the sp^2 hybridized (C=C) carbon from the sample. UV-vis absorption spectra were taken with a Thermo Scientific-Evolution 220 spectrophotometer. Photoluminescence (PL) spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer.

1.4 Photocatalytic water splitting reactions

Photocatalytic reactions were performed in a 250 mL reaction cell connected to a closed gas circulation and evacuation system (CEL-SPH2N, CEAULIGHT). A 300-W Xe lamp (CELHXF300) equipped with an optical cut-off filter ($\lambda \geq 420$ nm) was used as light source. In a typical experiment, 100 mg of the photocatalyst was dispersed into 120 mL of water. The pH of the reaction solution was adjusted by using dilute H_2SO_4 solution (0.1 M). Before light irradiation, the reaction system was thoroughly degassed by evacuation in order to remove the oxygen inside the reactor. The reaction solution was continuously stirred and maintained at 6 ℃ by a flow of

cooling anhydrous ethanol. The amount of evolved H_2 and O_2 gases was determined using an on-line gas chromatograph (CEL-GC-7920, TCD, Ar carrier).

1.5 Photoelectrochemical and electrochemical and measurements

All of the electrochemical and photoelectrochemical measurements were performed with an electrochemical analyzer (CS3103, Wuhan Corrtest Instruments Corp., Ltd) in a conventional three-electrode configuration. A Pt mesh (1 cm^2) and a Ag/AgCl (in saturated KCl solution) electrode were used as the counter electrode and the reference electrode, respectively. For the photoelectrochemical measurements, the supporting electrolyte was a phosphate buffer (PSB) solution (0.05 M, pH 7) and a 300-W Xe lamp equipped with a cut-off filter of 420 nm was used as a light source. The photocatalyst working electrodes were prepared by electrophoretic deposition on conducting glass supports (FTO) as following: 40 mg of photocatalyst powder and 10 mg of iodine were dispersed in 15 mL of acetone under stirring and sonicated for 10 min. After this process, two FTO electrodes (1 cm×3 cm) were inserted parallel with each other in the above homogeneous suspensions with *ca*. 8 mm of distance, and then 20 V of bias was applied between them for 30 min. After that, the photocatalyst electrodes were dried at 100 ℃ for 12 h in a vacuum oven. The transient photocurrent response was recorded at a bias of 0.01 V under visible light irradiation. Electrochemical impedance spectroscopy (EIS) was carried out at a forward bias of 0.01 V with an AC amplitude of 5 mV in the frequency range of 10 mHz to 100 kHz under the visible light irradiation. The Mott-Schottky (M-S) measurements were carried out in a 0.5 M Na_2SO_4 (pH 3.5) solution at a frequency of 1 MHz. The cyclic voltammetry (CV) curve of PANI were measured in a 0.5 M Na_2SO_4 solution (pH 3.5) with a scanning rate of 50 mV s^{-1}. The PANI-modified glassy carbon (GC, 3 mm) electrode was prepared as follows: 4 mg of PANI were dispersed in 50 μL of 5

wt% Nafion solution by at least 30 min sonication to form a homogeneous suspension. Then 10 μL of suspension was loaded onto a GC electrode with a loading 0.8 mg cm^2.

2. Additional figures

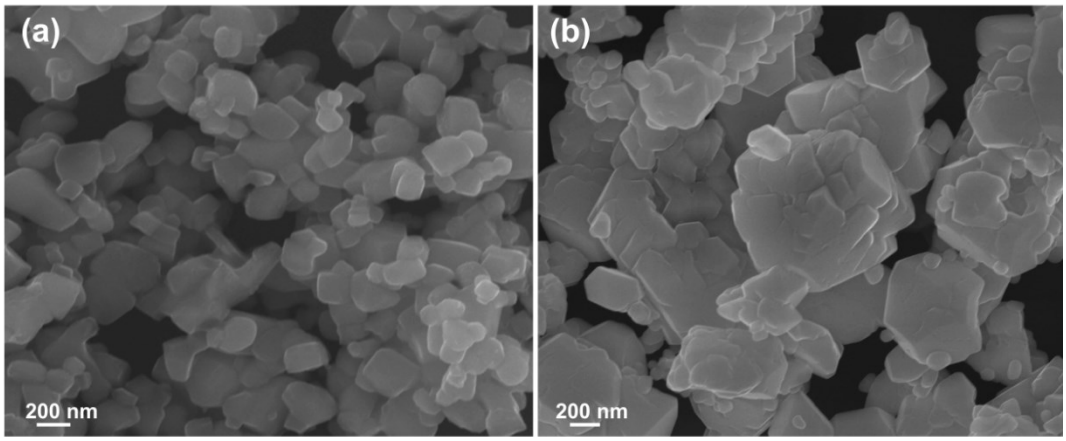

Fig. S1 SEM images of (a) Ru/$SrTiO_3$:Rh and (b) $BiVO_4$ particles.

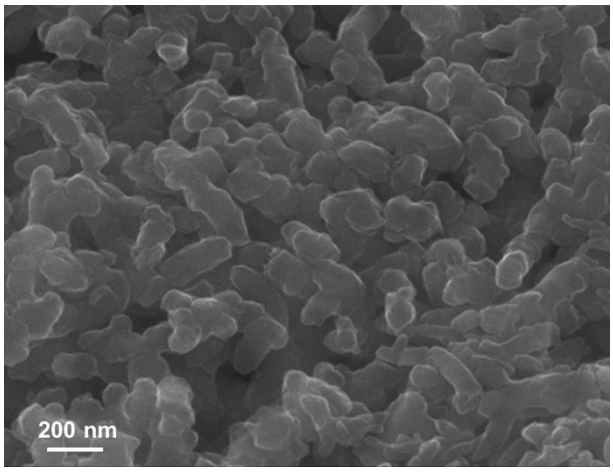

Fig. S2 SEM image of the pristine PANI.

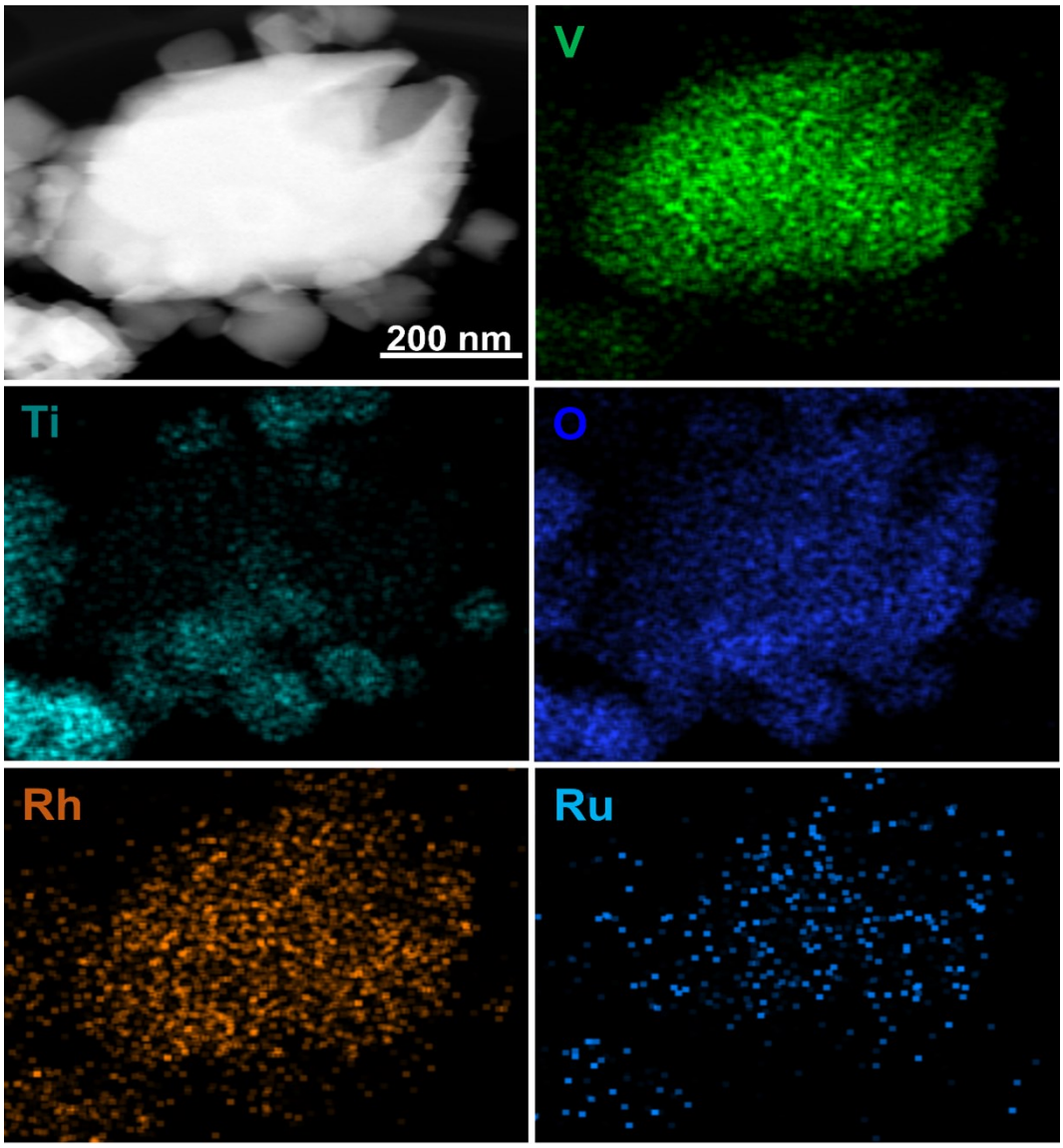

Fig. S3 Additional HAADF-SEM image of Ru/$SrTiO_3$:Rh/PANI/$BiVO_4$ and the corresponding EDX elemental maps (V, Ti, O, Rh, and Ru).

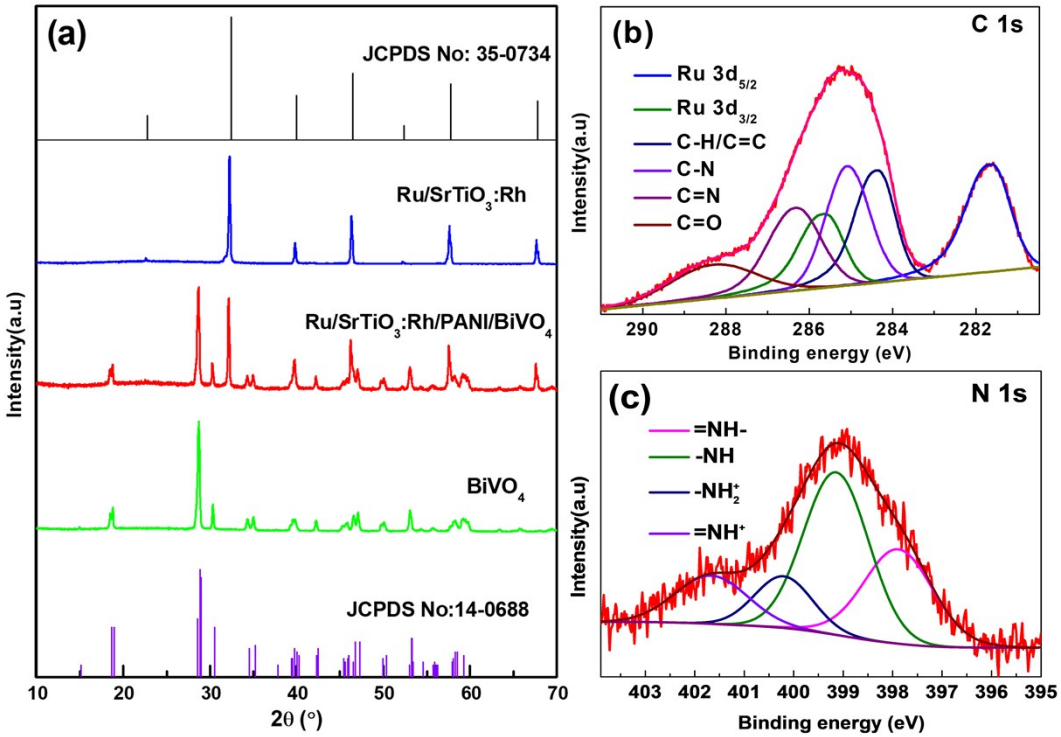

Fig. S4 (a) XRD patterns of $Ru/SrTiO_3$:Rh, $BiVO_4$, and $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$.

(b) C 1s and (c) N 1s XPS spectra of $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$.

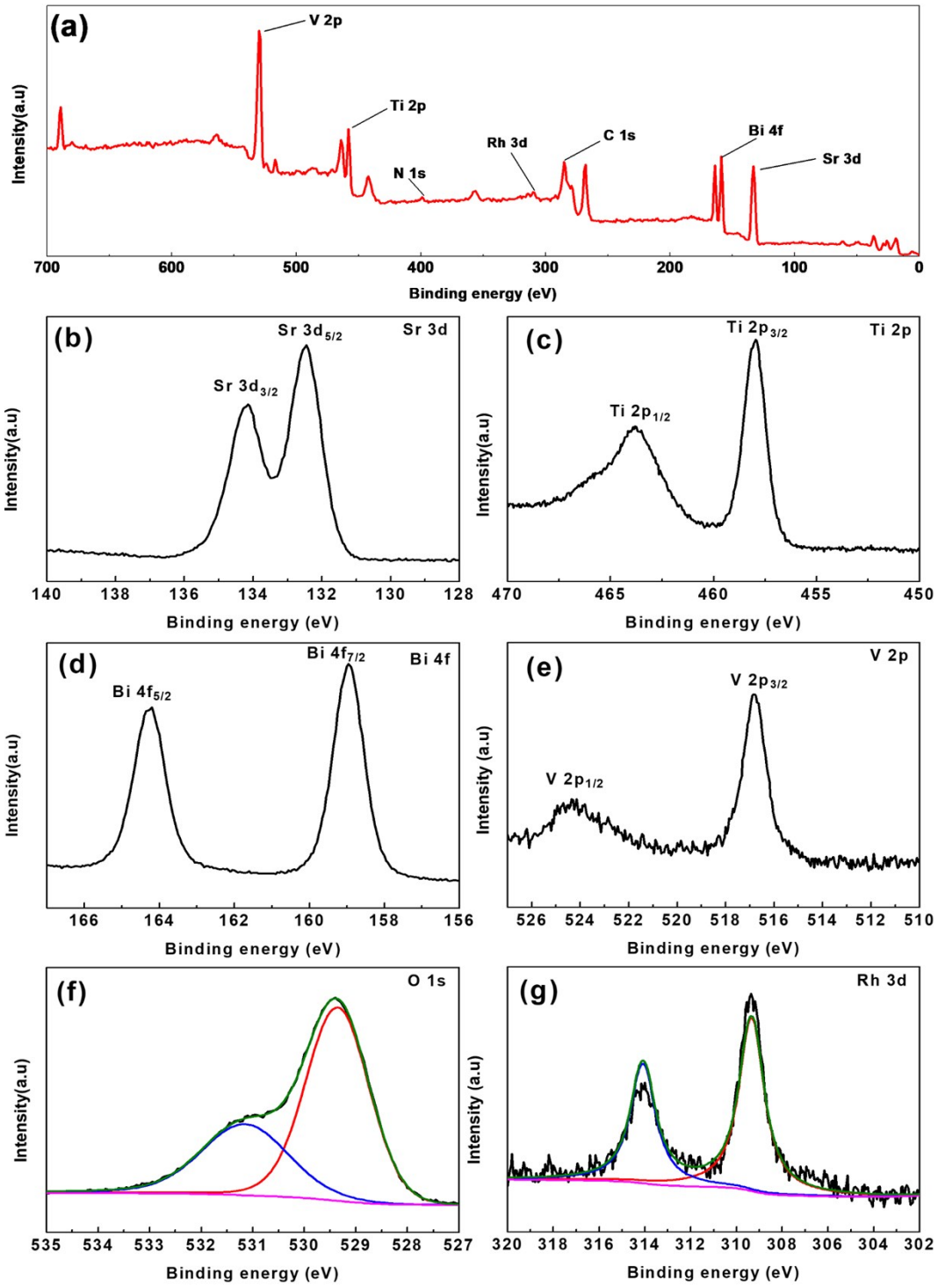

Fig. S5 (a) XPS survey spectrum and (b-g) high-resolution XPS spectra of (b) Sr 3d, (c) Ti 2p, (d) Bi 4f, (e) V 2p, (f) O 1s, and (g) Rh 3d of the $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$.

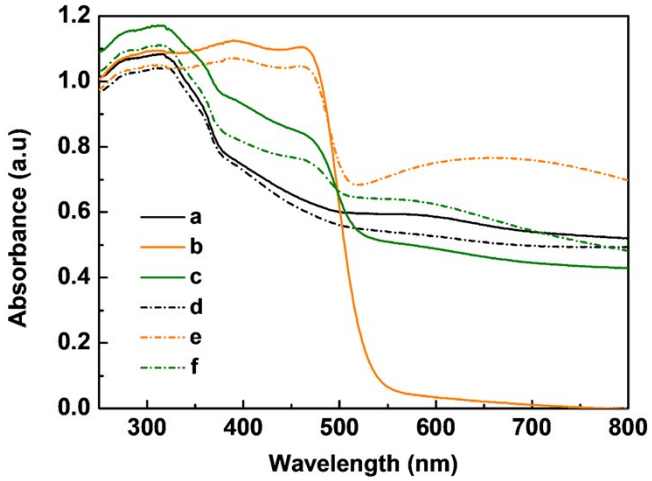

Fig. S6 UV-vis diffuse reflectance spectra (UV-vis-DRS) of (a) Ru/$SrTiO_3$:Rh, (b) $BiVO_4$, (c) Ru/$SrTiO_3$:Rh/$BiVO_4$, (d) Ru/$SrTiO_3$:Rh/PANI, (e) $BiVO_4$/PANI, and (f) Ru/$SrTiO_3$:Rh/PANI/$BiVO_4$.

In Fig. S6, it can be observed that the Ru/$SrTiO_3$:Rh has a steep absorption edge similar to $SrTiO_3$ at about 390 nm and a broad absorption in the visible light range due to the loading of Ru nanoparticles and the existence of the impurity levels of trivalent Rh species, while $BiVO_4$ exhibits an excellent absorption towards visible light with an steep edge at around 520 nm. The light absorption spectrum of the physical mixture of Ru/$SrTiO_3$:Rh and $BiVO_4$ is the simple sum of two components. After the incorporation of PANI, all of the Ru/$SrTiO_3$:Rh/PANI, $BiVO_4$/PANI, and Ru/$SrTiO_3$:Rh/PANI/$BiVO_4$ show enhanced light absorption ranging from 520 to 800 nm, which confirm the existence of PANI in the samples.

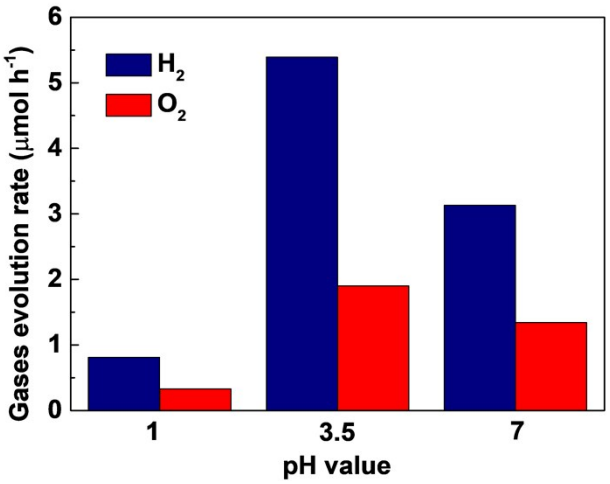

Fig. S7 Effect of the pH value on the H_2 and O_2 evolution activity of $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$ catalyst.

It has been previously reported that establishing an intimate physical interaction between the H_2 and O_2 photocatalysts is critical to allow the efficient interparticulate charge transfer and thus greatly improve the photocatalytic activity. In the previous studies, this can be realized by adjusting the pH value of the reaction solution to induce aggregation within the photocatalysts.[1] Similar to the previous findings for bare $BiVO_4$ and $Ru/SrTiO_3$:Rh, we also found that our $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$ photocatalyst showed the highest activity at pH 3.5 (Fig. S7) probably due to the close assembly of PANI, $BiVO_4$ and $Ru/SrTiO_3$:Rh. In addition, as can be seen from Fig. S7, $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$ photocatalyst also shows water splitting activity at pH 7, which is lower than the activity obtained at pH 3.5 due to the fact that the H_2 evolution reaction is thermodynamically unfavorable at higher pH values.

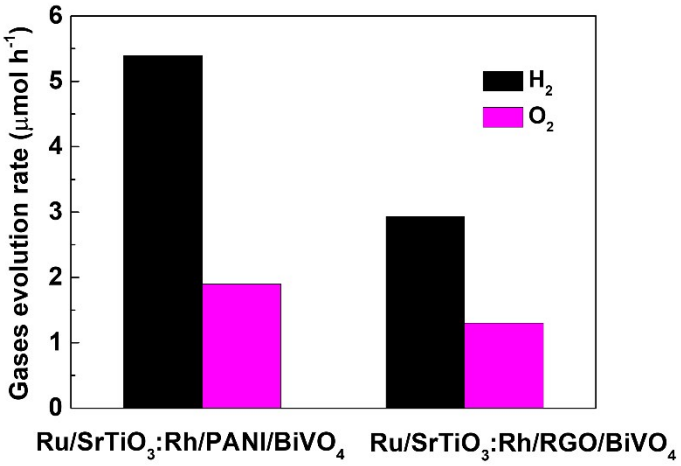

Fig. S8 Photocatalytic water splitting activity of $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$ and $Ru/SrTiO_3$:Rh/RGO/$BiVO_4$.

Table S1 Comparison of the overall water splitting performance of Z-scheme photocatalysts under visible light irradiation.

Photocatalyst	Photocatalyst dosage (mg)	H_2/O_2 evolution rate (μmol h^{-1})	Ref.
$Ru/SrTiO_3$:Rh/RGO/$BiVO_4$	30	11/5.5	1
$SrTiO_3$:Rh/np-ITO/$BiVO_4$	50	7.5/3.6	2
$SrTiO_3$:La,Rh/Au/$BiVO_4$:Mo	60	48/24	3
$Ru/SrTiO_3$:La,Rh/carbon/$BiVO_4$:Mo	20	8.6/4.4	4
$Ru/SrTiO_3$:Rh/PANI/$BiVO_4$	100	5.3/1.9	This work

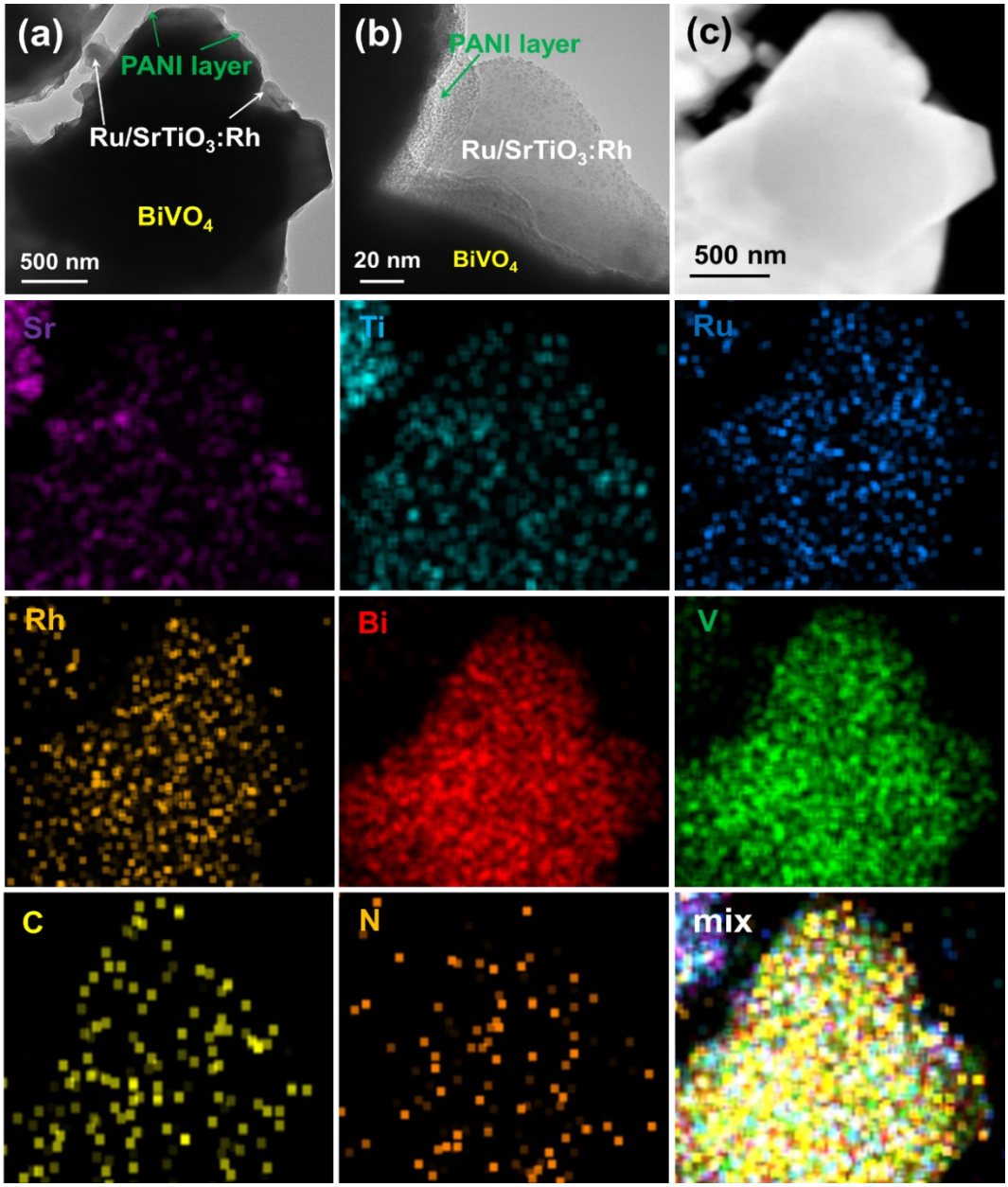

Fig. S9 (a, b) TEM and (c) HAADF-SEM images and the corresponding EDX elemental maps of the $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$ after stability test.

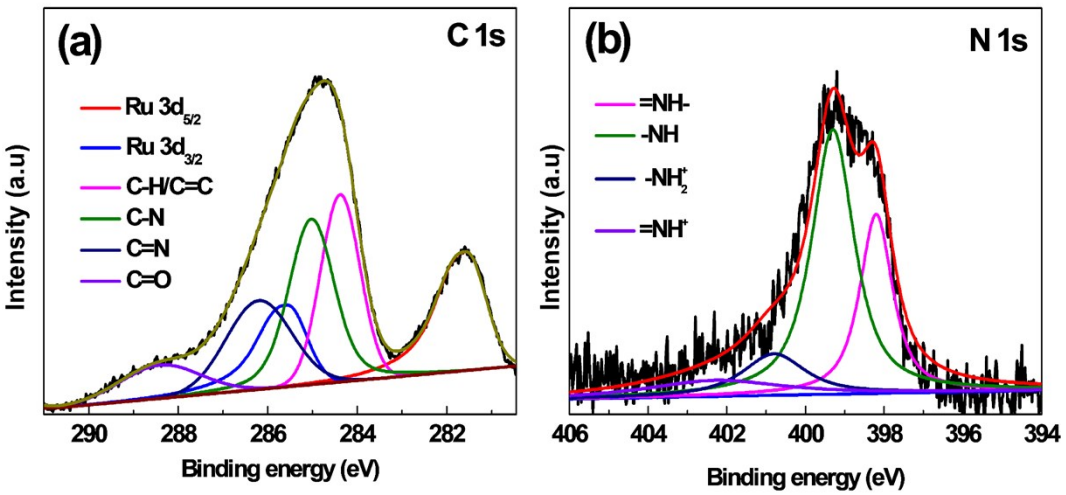

Fig. S10 (a) C 1s and (b) N 1s XPS spectra of the Ru/$SrTiO_3$:Rh/PANI/$BiVO_4$ photocatalyst after stability test.

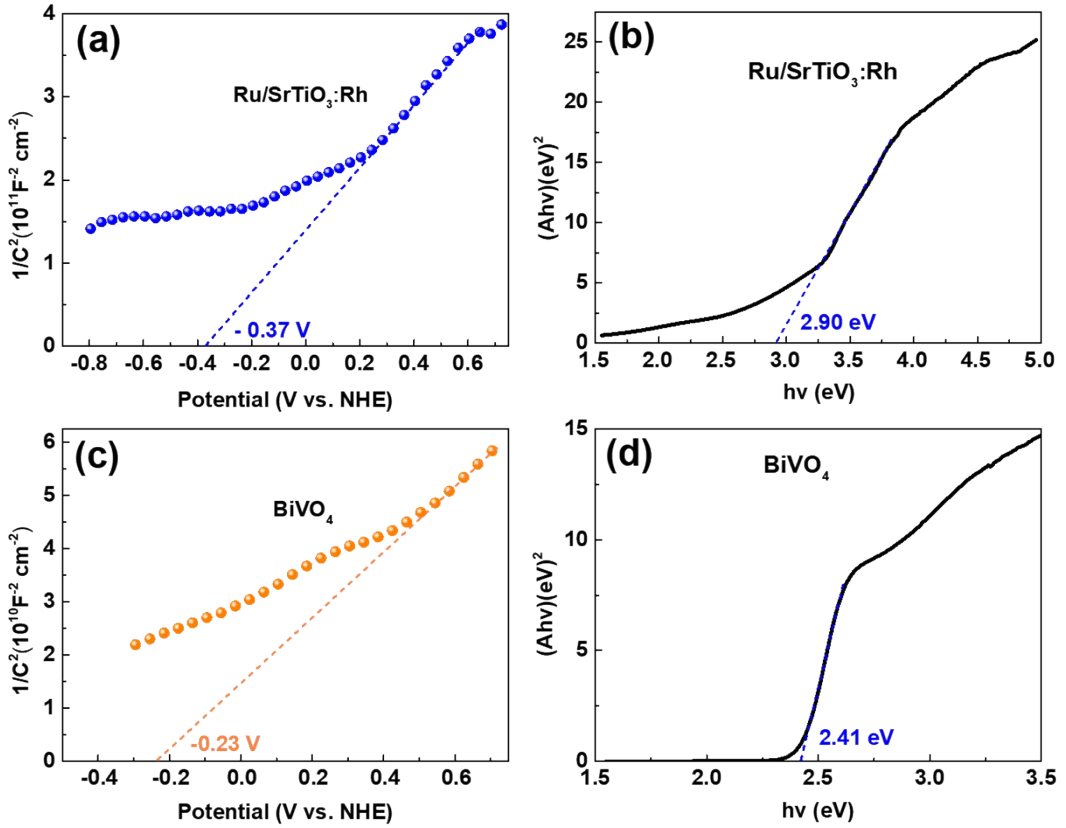

Fig. S11 Mott-Schottky plots of (a) Ru/$SrTiO_3$:Rh and (c) $BiVO_4$. Tauc plots of (b) Ru/$SrTiO_3$:Rh and (d) $BiVO_4$.

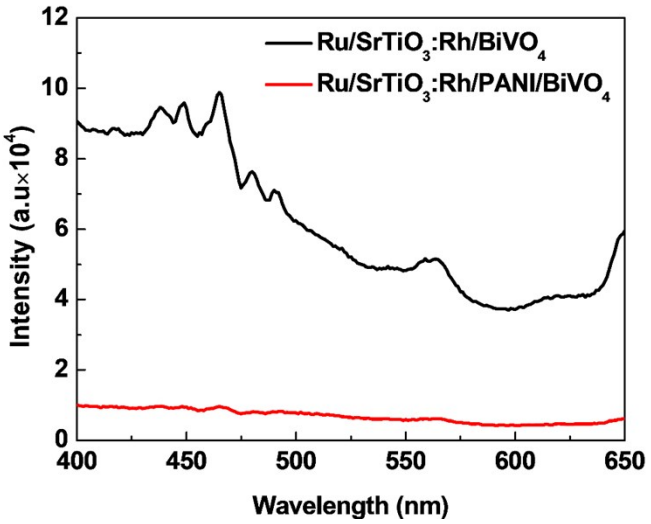

Fig. S12 PL spectra of $Ru/SrTiO_3$:Rh/$BiVO_4$ mixture and $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$. Excitation wavelength: 340 nm.

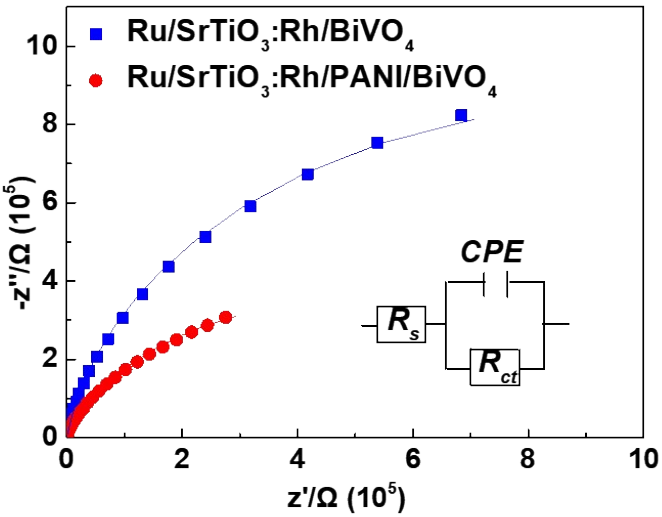

Fig. S13 Electrochemical impedance spectra of $Ru/SrTiO_3$:Rh/$BiVO_4$ mixture and $Ru/SrTiO_3$:Rh/PANI/$BiVO_4$. The inset is the equivalent circuit for simulating EIS curves.

References

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