PAPER



Cite this: DOI: 10.1039/d0cy00266f

Received 11th February 2020, Accepted 22nd April 2020

DOI: 10.1039/d0cy00266f

rsc.li/catalysis

Introduction

Currently, environmental and energy issues are of great concern. One of the most promising strategies for addressing these problems is the solar energy conversion for sustainable and renewable energy sources, as well as the development of effective and green technologies.^{1–6} In an attempt to achieve this aspect, researchers worldwide are making intensive efforts in photocatalysis, which has been viewed as the most promising approach for generating hydrogen (H₂) and/or oxygen (O₂) and reducing carbon dioxide (CO₂). However, very few examples can achieve overall water splitting under visible light irradiation using a single photocatalyst.^{7–9} Therefore, a *Z*-scheme system with a two-stage and double excitation



Tzu-Hsin Chen,^a Masaaki Yoshida,^{bc} Shun Tsunekawa,^b Jia-Hao Wu,^a Kun-Yi Andrew Lin^d and Chechia Hu ^b*^a

In this study, crystalline BiOI powders were prepared for photocatalytic O_2 evolution in the presence of NalO₃ as the electron mediator. BiOI with a microspherical morphology, a layered structure composed of $[Bi_2O_2]^{2+}$ and intercalated I⁻ ions, exhibited a suitable valence band level to generate photoexcited holes for O_2 evolution. Moreover, ruthenium was loaded using the impregnation or photodeposition method to produce RuO₂ as a co-catalyst to improve the photocatalytic activity of BiOI. Photodeposited RuO₂-loaded BiOI showed a high O_2 evolution rate of 2730 µmol h⁻¹ and can be reused eight times in the presence of NalO₃ under simulated solar irradiation. The high photocatalytic O_2 evolution can be attributed to the highly dispersed RuO₂, which could serve as an effective electron sink, on the surface of BiOI and its enhanced visible light-harvesting ability. Besides, the presence of NalO₃ in the system was effective to receive photoexcited electrons from RuO₂-loaded BiOI for improving charge separation and hence the O_2 evolution from RuO₂ sites on the BiOI surface. The RuO₂-loaded BiOI with high photocatalytic activity and stability for generating O_2 could be a potential candidate for achieving overall water splitting in a *Z*-scheme system in the presence of NalO₃ for solar utilization in the future.

process, which mimicked the natural photosynthesis of green plants, has been extensively studied in past decades.^{10–16} This Z-scheme system can be used for overall water splitting by coupling two semiconductors with a band gap suitable for visible light-harvesting to respectively act as an O2-evolved photocatalyst (OEP) and H2-evolved photocatalyst (HEP) in the presence of an electron mediator. Briefly, photoinduced electrons and holes at the HEP and OEP sides would reduce protons and simultaneously oxidize water to produce H₂ and O₂, respectively. Meanwhile, photoexcited holes and electrons at HEP and OEP would oxidize and reduce the electron mediator for electron-hole transfer to achieve charge neutrality (Fig. 1). Over the past 20 years, approximately 500 papers on "Z-scheme" and "water splitting" have been published with more than 23 300 citations (Fig. 1b), indicating that the Z-scheme system is of particular interest in photocatalytic water splitting.

In this aspect, both OEP and HEP should be carefully constructed to strengthen the charge separation to obtain high solar conversion efficiency and maintain its stability. Many OEPs and HEPs have been used in the Z-scheme system, such as Ru/SrTiO₃:Rh–BiVO₄,¹⁷ SrTiO₃:Rh–BiVO₄,¹⁸ Ag₃PO₄-AgI,¹⁹ TiO₂-CdS,²⁰ ZnO-CdS,²¹ Pt/SrTiO₃:Cr,Ta–Pt/WO₃,²² CdS-Au–TiO₂,²³ Ag/AgX/BiOX (X = Cl, Br),²⁴ and α -Fe₂O₃-Cu₂O.²⁵ The development of HEPs and OEPs is urgently required to achieve overall water splitting in a

ROYAL SOCIETY OF **CHEMISTRY**

View Article Online

^a Department of Chemical Engineering, R&D Center for Membrane Technology and Luh Hwa Research Center for Circular Economy, Chung Yuan Christian University, Chungli Dist., Taoyuan City, 32023, Taiwan. E-mail: chechiahu@cycu.edu.tw; Fax: +886 3 2654199; Tel: +886 3 2654152

^b Applied Chemistry, Graduate School of Sciences and Technology for Innovation, Yamaguchi University, Ube, Yamaguchi, 755-8611, Japan

^c Blue Energy Center for SGE Technology (BEST), Yamaguchi University, Ube, Yamaguchi, 755-8611, Japan

^d Department of Environmental Engineering & Innovation and Development Center of Sustainable Agriculture, National Chung Hsing University, Taichung City, 40227, Taiwan

 $[\]dagger$ Electronic supplementary information (ESI) available. See DOI: 10.1039/ d0cy00266f





Fig. 1 (a) Schematic diagram of a Z-scheme system containing H_2 - and O_2 -evolved photocatalysts in the presence of an electron mediator to produce H_2 and O_2 . The number of publications searched by keywords (b) "Z scheme" and "water splitting" and (c) BiOI and Photocat* using the web of science on 12/04/2019.

Z-scheme system. However, materials used for effective photocatalytic O₂ evolution have been rarely considered. Bismuth-based materials, including BiVO₄ and BiOX (X = F, Cl, Br, and I), have a valence band composed of Bi 6 s and O 2p states that could serve as a potential candidate for OEPs.²⁶⁻²⁹ Among these samples, BiOI with a unique layered structure, band gap energy of ca. 1.8-2.0 eV, and intercalated I^{-} ions stacked inside the $[Bi_2O_2]^{2+}$ layers is considered a promising photocatalyst. Vacancy and ionic engineering in BiOI can alternate the light-harvesting ability and enhance the charge separation to improve the photocatalytic activity.30-33 However, to the best of our knowledge, only a few reports studied the photocatalytic H₂ or O₂ evolution using BiOI (see Fig. 1c). Zhang reported that BiOI has negligible photocatalytic activity in the degradation of rhodamine B and O₂ evolution in 2008,³⁴ whereas Wu et al. produced H₂ using BiOI from water splitting with a rate of about 1316.9 μ mol h⁻¹ g⁻¹ at pH 7 under visible light irradiation in 2018.35 Zhao discussed the band edge engineering of BiOI through the introduction of vacancies and defects, showing that pure BiOI has a conduction band (CB) and a valence band (VB) energy of -5.02 eV and -6.91 eV, respectively.33 This implies that BiOI has a relatively narrow band gap of ca. 1.9 eV, enabling an enhanced visible light response and could use more sunlight compared to that of BiOCl and BiOBr. However, the CB position of BiOI cannot satisfy the reduction potential of H^+/H_2 (-4.44 eV). In contrast, the VB edge of BiOI is much lower than the oxidation potential of O2/H2O (-5.67 eV).33 This result indicates that BiOI has a strong potential to produce O₂ and serve as a promising OEP in a Z-scheme system. Furthermore, the addition of electron mediators, including solution type (Fe³⁺/Fe²⁺ and IO₃⁻/I⁻) or solid-state type (reduced graphene oxide),¹⁷ as a redox couple could significantly assist the electron-hole transfer, thereby enhancing the photocatalytic activity in a Z-scheme system by suppressing the backward reaction. Moreover, metal-loading as a co-catalyst, such as Pt, Pd, Rh, and Ru, could be the most effective method for further improving the photocatalytic performance of a catalyst by acting as an electron sink. In previous works, ruthenium (Ru) in the form

of metallic Ru or metal oxide (RuO₂) exhibits remarkable photocatalytic activity because it can effectively facilitate charge separation to attract photoexcited holes from the photocatalyst to Ru/RuO2 sites.36,37 Many methods, including photodeposition, impregnation, sputtering, direct mixing, electrodeposition, or reduction, are widely employed to load nanoparticles onto the surface of the photocatalyst. Among these methods, the photodeposition method is an alternative one because the in situ formation of the well-defined particles on the surface of the photocatalyst as well as the H₂ generation could be achieved at the same time during the photocatalytic reaction.38 However, no studies have been reported to explore the loading method of Ru on BiOI and their correlation to the photocatalytic O₂ evolution reaction in the presence of the electron mediator, and this is worth investigating.

In the present study, BiOI is subjected to a photocatalytic O2 evolution reaction in the presence of sacrificial reagents (AgNO₃) or electron mediators (NaIO₃ or FeCl₃) to examine the O₂ production efficiency. In addition, a conventional cocatalyst, Ru, was used in an attempt to enhance the photocatalytic activity of BiOI. The preparations of RuO2loaded BiOI in two different manners, including impregnation and photodeposition, have a strong influence on the photocatalytic O2 evolution activity. The RuO2-loaded BiOI sample obtained from the photodeposition method exhibits the highest O₂ production amounts (13650 µmol) in 5 h and can be reused for at least eight cycles under xenon lamp irradiation. The determination of structural and optical changes and the effect of electron mediators in a BiOI system is of vital importance in the photocatalytic water splitting field, particularly in a Z-scheme system.

Materials and methods

An *in situ* growth method was conducted to synthesize BiOI in this study. Bi(NO₃)₃·5H₂O was added to 200 mL of absolute ethyl alcohol, followed by the addition of a certain amount of 0.1 mol L⁻¹ KI solution gradually. The pH value was adjusted to 8 using an ammonia solution (NH₄OH) to ensure its stability. The solution was subsequently stirred at 80 °C using

a magnetic agitator for 4 h, and, thereafter, filtered and washed with deionized water three times. The samples were collected and dried at 60 °C overnight. All chemicals were purchased from Alfa Aesar and used without any purification.

To improve the photocatalytic activity, Ru was loaded onto the BiOI surface as a co-catalyst using the impregnation or photodeposition method. Typically, certain amounts of RuCl₃ were added dropwise into aqueous BiOI suspension (1000/50 mg mL⁻¹) with continuous stirring at 80 °C. Until the evaporation of excess water, the yielding sample was subjected to a furnace for heat treatment at 300 °C for 1 h (ramp rate 2 °C min⁻¹), and denoted as *x*Ru_{im}/BiOI, where im and *x* indicate the impregnation method and weight ratio of Ru to BiOI, respectively. For the photodeposition of Ru on BiOI, RuCl₃ was added to aqueous BiOI suspension (1000/50 mg mL⁻¹) with continuous stirring and subjected to light irradiation using a metal halide lamp for 2 h. Thereafter, the sample was collected, dried at 60 °C overnight, and denoted as *x*Ru_{pd}/BiOI, where pd refers to photodeposition.

In this study, we used X-ray diffraction (XRD) to determine the crystalline structure of the specimens with a diffractometer (Bruker D8 advance, USA) at 2θ of 10-80° and a scan rate of 6° min⁻¹. The morphologies and appearances of the samples were observed by scanning electron microscopy (SEM; Hitachi S-4800N, Japan) and highresolution transmission electron microscopy (HR-TEM; Hitachi H-7100, Japan, JEOL JEM-2100, Japan). Elemental compositions of the specimens were examined by energydispersive X-ray spectroscopy (EDS) equipped with SEM. A thermogravimetric analyzer (TGA, TA-Q50, DuPont, USA) was used to determine the thermal behavior of the samples. The N2 surface area was determined with the Brunauer-Emmett-Teller (BET) method at -196 °C using an adsorption apparatus (Micromeritics ASAP 2010, USA). Fourier transform infrared spectroscopy (FTIR; Tensor 27, Bruker, USA) was used to investigate the functional groups of the samples. The light absorption properties of the samples were identified using an ultraviolet-visible (UV-vis; Hitachi U-3900, Japan) spectrometer equipped with an integrating sphere. The oxidation states and chemical binding energy of the samples were measured using X-ray photoelectron spectroscopy (XPS; VG Scientific ESCALAB 250, Electron Spectroscopy for Chemical Analysis, UK) with Al K α radiation, which was calibrated using the C 1s peak as the reference energy at 284.8 eV. The VB of the samples were determined by ultraviolet photoemission spectroscopy (UPS; Thermo VG-Scientific/Sigma Probe, UK) using He I (0-21.2 eV) as UV source. The Ru L_{III}-edge X-ray absorption fine structure (XAFS) measurements were carried out at BL-9A in KEK-PF (Ibaraki, Japan) using radiation that has been with monochromatized а Si (111)double-crystal monochromator. The sample and reference powders were placed on a sample holder using carbon tape in a small chamber under He atmosphere. The intensity of the incident X-ray beam was monitored by an ion chamber filled with He gas positioned in front of the sample to obtain I_0 . The XAFS

spectra were acquired in fluorescence mode by detecting fluorescence X-ray from the samples in an Ar atmosphere using a Lytle detector. The photon energies were calibrated with the first inflection point of Ru metal (2838 eV) powder according to previous work.³⁹

Photocatalytic O₂ evolution reactions were performed using 0.25 g of the pristine BiOI, xRu_{pd} -BiOI, or xRu_{im} -BiOI catalysts suspended in 250 mL of an aqueous solution containing an electron mediator, such as AgNO₃ (1×10^{-2} , $5 \times$ 10^{-3} , 1×10^{-3} , 5×10^{-4} M), NaIO₃ (1×10^{-2} , 5×10^{-3} , 1×10^{-3} , 5×10^{-4} M), or FeCl₃ (1×10^{-2} M), in a Pyrex glass reactor cell with a magnetic stirrer. A 250 W metal halide lamp and a 300 W xenon lamp without any filter were used as the light source (Fig. S1†). The gas evolutions were determined by gas chromatography (Shimadzu GC-2014, Japan).

Results and discussion

The crystalline structure of BiOI was examined by XRD (Fig. 2a), revealing its pure tetragonal system with a space group of *P*4/*nmm*, and its lattice constant along the *a*- and *c*-axes are 3.98 and 9.13 Å (JCPDS #73-2062), respectively, without any impurity. The sample was investigated by SEM and TEM, and the images are shown in Fig. 2b–d. It can be seen that the BiOI sample is composed of a sheet-like structure forming a flower-shaped microsphere approximately 5–6 μ m in size (Fig. 2b and its inset). From the EDS spectra shown in the inset of Fig. 2b, only the Bi, O, and I elements could be found. This confirms its pure BiOI configuration. In Fig. 2c, BiOI has a thin and transparent layered structure,



Fig. 2 (a) XRD, (b) SEM, (c) TEM, and (d) HRTEM images of BiOI. Insets of (b) show the SEM image with a scale bar of 5 μ m and its EDS spectrum. Insets of (d) show the SAED patterns and schematic crystalline structure of BiOI.

Paper

which staked into a nanosheet-like configuration that can easily be observed. In addition, the lattice fringes of the interplane were estimated to be 0.28 nm, which corresponded to the d-spacing of (110) in BiOI (Fig. 2d). The selected area electron diffraction (SAED) patterns indicate the presence of the (110), (114), and (122) planes, supporting the diffraction peaks in XRD. According to the crystalline geometry, BiOI consisted of $[Bi_2O_2]^{2+}$ layers containing I atoms along the c axis, where I atoms were situated within the unit cell without forming a covalent bond. Instead, they formed an asymmetric decahedral geometry with electrostatic forces.40 As a result, the strong intralayer bonding and interlayer forces in the I atom-intercalated [Bi2O2]2+ layers could construct a platelet configuration. Fig. S2[†] shows the N₂ adsorption-desorption isotherm, pore width, and TGA plot of BiOI. It can be noted that BiOI is a mesoporous material with a typical type IV isotherm and a H3 hysteresis loop at a relative pressure of 0.8-0.98,⁴¹ and its BET specific surface area is 5.8 m² g⁻¹ (Fig. S2a[†]). It can be seen in Fig. S2b[†] that BiOI begins to decompose in the airflow at an elevated temperature of 280 °C. From 280 to 450 °C, the total weight decreases by approximately 25%. By increasing the temperature from 450 to 650 °C, the weight loss could be ascribed to the phase transformation for producing a metastable Bi₅O₇I. Finally, it is in good agreement with the previous report that the sample transforms from Bi₅O₇I to Bi₂O₃ with ca. 2-3% of weight loss beyond 700 °C.42 We also determined the chemical functional groups of BiOI using the FTIR technique (Fig. S2c⁺), displaying several peaks located at approximately 1000-2000 cm⁻¹ and broadband at 3000–3600 cm⁻¹. These peaks at 1070, 1300, and 1600 cm⁻¹ are identical to those characteristic peaks of BiOI in the previous report,43 and the band at 3000-3600 cm⁻¹ can be associated with the hydroxyl groups of the surface-adsorbed H₂O on the BiOI surface.

The chemical states of BiOI were determined by XPS (Fig. 3), showing a typical survey spectrum composed of Bi 4d, Bi 4p, Bi 4f, I 3d, and O 1s states for BiOI (Fig. 3a). The XPS spectra of the Bi 4f, I 3d, and O 1s core states are shown

in Fig. 3b–d. The peaks at the binding energies of *ca.* 159 eV and 164 eV could be attributed to Bi $4f_{7/2}$ and Bi $4f_{5/2}$ (Fig. 3b), respectively, which are the characteristics of Bi³⁺ in BiOI.⁴⁴ In addition, two peaks at approximately 620 eV and 631.5 eV, which can be assigned to the I $3d_{5/2}$ and I $3d_{3/2}$ states, were observed. These peaks can be ascribed to the –1 valence state of I in the BiOI sample.⁴⁵ Moreover, the spectrum for the O 1s core level of BiOI can be deconvoluted into two peaks located at 530.7 eV and 532.8 eV, corresponding to Bi–O bonding in the [Bi₂O₂]²⁺ layer of BiOI and the OH group. This OH group mainly results from surface-adsorbed H₂O molecules.⁴⁶ Therefore, it is confirmed to be the pure BiOI phase and its I-intercalated [Bi₂O₂]²⁺ layered nature.

Fig. 4 shows the time courses of O_2 evolution from a water solution containing different electron mediators and pH adjusters, such as NaIO₃, FeCl₃, AgNO₃, and HNO₃, using BiOI as the photocatalyst under metal halide lamp irradiation. In principle, O2 evolved steadily at a rate of 1540 μ mol h⁻¹ for the BiOI sample in the presence of 1 × 10⁻² M NaIO₃ as an electron mediator. Different concentrations of NaIO₃ were applied to investigate the O₂ evolution using BiOI (Fig. S3a^{\dagger}), revealing that the O₂ evolution is in proportion to the NaIO3 concentration. However, no O2 gases could be detected without the addition of a catalyst even in the presence of NaIO3 as an electron mediator. For the other electron mediator and pH adjuster, the O₂ evolution amounts reached a steady value of less than 1800 µmol and 3000 µmol, respectively. Fig. S3b and c† showed the concentration and pH-dependent time courses of O₂ evolution for AgNO₃ and HNO₃, respectively, showing that AgNO₃ and FeCl₃ are not good candidates for promoting O2 evolution for BiOI. In the cases of AgNO₃, FeCl₃, and HNO₃, the low O₂ evolutions indicated the deactivation of the sample. Fig. S4[†] shows the XRD and XPS plots of BiOI after the photocatalytic reaction using FeCl₃ and AgNO₃, revealing that the crystalline structure of BiOI was destroyed. We can observe the presence of AgI- and Fe-based iodide compounds after the reaction. This agrees with the deactivation of the sample in the photocatalytic reaction with prolonged time. Most



Fig. 3 XPS spectra for (a) survey scan, (b) Bi 4f, (c) I 3d, and (d) O 1s level of BiOI.



Fig. 4 Photocatalytic O_2 evolution using BiOI in the presence of different electron mediators (1 \times 10⁻² M) and pH adjuster under metal halide lamp irradiation.

importantly, the high activity of BiOI in the presence of the NaIO₃ solution could be attributed to the IO_3^-/I^- redox potential of 0.67 V (*vs.* $E_{\rm NHE}$), which is suitable for receiving photoexcited electrons from BiOI for reduction (see eqn (1)), thus, enhancing the charge separation to trigger the photoinduced hole at the BiOI side for oxidizing H₂O to produce O₂ (see eqn (3)). The proposed reaction mechanism is shown as follows:

 $BiOI + light \rightarrow e_{CB}^{-} + h_{VB}^{+}$

$$IO_3^- + 3H_2O + 6e_{CB}^- \rightarrow I^- + 6OH^-$$
 (1)

$$I^{-} + 6OH^{-} + 6h^{+} \rightarrow IO_{3}^{-} + 3H_{2}O$$
 (2)

$$H_2O + h_{VB}^{+} \rightarrow O_2 + 4H^+$$
 (3)

$$2H^{+} + 2e_{CB}^{-} \rightarrow H_2 \tag{4}$$

It is important to determine the photocatalytic cycle test for a sustainable photocatalyst. The long-term photocatalytic stability to produce O₂ using BiOI in the presence of NaIO₃ as an electron mediator using xenon lamp to simulate solar irradiation is shown in Fig. 5. Evidently, BiOI has high photocatalytic stability to produce around 7500-9000 µmol in 5 h for each cycle, and the production rate is almost unchanged, indicating that BiOI could be a potential photocatalyst. Moreover, the XRD, SEM, and XPS measurements of BiOI after the photocatalytic reaction are shown in Fig. 6, indicating that the crystalline structure, appearance and morphology, and the binding energy for the Bi 4f level of BiOI all remain unchanged. The chemical composition obtained from the elemental analysis (Fig. 6d) also suggested that the stoichiometric ratio of BiOI after the reaction is consistent with that before the reaction.

To further improve the photocatalytic activity of BiOI, Ru was loaded onto the BiOI surface to increase the active sites for water splitting. Two methods, impregnation and photodeposition, were employed for loading Ru on BiOI. Fig. 7a shows the XRD patterns of $1Ru_{im}/BiOI$ and $1Ru_{pd}/$



20

Time (h)

30

10

8000

6000

4000

2000

0

O, amount (µmol)



Fig. 6 (a) XRD patterns, (b) SEM image, (c) Bi 4f level for XPS spectrum, and (d) chemical composition obtained from XPS for BiOI after the photocatalytic O_2 production reaction. The inset of (b) shows the EDS spectrum of BiOI.

BiOI, revealing that the samples exhibit pure BiOI tetragonal phase without any impurity, which is mainly because the Ru content is relatively low. In addition, the main diffraction peaks of 1Ruim/BiOI and 1Rupd/BiOI at approximately 29.7° did not shift toward higher or lower degrees (Fig. S5⁺), indicating the lattice of BiOI did not expand or shrink after Ru loading. The XPS survey spectra of these samples also suggest that there are Bi 4d₃, 4d₅, and 4f and I 3d, 3p₃, and 3p1 levels for the BiOI sample without any impurity. Interestingly, the Bi 4f, I 3d, and O 1s states in Fig. 7c-e shifted toward relatively high binding energies compared to those peaks in Fig. 3. This can be attributed to the higher electronegativity of Ru (2.2) compared to that of Bi (2.02), which may lead to electrons near the Bi, I, and O states moving toward Ru sites, thereby increasing the binding energy of the Bi 4f and I 3d levels. And the electron movement and the increasing binding energy of the Bi 4f level in 1Ru_{pd}/BiOI suggest the photoexcited electrons could probably flow toward Ru sites more easily, thereby improving its photocatalytic activity. The Bi $4f_{7/2}$, $4f_{5/2}$, $13d_{5/2}$, and $3d_{3/2}$ levels and the Bi-O bond can still be observed in Fig. 7c-e, suggesting the well-preserved structure of BiOI after Ru modification. A small peak at around 625.6 eV was observed to $1Ru_{im}/BiOI$ in Fig. 7d. The peak could be attributed to the oxidized specie, *i.e.*, I₂O₅,⁴⁷ on the sample surface after heat treatment of 300 °C of the impregnation method. The Ru 3d_{5/2} and 3d_{3/2} states can be seen in Fig. 7f, and these states indicate the coexistence of the metal Ru phase and the RuO₂ phase on BiOI. The C-C bond at approximately 284.7 eV is set to fill the region envelope. Most importantly, the presence of Ru and RuO2 on BiOI could serve as accommodating sinks for photoexcited holes to further improve the charge separation and photocatalytic O₂ evolution.^{36,37}



Fig. 7 (a) XRD and XPS spectra for (b) survey scan, (c) Bi 4f, (d) I 3d, (e) O 1s, and (f) Ru 3d levels of the 1Ru_{im}/BiOI and 1Ru_{pd}/BiOI samples.

The 1Ruim/BiOI and 1Rupd/BiOI samples were investigated by HRTEM images (Fig. 8a and b). The lattice fringes of 1Ruim/BiOI and 1Rund/BiOI samples are visible, showing the good crystallinity. The d-spacing of 1Rupd/BiOI and 1Ruim/ BiOI samples were estimated to be around 0.88 nm and 0.3 nm, which referred to the (001) and (012) of BiOI, respectively. It can be seen that numerous small circular particles, which are attributed to Ru, were homogeneously distributed on the surface of the BiOI sample with a size of approximately 1-3 nm. This suggested that these Ru particles at the BiOI surface could act as a cocatalyst to receive photoexcited charges for the photocatalytic reaction. In the inset of Fig. 8a and b, these samples consist of thin and transparent sheet-like structure, which is similar to the HRTEM result in Fig. 2c. Moreover, as shown in Fig. 8c, we employed Ru Lui-edge XAFS to determine the oxidative states



Fig. 8 (a and b) HRTEM images and (c) XAFS spectrum of $1Ru_{pd}/BiOI$ and $1Ru_{im}/BiOI$ samples. Inset of (a) and (b) shows the TEM images of the corresponding samples. Metallic Ru and RuO₂ were used as references in the XAFS spectrum.

of Ru on the BiOI surface. The white-line peaks for the $1Ru_{im}/BiOI$ and $1Ru_{pd}/BiOI$ samples were observed around 2842 eV, as well as that of RuO_2 . The result indicates that the oxidation state of Ru cocatalyst is mainly composed of RuO_2 (Ru^{4+}), which is generally considered to be an active oxidative cocatalyst.⁴⁸

Different weight contents of Ru were employed to be individually impregnated or photodeposited onto the surface of BiOI, followed by the photocatalytic O2 production. Fig. 9 shows the time courses of O₂ evolution from a water solution containing NaIO3 as an electron mediator using Ruim/- or Ru_{pd}/BiOI as a photocatalyst under metal halide lamp irradiation. Interestingly, all BiOI samples after Ruimpregnation showed significantly decreased activities. This is mainly because the appearance of BiOI had been destroyed from the flower-like structure to an irregular sheet-like stacking configuration (Fig. S6a†), resulting from heat treatment, which is certainly required in impregnation to influence the morphology of BiOI and hence its photocatalytic activity. This is consistent with the above TGA that BiOI is metastable between heating temperatures of 250-450 °C (Fig. S2b⁺). Conversely, the photodeposited Ru on the BiOI surface could extensively improve the photocatalytic O₂ production. Particularly, 1Rupd/BiOI and 0.5Rupd/BiOI had O2 production rates of approximately 2730 µmol h⁻¹ and 2360 μ mol h⁻¹, respectively, which are much higher than that of pristine BiOI (1540 µmol h⁻¹) under metal halide lamp irradiation. The high activity to produce O2 for Rupd/BiOI samples could be attributed to that the RuO₂ cocatalyst can effectively receive photoexcited holes from BiOI to enhance the charge separation owing to its partially filled π^* band at metal-oxygen (d-p) level, which is similar to that in the reported studies.37,49 In addition, we also evaluated the photocatalytic stability of 1Rupd/BiOI in the presence of



Fig. 9 Photocatalytic O_2 production using different weight contents of Ru on BiOI through the (a) impregnation and (b) photodeposition method in the presence of NaIO₃ as an electron mediator under metal halide lamp irradiation.

NaIO₃ under xenon lamp irradiation (Fig. 10), revealing that O2 evolved steadily with time and that the sample can be reused for at least eight cycles. The O₂ evolution amount of Ru_{pd}/BiOI in this study is higher than the reported values Pt-doped α -Fe₂O₃⁵⁰ doped TiO₂⁵¹ using decorated g-C₃N₄,^{52,53} and conjugated polymers.⁵⁴ Fig. S6b⁺ shows the XRD patterns of 1Rupd/BiOI before and after the photocatalytic O₂ production, revealing the structural stability and that no impurities can be found. In addition, Fig. S7⁺ displays the SEM images and the corresponding EDS mapping of Bi, O, I, and Ru elements for 1Rupd/BiOI before and after the reaction. Evidently, the appearance and morphology of 1Rupd/BiOI remained unchanged as a sheetstacked flower-like configuration (Fig. S7a and f⁺). In the elemental mapping, Bi, O, I, and Ru elements were homogeneously distributed before and after the reaction. But in the high-resolution XPS spectra for the used sample (Fig. S8[†]), the peak of Bi 3d level moved toward lower binding energy compared to that in Fig. 7, indicating its reduced state.⁵⁵ Besides, the O 1s level shifted to high binding energy (Fig. S8b⁺), showing the formation of O-I bond (electronegativity of I is larger than that of Bi). Moreover, the I 3d level in Fig. S8c† also shifted to larger binding energy than that in the fresh sample, which means the presence of anionic vacancies.^{56,57} On the other hand, the additional two



Fig. 10 Cycle test of photocatalytic O₂ evolution using $1Ru_{pd}/BiOI$ in the presence of NalO₃ as an electron mediator with intermediate evacuation using xenon lamp to simulate solar irradiation.

peaks at around 625 and 637 eV were assigned to iodate or iodide,⁵⁸ indicating the surface adsorbed redox-couples. These results suggest that Bi could be reduced by photoexcited electrons, and the I atom of BiOI could leach during the photocatalytic reaction to react with the surface adsorbed O^{2-} to form a weak O–I bond to proceed with an interfacial reduction, which may contribute to improving the *Z*-scheme water splitting for O₂ generation in our case. At the same time, generated I⁻ could compensate for the vacancies of BiOI, which means this could only occur in the BiOI case in the presence of NaIO₃ as a mediator. But the interfacial reduction–oxidation still needs further determination. Nevertheless, the I-contained RuO₂/BiOI still could be an effective photocatalyst for O₂ production, especially in the presence of NaIO₃ as an electron mediator.

This study presents the UV-vis spectroscopic measurement for the RuO₂-loaded BiOI samples in Fig. 11a, showing that the absorption edges of these samples were similar, with values of approximately 660 nm. The calculated band gap values of BiOI and 1Rupd/BiOI were obtained to be 2.02 eV and 1.92 eV, respectively, from the Tauc plot in the inset of (a). Interestingly, Ru modification did not change the absorption shoulder and its band gap energy. Instead, Ru modification on BiOI only resulted in a significant increase in absorption in the range of 680-800 nm, and the intensity became relatively strong when the Ru content increased. This interesting feature can be ascribed to the surface plasmonic effect associated with the excitation of collective electron oscillation on the metallic Ru/RuO2 surface.49 Moreover, this surface plasmonic effect could not only attract the photoexcited hole but also produce an extra trap state to improve the visible light-harvesting ability of the Ru_{nd}/BiOI sample. The UPS was employed to elucidate the band edge of BiOI (Fig. 11b), revealing that the linear extrapolation of the tangent line was located at approximately 6.2 eV (inset of Fig. 11b). This value is consistent with the reported values of 5.9–6.1 eV.⁵⁹ In combination with the band gap energy obtained from the UV-vis spectra, an energy band structure of BiOI along with the redox potentials of H^+/H_2 , IO_3^-/I^- , and O₂/H₂O was proposed in Fig. 11c. It can be noted that the CB



Fig. 11 (a) UV-vis, (b) UPS spectra, and (c) proposed energy band position of RuO₂-loaded BiOI.

of BiOI is very close to the redox potential of H_2 production but much higher than that of IO_3^-/I^- , indicating that the photoexcited electrons have sufficient over-potential to react with IO_3^- to produce I^- . Conversely, with Ru modification, the photoexcited holes could move toward the RuO₂ site to oxidize H_2O to produce O_2 because the reactive potential position of BiOI is much lower than the oxidative potential of O_2/H_2O . As a result, RuO₂-loaded BiOI can be an effective photocatalyst for photocatalytic O_2 evolution but is not suitable for producing H_2 .

Conclusions

In the present study, RuO₂-loaded BiOI was first used as an effective photocatalyst for O₂ evolution in the presence of NaIO₃ as the electron mediator under simulated solar irradiation. The XAFS and HR-TEM results revealed that RuO₂ was homogeneously distributed on the BiOI surface as a co-catalyst; the UPS and UV-vis spectra showed that RuO₂-loaded BiOI exhibited an appropriate valence band potential for generating O₂. Highly dispersed RuO₂ on the BiOI surface could serve as an electron sink for enhancing light-harvesting ability while improving the photocatalytic activity for O₂ evolution at a rate of approximately 2730 μ mol h⁻¹ for eight cycle tests. In summary, this study prepared an effective RuO₂-loaded BiOI as an OEP to promote light-harvesting and charge separation to boost the photocatalytic O₂ evolution under simulated solar irradiation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the Ministry of Science and Technology, Taiwan (MOST 107-2221-E-033-032-MY3, 108-2221-E-033-034-MY3). The Ru L_{III} -edge XAFS measurements were carried out at BL-9A in KEK-PF (2018G589), and Prof. Masaaki Yoshida was financially supported by Kiban C (17K05843) and the Electric Technology Research Foundation of Chugoku.

References

- 1 C. W. Chang and C. Hu, *Chem. Eng. J.*, 2019, **383**, 12116, DOI: 10.1016/j.cej.2019.123116.
- 2 C. Hu, Y. R. Lin and H. C. Yang, *ChemSusChem*, 2019, 12, 1794–1806, DOI: 10.1002/cssc.201802257.
- 3 Z. Ni, Y. Sun, Y. Zhang and F. Dong, *Appl. Surf. Sci.*, 2016, **365**, 314–335, DOI: 10.1016/j.apsusc.2015.12.231.
- 4 M. Arumugam and M. Y. Choi, *J. Ind. Eng. Chem.*, 2020, **81**, 237–268, DOI: 10.1016/j.jiec.2019.09.013.
- 5 C. Karthikeyan, P. Arunachalam, K. Ramachandran, A. M. Al-Mayouf and S. Karuppuchamy, J. Alloys Compd., 2020, 828, 154281, DOI: 10.1016/j.jallcom.2020.154281.
- 6 A. Malathi, J. Madhavan, M. Ashokkumar and P. Arunachalam, *Appl. Catal.*, A, 2018, 555, 47–74, DOI: 10.1016/j.apcata.2018.02.010.
- 7 G. Zhang, Z. A. Lan, L. Lin, S. Lin and X. Wang, *Chem. Sci.*, 2016, 7, 3062–3066, DOI: 10.1039/C5SC04572J.
- 8 S. Chen, T. Takata and K. Domen, *Nat. Rev. Mater.*, 2017, 2, 17050, DOI: 10.1038/natrevmats.2017.50.
- 9 H. F. Liang, A. N. Gandi, D. H. Anjum, X. B. Wang, U. Schwingenschlögl and H. N. Alshareef, *Nano Lett.*, 2016, 16, 7718–7725, DOI: 10.1021/acs.nanolett.6b03803.
- 10 K. Maeda, ACS Catal., 2013, 3, 1486–1503, DOI: 10.1021/ cs4002089.
- 11 Y. O. Wang, H. Suzuki, J. J. Xie, O. Tomita, D. J. Martin, M. Higashi, D. Kong, R. Abe and J. W. Tang, *Chem. Rev.*, 2018, **118**, 5201–5241, DOI: 10.1021/acs.chemrev.7b00286.
- 12 Q. L. Xu, L. Y. Zhang, J. G. Yu, S. Wageh, A. A. Al-Ghamdi and M. Jaroniec, *Mater. Today*, 2018, 21, 1042–1063, DOI: 10.1016/j.mattod.2018.04.008.
- 13 M. S. Zhu, Z. C. Sun, M. Fujitsuka and T. Majima, Angew. Chem., Int. Ed., 2018, 57, 2160–2164, DOI: 10.1002/ anie.201711357.
- R. B. Chandran, S. Breen, Y. X. Shao, S. Ardo and A. Z. Weber, *Energy Environ. Sci.*, 2018, 11, 115–135, DOI: 10.1039/C7EE01360D.
- 15 H. J. Li, W. G. Tu, Y. Zhou and Z. G. Zou, *Adv. Sci.*, 2016, 3, 1500389, DOI: 10.1002/advs.201500389.
- 16 Y. R. Lin, G. V. C. Dizon, K. Yamada, C. Y. Liu, A. Venault, H. Y. Lin, M. Yoshida and C. Hu, J. Colloid Interface Sci., 2020, 567, 202–212, DOI: 10.1016/j.jcis.2020.02.017.

- 17 A. Iwase, Y. H. Ng, Y. Ishiguro, A. Kudo and R. Amal, *J. Am. Chem. Soc.*, 2011, **133**, 11054–11057, DOI: 10.1021/ja203296z.
- 18 H. Kato, M. Hori, R. Konta, Y. Shimodaira and A. Kudo, *Chem. Lett.*, 2004, 33, 1348, DOI: 10.1246/cl.2004.1348.
- 19 Z. H. Chen, W. L. Wang, Z. G. Zhang and X. M. Fang, J. Phys. Chem. C, 2013, 117, 19346–19352, DOI: 10.1021/jp406508y.
- 20 J. X. Low, B. Z. Dai, T. Tong, C. J. Jiang and J. G. Yu, Adv. Mater., 2019, 31, 1802981, DOI: 10.1002/adma.201802981.
- 21 S. Wang, B. C. Zhu, M. J. Liu, L. Y. Zhang, J. G. Yu and M. H. Zhou, *Appl. Catal.*, *B*, 2019, 243, 19–26, DOI: 10.1016/j. apcatb.2018.10.019.
- 22 K. Sayama, K. Mukasa, R. Abe, Y. Abe and H. Arakawa, J. Photochem. Photobiol., A, 2002, 148, 71–77, DOI: 10.1016/ S1010-6030(02)00070-9.
- 23 H. M. Zhu, B. F. Yang, J. Xu, Z. P. Fu, M. W. Wen, T. Guo,
 S. Q. Fu, J. Zuo and S. Y. Zhang, *Appl. Catal.*, *B*, 2009, 90, 463–469, DOI: 10.1016/j.apcatb.2009.04.006.
- 24 Y. Yu, C. Y. Cao, H. Liu, P. Li, F. F. Wei, Y. Jiang and W. G. Song, ACS Catal., 2012, 28, 1677–1683, DOI: 10.1039/ C3TA14494A.
- 25 J. C. Wang, L. Zhang, W. X. Fang, J. Ren, Y. Y. Li, H. C. Yao, J. S. Wang and Z. J. Li, ACS Appl. Mater. Interfaces, 2015, 71, 8631–8639, DOI: 10.1021/acsami.5b00822.
- 26 A. Malathi, P. Arunachalam, A. N. Grace, J. Madhavan and A. M. Al-Mayouf, *Appl. Surf. Sci.*, 2017, **412**, 85–95, DOI: 10.1016/j.apsusc.2017.03.199.
- 27 A. Malathi, P. Arunachalam, J. Madhavan, A. M. Al-Mayouf and M. A. Ghanemb, *Colloids Surf.*, A, 2018, 537, 435–445, DOI: 10.1016/j.colsurfa.2017.10.036.
- 28 Y. Bu, J. Xu, Y. Li, Q. Liu and X. Zhang, *RSC Adv.*, 2017, 7, 42398–42406, DOI: 10.1039/C7RA06462D.
- 29 A. Malathi, P. Arunachalam, V. S. Kirankumar, J. Madhavan and A. M. Al-Mayouf, *Opt. Mater.*, 2018, 84, 227–235, DOI: 10.1016/j.optmat.2018.06.067.
- 30 Y. C. Huang, H. B. Li, M. S. Balogun, W. Y. Liu, Y. X. Tong,
 X. H. Lu and H. B. Ji, ACS Appl. Mater. Interfaces, 2014, 6,
 22920–22927, DOI: 10.1021/am507641k.
- 31 Y. C. Huang, H. B. Li, W. J. Fan, F. Y. Zhao, W. T. Qiu, H. B. Ji and Y. X. Tong, ACS Appl. Mater. Interfaces, 2016, 8, 27859–27867, DOI: 10.1021/acsami.6b10653.
- 32 Y. C. Huang, H. X. Hu, S. X. Wang, M. S. Balogun, H. B. Ji and Y. X. Tong, *Appl. Catal.*, *B*, 2017, 218, 700–708, DOI: 10.1016/j.apcatb.2017.07.028.
- W. W. Dai and Z. Y. Zhao, J. Am. Ceram. Soc., 2016, 99, 3015–3024, DOI: 10.1111/jace.14311.
- J. An, Y. Du, T. Wang, C. Wang, W. Hao and J. Zhang, *Rare Met.*, 2008, 27, 243–250, DOI: 10.1016/S1001-0521(08)60123-0.
- 35 G. J. Lee, Y. C. Zheng and J. J. Wu, *Catal. Today*, 2018, 307, 197–204, DOI: 10.1016/j.cattod.2017.04.044.
- 36 S. Y. Mi, Y. X. Liu and W. D. Wang, Chin. J. Chem. Phys., 2016, 29, 585–590, DOI: 10.1063/1674-0068/29/cjcp1603057.
- 37 Q. Gu, Z. Gao, S. Yu and C. Xue, Adv. Mater. Interfaces, 2016, 3, 1500631, DOI: 10.1002/admi.201500631.
- 38 K. Wenderich and G. Mul, *Chem. Rev.*, 2016, **116**, 14587–14619, DOI: 10.1021/acs.chemrev.6b00327.

- 39 I. C. Stefan, Y. B. Mo, M. R. Antonio and D. A. Scherson, J. Phys. Chem. B, 2002, 106, 12373–12375, DOI: 10.1021/ jp026300f.
- 40 Y. N. Wang, K. J. Deng and L. Z. Zhang, J. Phys. Chem. C, 2011, 115, 14300–14308, DOI: 10.1021/jp2042069.
- 41 O. Mehraj, B. M. Pirzada, N. A. Mir, M. Z. Khan and S. Sabir, *Appl. Surf. Sci.*, 2016, **387**, 642–651, DOI: 10.1016/j. apsusc.2016.05.166.
- 42 L. Q. Ye, L. H. Tian, T. Y. Peng and L. Zan, *J. Mater. Chem.*, 2011, **21**, 12479–12484, DOI: 10.1039/C1JM11005E.
- 43 L. H. Ai, Y. Zeng and J. Jiang, Chem. Eng. J., 2014, 235, 331–339, DOI: 10.1016/j.cej.2013.09.046.
- 44 H. Liu, W. R. Cao, Y. Su, Y. Wang and X. H. Wang, *Appl. Catal.*, *B*, 2012, **111**, 271–279, DOI: 10.1016/j.apcatb.2011.10.008.
- 45 W. E. Morgan, J. R. Vanwazer and W. J. Stec, J. Am. Chem. Soc., 1973, 95, 751–755, DOI: 10.1021/ja00784a018.
- 46 L. A. Brook, P. Evans, H. A. Foster, M. E. Pemble, A. Steele,
 D. W. Sheel and H. M. Yates, *J. Photochem. Photobiol., A*,
 2007, 187, 53–63, DOI: 10.1016/j.jphotochem.2006.09.014.
- 47 D. K. Smith, J. McCollum and M. L. Pantoya, *Phys. Chem. Chem. Phys.*, 2016, 18, 11243–11250, DOI: 10.1039/C5CP06998J.
- 48 Z. U. Rahman, N. Wei, M. Feng and D. A. Wang, Int. J. Hydrogen Energy, 2019, 44, 13221–13231, DOI: 10.1016/j. ijhydene.2019.03.176.
- 49 M. T. Uddin, Y. Nicolas, C. Olivier, T. Toupance, M. M. Muller, H. J. Kleebe, K. Rachut, J. Ziegler, A. Klein and W. Jaegermann, *J. Phys. Chem. C*, 2013, **117**, 22098–22110, DOI: 10.1021/jp407539c.
- 50 H. Liu, K. Tian, J. Ning, Y. Zhong, Z. Zhang and Y. Hu, ACS Catal., 2019, 9, 1211–1219, DOI: 10.1021/acscatal.8b03819.
- 51 F. Amano, R. Tosaki, Y. Sato and Y. Higuchi, *J. Solid State Chem.*, 2018, **258**, 79–85, DOI: 10.1016/j.jssc.2017.09.030.
- 52 C. Ye, J. X. Li, Z. J. Li, X. B. Li, X. B. Fan, L. P. Zhang, B. Chen, C. H. Tung and L. Z. Wu, ACS Catal., 2015, 5, 6973-6979, DOI: 10.1021/acscatal.5b02185.
- 53 C. Ye, X. Z. Wang, J. X. Li, Z. J. Li, X. B. Li, L. P. Zhang, B. Chen, C. H. Tung and L. Z. Wu, ACS Catal., 2016, 6, 8336–8341, DOI: 10.1021/acscatal.6b02664.
- 54 L. Wang, Y. Wan, Y. Ding, Y. Niu, Y. Xiong, X. Wu and H. Xu, *Nanoscale*, 2017, **9**, 4090–4096, DOI: 10.1039/C7NR00534B.
- 55 Y. Li, Y. Hu, C. A. Morrison, W. Wu, H. Han and N. Robertson, *Sustainable Energy Fuels*, 2017, 1, 308–316, DOI: 10.1039/C6SE00061D.
- 56 M. Zi, J. Li, Z. Zhang, X. Wang, J. Han, X. Yang, Z. Qiu, H. Gong, Z. Ji and B. Cao, *Phys. Status Solidi A*, 2015, 212, 1466–1470, DOI: 10.1002/pssa.201532015.
- 57 A. Liu, H. Zhu, W. T. Park, S. J. Kang, Y. Xu, M. G. Kim and Y. Y. Noh, *Adv. Mater.*, 2018, **30**, 1802379, DOI: 10.1002/ adma.201802379.
- 58 K. Li, Y. Zhao, P. Zhang, C. He, J. Deng, S. Ding and W. Shi, *Appl. Surf. Sci.*, 2016, **390**, 412-421, DOI: 10.1016/j.apsusc.2016.08.095.
- 59 R. L. Z. Hoye, L. C. Lee, R. C. Kurchin, T. N. Huq, K. H. L. Zhang, M. Sponseller, L. Nienhaus, R. E. Brandt, J. Jean, J. A. Polizzotti, A. Kursumović, M. G. Bawendi, V. Bulović, V. Stevanović, T. Buonassisi and J. L. MacManus-Driscoll, *Adv. Mater.*, 2017, **29**, 1702176, DOI: 10.1002/adma.201702176.