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Self-activated Rh–Zr mixed oxide as a nonhazardous cocatalyst for photocatalytic hydrogen evolution†

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Efficient, robust and environmentally friendly cocatalysts for photocatalysts are important for large-scale solar hydrogen production. Herein, we demonstrate that a Rh–Zr mixed oxide is an efficient cocatalyst for hydrogen evolution. Impregnation of Zr and Rh precursors (Zr/Rh = 5 wt/wt%) formed RhZrO_x cocatalyst particles on Al-doped SrTiO₃, which exhibited 31× higher photocatalytic water-splitting activity than a RhO_x cocatalyst. X-ray photoelectron spectroscopy proved that the dissociation of Cl[−] ions from preformed Rh–Cl–Zr–O solid led to formation of the active phase of RhZrO_x, in which the Zr/Rh ratio was critical to high catalytic activity. Additional CoO_x loading as an oxygen evolution cocatalyst further improved the activity by 120%, resulting in an apparent quantum yield of 33 (±4)% at 365 nm and a long durability of 60 h. Our discovery could help scale up photocatalytic hydrogen production.

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Introduction

Photocatalytic water-splitting is a promising technology for sustainable hydrogen production.^{1,2} Various photocatalysts, such as TiO₂, SrTiO₃, TaON, GaN:ZnO, Ta₃N₅ and Y₂Ti₂O₅S₂, have been developed for effective utilization of solar energy.^{3–8} Developing cocatalysts for photocatalysis is equally indispensable for improving photocatalytic activity;⁹ this is because the cocatalysts promote extraction of excited charges from the photocatalysts and reduce the overpotential of the water-splitting reaction. Noble metals, particularly platinum group metals, are widely used for the hydrogen evolution reaction (HER); they reduce H₂O because of the metals' high activity and

stability.¹⁰ However, noble metals also catalyze backward reactions, such as O₂ photoreduction and H₂O formation, from evolved H₂ and O₂.¹¹ Suppressing the backward reactions is central for developing an efficient HER cocatalyst. Based on this concept, Pt@SiO₂ core@shell,¹² Rh@Cr₂O₃ core@shell^{11,13} and Rh–Cr mixed oxide (RhCrO_x)¹⁴ cocatalysts have been developed. In these systems, H₂O can access the noble metal surface, whereas oxygen access is prevented to dramatically suppress the backward reactions. Although both Rh@CrO_x and RhCrO_x are commonly used because of their excellent activity, long-duration photo-irradiation causes dissolution of Cr⁶⁺ ions,¹⁵ resulting in not only decreased catalytic activity but also environmental damage and health hazards. To meet increasing demands on solar-to-energy conversion, many scientists are trying to replace hazardous elements in solar active materials, as observed in organic–inorganic lead halide perovskite solar cells (e.g., replace Pb with Sn or Bi).¹⁶ Similarly, alternatives to Cr are necessary for large-scale, environmentally friendly photocatalytic water-splitting systems.¹⁷

In this paper, we demonstrate that a novel Rh–Zr mixed oxide (RhZrO_x) is an efficient HER cocatalyst for an Al-doped SrTiO₃ (SrTiO₃:Al) photocatalyst. SrTiO₃:Al is the best water-splitting photocatalyst under UV irradiation to date,¹⁸ and can work in sunlight because of the high apparent quantum yield (AQY) in the UV region. Therefore, we chose SrTiO₃:Al synthesized by the flux-mediated method¹⁵ as a model photocatalyst to explore new efficient cocatalysts. Surface characterizations of the cocatalysts using HRTEM, STEM-EDS and XPS indicate that the active RhZrO_x phase forms by activation of the Rh–Cl–Zr–O mixed solid. A systematic study of loading conditions and

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electrocatalytic activity assessments of the cocatalyst uncovered the effect of Zr in the cocatalyst. Our novel, robust and nonhazardous Zr-based HER cocatalysts will be useful for large-scale solar hydrogen production.

Results and discussion

To find a new partner metal for Rh, we conducted element screening experiments (Fig. S1†). We chose impregnation to deposit cocatalysts on SrTiO₃:Al because impregnation is the easiest way to test a number of combinations without varying other experimental conditions. We fixed the weight ratio of metal to Rh (0.1 wt% *vs.* SrTiO₃:Al) at 5. Of 18 elements except for Cr, only five (Zr, Fe, Sm, La and Ce) showed higher activity than Rh alone. Among them, Zr exhibited outstanding H₂ evolution activity, 3.6× higher than the next most active element, Fe. The H₂/O₂ evolution molar ratio was approximately 2, indicating efficient overall water splitting. Zr is a nonhazardous element and its oxide is widely used in functional ceramics for bio-related applications. Therefore, Zr is a promising environmentally friendly alternative to Cr.

Then we optimized various parameters of RhZrO_x cocatalysts on SrTiO₃:Al. We first varied the Zr/Rh weight ratio from 0 to 7 at a constant weight percent Rh of 0.1 wt% *vs.* SrTiO₃:Al (Fig. 1a). The catalytic activity increased in accordance with increasing Zr/Rh weight ratio from 0 to 5, and showed the highest H₂ evolution rate of 249 μmol h⁻¹ at Zr/Rh = 5 wt/wt%, which is 31× higher than RhO_x/SrTiO₃:Al (Zr/Rh = 0). At Zr/Rh < 3 wt/wt%, the H₂ evolution rate drastically decreased after 1.5 h, indicating a Zr/Rh weight ratio >3 improves the catalyst's

stability. Although the sample synthesized at Zr/Rh = 7 wt/wt% was stable, the overall activity was less than half (110 μmol h⁻¹) that at Zr/Rh = 5 wt/wt%. We also optimized the total quantity of cocatalyst at a fixed Zr/Rh weight ratio of 5 wt/wt% (Fig. 1b). When the loading quantity of cocatalyst was less than standard (Rh = 0.1 and Zr = 0.5 wt%), the H₂ evolution activity decreased considerably (22 μmol h⁻¹) because of the insufficient number of water reduction sites. However, loading a larger quantity of cocatalyst (Rh = 0.2 and Zr = 1.0 wt%) only slightly lessened the activity (221 μmol h⁻¹). Based on these results, the optimum quantity of cocatalyst for SrTiO₃:Al is Rh = 0.1 wt% and Zr = 0.5 wt%.

Then we investigated the effect of calcination temperature in the range of 300–450 °C. RhZrO_x/SrTiO₃:Al calcined at 350 °C showed the highest H₂ evolution (Fig. 1c). A calcination temperature of 300 °C is too low to transform ZrOCl₂·8H₂O into ZrO₂ (Fig. S2 and Table S1†). The Cl/Zr molar ratio decreases with increasing the calcination temperature (Table S1†), indicating that higher calcination temperature assists the formation of ZrO₂. SEM images revealed that the cocatalyst size increased from several nanometres to hundreds of nanometres when we calcined the sample at a temperature higher than 400 °C, which decreased the number of active sites on the photocatalyst (Fig. S3†). The order of impregnation of two metal species is important, because the nanostructure of the cocatalyst affects the catalytic activity.¹¹ We compared a co-impregnated (Rh and Zr precursors mixed and loaded simultaneously) with sequentially impregnated (Rh and Zr precursors loaded sequentially) photocatalyst. The co-impregnated photocatalyst showed much higher activity than the sequentially impregnated photocatalyst (Fig. 1d), implying that the Rh–Zr mixed oxide was the active species for overall water splitting rather than the mixture of RhO_x and ZrO_x. Fig. S4† summarizes all aforementioned catalytic activities including O₂ evolution activity.

Next, we characterized the optimized RhZrO_x cocatalysts on SrTiO₃:Al. We conducted HRTEM to observe the hetero-interface between RhZrO_x and SrTiO₃:Al phases. We observed no appreciable spots in a FFT image from the cocatalyst region (light-blue square), whereas the SrTiO₃:Al region (orange square) exhibited spots that are attributable to crystalline SrTiO₃:Al (Fig. 2a), which indicates that the RhZrO_x cocatalyst is amorphous. STEM-EDS elemental mapping analysis revealed that the elements Rh, Zr and O coexist in the cocatalysts and uniformly disperse on the photocatalysts (Fig. 2b).

For loading cocatalysts, we used RhCl₃·3H₂O and ZrOCl₂·8H₂O as Rh and Zr precursors, respectively. Considering the exceptional stability of anhydrous RhCl₃,¹⁹ Cl may contaminate the Rh–Zr mixed oxide cocatalysts. At the impregnation conditions (350 °C for 1 h), ZrOCl₂·8H₂O was mostly converted into ZrO₂ (Fig. S2†), whereas RhCl₃·3H₂O released only H₂O to give anhydrous RhCl₃ (Fig. S5†), which is stable until 600 °C in air.¹⁹ Thus Cl should exist in the RhZrO_x cocatalyst; however, the XRD measurement for RhZrO_x solid (Zr/Rh = 5 wt/wt%) did not indicate any metal chloride peaks (Fig. S6†). EDS analysis cannot indicate the coexistence of Rh and Cl, because the

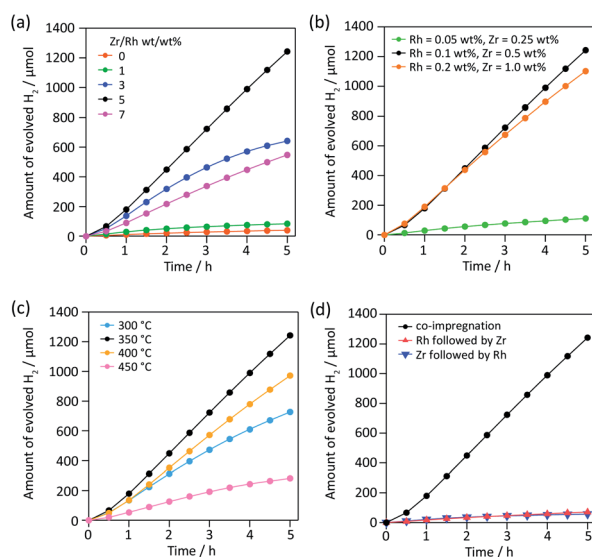


Fig. 1 Photocatalytic activities of RhZrO_x/SrTiO₃:Al synthesized in various experimental conditions. The quantity of evolved H₂ of RhZrO_x/SrTiO₃:Al synthesized (a) at various Zr/Rh weight ratios (Rh = 0.1 wt%), (b) at various quantities of Rh (Zr/Rh = 5 wt/wt%), (c) at various annealing temperatures (Rh = 0.1, Zr = 0.5 wt%) and (d) by co-impregnation and sequential impregnation (Rh = 0.1, Zr = 0.5 wt%). Reaction conditions: catalyst, 10 mg; solution, 20 mL of H₂O; light source, 300 W Xe lamp (λ = 300–450 nm).



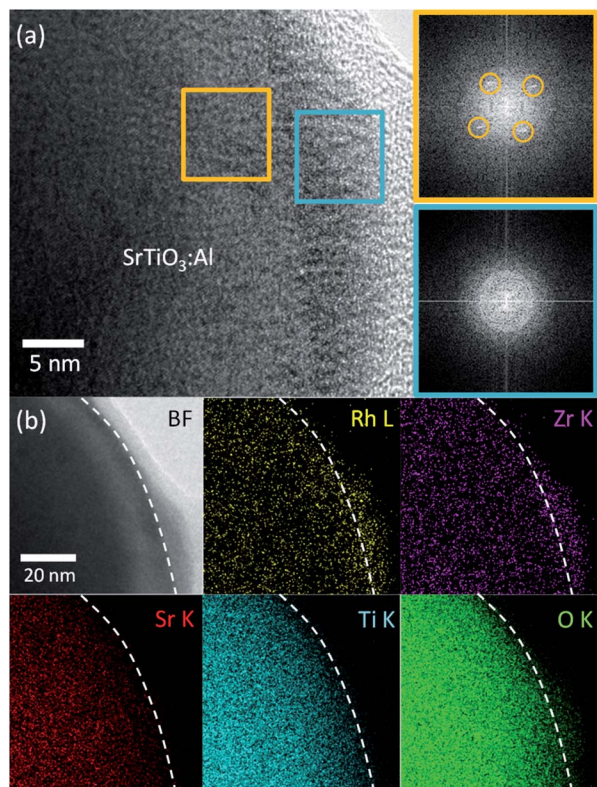


Fig. 2 Electron microscopy analyses of Rh–Zr oxide cocatalyst on SrTiO₃:Al. (a) HRTEM image and FFT images of RhZrO_x/SrTiO₃:Al at the interface. Outer bright layer: carbon-related contamination formed during observation. Orange and light-blue squares: SrTiO₃:Al and cocatalyst, respectively. (b) STEM-EDS elemental mapping images of RhZrO_x/SrTiO₃:Al at the interface. White broken lines: surface of SrTiO₃:Al.

characteristic X-ray energies from Rh-L and Cl-K largely overlap (2.6–2.9 keV). Therefore, we used XPS to confirm the presence of Cl in the cocatalyst, because the Rh 3d and Cl 2p peaks separately appear at approximately 310 and 198 eV, respectively. The XPS spectra of RhZrO_x/SrTiO₃:Al showed Cl 2p peaks along with Rh 3d and Zr 3d peaks (Fig. 3), indicating the presence of Cl in the cocatalyst. Rh 3d peaks have an intermediate feature between Rh₂O₃ and RhCl₃·3H₂O, suggesting that the Rh is partially oxidized to a Rh–Cl–O species. Zr 3d and Cl 2p peaks can be assigned to Zr⁴⁺ of ZrO₂ and Cl[−] of RhCl₃·3H₂O, respectively. These results indicate the formation of Rh–Cl and Zr–O bonds. In addition, water-washed RhZrO_x/SrTiO₃:Al still has clear Cl 2p peaks along with Rh 3d and Zr 3d peaks, which is consistent with the intrinsic insolubility of anhydrous RhCl₃ in water. We also applied Ar bombardment to remove a several-nanometre surface extract of the samples to obtain the XPS spectra in the inner regions of the cocatalyst.²⁰ We detected three elements after Ar bombardment, indicating they were uniformly distributed in the cocatalyst. Thus, as-prepared cocatalyst can be described as a Rh–Cl–Zr–O solid. Because the Ar bombardment sometimes induces an XPS peak shift, we do not discuss the valence state of the elements in these experiments.

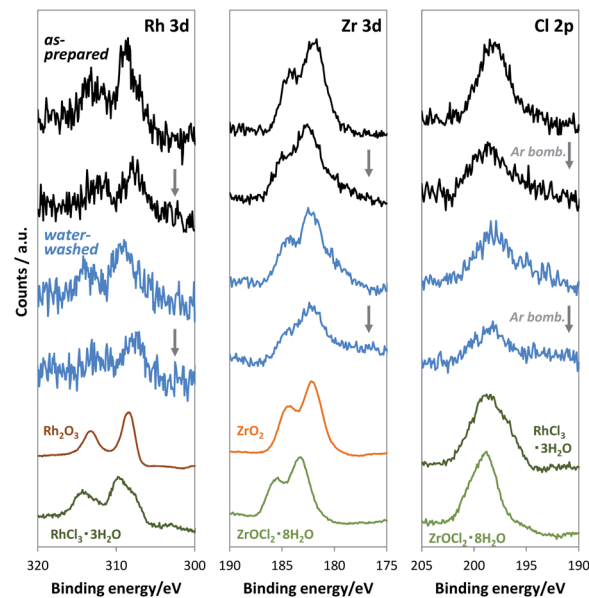


Fig. 3 XPS spectra of RhZrO_x/SrTiO₃:Al and reference materials at the energy ranges of (left) Rh 3d, (middle) Zr 3d and (right) Cl 2p. Black and blue spectra: as-prepared and water-washed samples, respectively, before and after Ar bombardment.

To understand why Rh–Cl–Zr–O solid-loaded SrTiO₃:Al exhibits high catalytic activity and durability, we investigated the structural change of Rh–Cl–Zr–O during the photocatalytic reaction. First, we examined the valence state of Rh during the photocatalytic reaction by *in situ* XANES measurements (Fig. S7†). We obtained XANES spectra every 11 min over the course of a 200 min photocatalytic reaction. The Rh K-edge spectra indicates that the valence of Rh retained nearly a trivalent state, which in turn indicates that the photo-excited electrons in SrTiO₃:Al do not reduce Rh³⁺ into Rh⁰, as observed in previously reported RhCrO_x cocatalysts.²¹

We conducted XPS measurements of RhZrO_x/SrTiO₃:Al after a 5 h reaction to further clarify the valence and composition

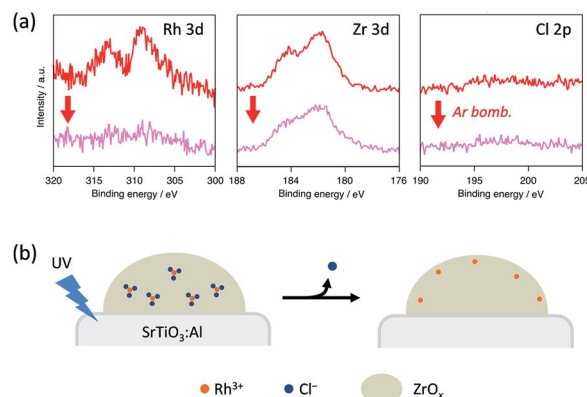


Fig. 4 (a) XPS spectra of Rh 3d, Zr 3d and Cl 2p peaks in a RhZrO_x cocatalyst on SrTiO₃:Al after the reaction. (b) Schematic of the atomic rearrangement in Rh–Cl–Zr–O solid during photocatalysis.



changes of the elements in the cocatalyst (Fig. 4a). The Rh 3d_{5/2} peak at 309 eV showed no considerable shift after the reaction, which is consistent with our *in situ* XANES results. The Zr 3d_{5/2} peak at 182 eV was also unchanged after the reaction. However, the Cl 2p peak completely disappeared after the reaction, indicating the dissolution of Cl[−] ions into the water during the reaction. Notably, the Rh 3d peak intensity considerably decreased after Ar bombardment, whereas the Zr 3d peak intensity remained unchanged. We did not observe the Cl 2p peak even inside the cocatalyst. ICP measurements revealed that the Zr/Rh weight ratio in the entire cocatalyst was retained after the reaction (Table S2†). These results strongly suggest that the Rh³⁺ ions are concentrated at the outer surface of the cocatalysts during the reaction without eluting into the water. This noteworthy concentration phenomenon does not result from the photoreduction of once-eluted Rh³⁺ on SrTiO₃:Al; this is because *in situ* XANES and XPS measurements revealed that Rh³⁺ was not reduced during the photocatalysis.

Considering the aforementioned results, we summarize the structural change of RhZrO_x cocatalysts during photocatalysis as follows (Fig. 4b). Both Rh and Zr are uniformly dispersed in as-synthesized Rh–Cl–Zr–O solid in the forms of RhCl₃ and ZrO₂, respectively. As the reaction proceeds, the Cl[−] ions move to the surface and elute to water. The Rh³⁺ ions also migrate together with Cl[−] ions to the surface because of the strong Rh–Cl bond. As a result, the Rh³⁺ ions are condensed near the water/cocatalyst interface. However, the driving force for Cl[−] dissolution remains to be clarified. In the resulting structure, the insulating ZrO_x layer may hinder the electron transfer from SrTiO₃:Al to Rh³⁺ reaction centres. Recently, it has been reported that the photoelectrodes coated with the insulating layers (ZrO₂, SiO_x, Al₂O₃, HfO₂, Ta₂O₅, etc.) exhibited enhanced photocatalytic activity, in which the photoexcited electrons can penetrate a few nanometre insulating overlayers.^{22–26} Because our RhZrO_x cocatalysts are several nanometres in size, it is reasonable that the photoexcited electrons can migrate through ZrO_x layers to reach Rh³⁺.

The atom migration (induced by Cl[−]) in the cocatalysts seems to affect the catalysts' catalytic properties. To confirm this migration effect, we synthesized RhZrO_x/SrTiO₃:Al catalysts from Cl-free precursors, such as Rh(NO₃)₃·xH₂O and ZrO(NO₃)₂·2H₂O, which were converted into mixed oxide cocatalysts through co-impregnation (Fig. S8†). The photocatalysts synthesized from Rh(NO₃)₃·xH₂O have considerably lower activity than those from RhCl₃·3H₂O (Fig. S9†). Because the diameters of the cocatalysts were similar regardless of the precursors, a morphological effect on the activity can be excluded (Fig. S10†). These results strongly suggest that Cl[−] elution from the Rh–Cl–Zr–O solid formed the RhZrO_x active species with the optimal spatial distribution of Rh, Zr and O for the overall water-splitting reaction.

The ZrO_x-loaded SrTiO₃:Al showed almost no H₂ evolution activity (1 μmol h^{−1}), therefore, the ZrO_x does not function as a HER-active centre (Fig. S11†). To understand how Zr contributes to the activity enhancement, we conducted electrochemical catalysis measurements of RhZrO_x. We loaded the RhZrO_x cocatalysts on carbon powder (XC-72) by the same

impregnation method adopted for SrTiO₃:Al. We evaluated the catalytic activity of the backward reaction by measuring the current density of the oxygen reduction reaction (ORR) in O₂-saturated 1 M aqueous Na₂SO₄. Linear sweep voltammograms showed that the onset potential for the ORR shifted in the negative direction, and the current density at 0.4 V vs. reversible hydrogen electrode decreased from 2.5 to 1.3 mA cm^{−2} as the Zr/Rh weight ratio increased from 0 to 7 (Fig. S13a and b†). This indicates that increasing the Zr/Rh weight ratio suppresses the ORR. We also evaluated the HER activity from an overpotential for the water reduction reaction in Ar-saturated 1 M aqueous Na₂SO₄. Overpotential of HER at −8 mA cm^{−2} increased from 445 to 524 mV in accordance with increasing Zr/Rh weight ratio (Fig. S13c and d†), which suggests that the larger quantity of Zr also suppresses the water reduction activity. This tendency accounts for the reason why Zr/Rh = 5 wt/wt% showed the highest water-splitting activity; that is, at Zr/Rh = 0–5 wt/wt%, suppression of the backward reaction is the main contributor to the improvement of the catalytic activity. In the range of Zr/Rh > 5 wt/wt%, deactivation of HER exceeds the suppression of the backward reaction.

From the structural point of view, we have to mention that it is hard to clarify whether the structure of RhZrO_x on XC-72 is exactly the same as that of activated RhZrO_x on SrTiO₃:Al, because the amount of RhZrO_x used in the electrochemical test was not enough for XPS measurement (Rh + Zr = 0.12 μg). Although the Cl[−] effect is unclear in electrochemical catalyses without structural characterization, the RhZrO_x/XC-72 prepared from Rh(NO₃)₃·xH₂O showed different ORR and HER activities from that prepared from RhCl₃·3H₂O (Fig. S13b and d†). One clear trend is that both ORR and HER activities decrease with increasing the Zr/Rh weight ratio for each catalyst (Fig. S13b and d†), which suggests that the addition of ZrO_x hinders both ORR and HER of Rh³⁺ regardless of the Cl[−]-mediated activation.

The ORR blocking ability of ZrO_x was confirmed in the photocatalysis of RhZrO_x/SrTiO₃:Al (Zr/Rh = 5 wt/wt%) by monitoring the concentrations of accumulated H₂ and O₂ in a reaction vessel after turning off the light irradiation (Fig. S14†). H₂ and O₂ concentrations in the reactor remained almost unchanged (>95%) over the subsequent 9 h in the dark, indicating that the backward reaction was strongly suppressed on RhZrO_x/SrTiO₃:Al with Zr/Rh = 5 wt/wt%. This result also suggests that the ratio of Zr/Rh = 5 wt/wt% is sufficient to suppress the backward reaction, which is qualitatively linked to the less ORR activity of RhZrO_x cocatalyst with Zr/Rh = 5 wt/wt% in electrochemical results (Fig. S13a†). Additionally, this result also supports the conclusion that the less activity of RhZrO_x/SrTiO₃:Al with Zr/Rh = 7 wt/wt% results from the decreased HER activity, as shown in Fig. S13c.†

Co-loading of both HER and oxygen evolution reaction (OER) cocatalysts synergistically enhances the photocatalytic overall water splitting.²⁷ For example, co-loading of cobalt oxide (CoO_x) with RhCrO_x on SrTiO₃:Al enhances both the catalytic activity and durability.¹⁵ Encouraged by these results, we co-loaded CoO_x and RhZrO_x on SrTiO₃:Al (CoO_x + RhZrO_x/SrTiO₃:Al) by sequential impregnation. Initially, we loaded CoO_x (Co = 0.1 wt% vs. SrTiO₃:Al) on SrTiO₃:Al, followed by loading RhZrO_x



(Rh = 0.1 and Zr = 0.5 wt% vs. SrTiO₃:Al). The HER activity of CoO_x + RhZrO_x/SrTiO₃:Al was 296 μmol h⁻¹, which is 1.2× higher than that of RhZrO_x/SrTiO₃:Al (Fig. 5a). We confirmed that 0.1 wt% vs. SrTiO₃:Al is an optimum amount of Co in the range of 0.05–0.2 wt% (Fig. S15[†]). Other well-known OER cocatalysts like NiO_x and IrO_x were also tested as additives on RhZrO_x/SrTiO₃:Al but their activities did not exceed the CoO_x + RhZrO_x/SrTiO₃:Al (Fig. S16[†]). We calculated the AQY of CoO_x + RhZrO_x/SrTiO₃:Al to be 33 (±4)% at 365 nm. The solar-to-hydrogen efficiency (STH) was estimated to be 0.21% (Fig. S17[†]). The stability was also improved by co-loading CoO_x with RhZrO_x (Fig. 5b). Because CoO_x/SrTiO₃:Al showed much lower activity for HER (Fig. 5a and b), we conclude that coexistence of CoO_x and RhZrO_x has a synergetic effect on the catalytic activity. In the case of the CoO_x + RhCrO_x combination, CoO_x promotes hole extraction from SrTiO₃:Al, which disrupts hole migration to RhCrO_x to suppress the degradation,²¹ and also catalyzes water oxidation. We consider that this positive effect would also be effective for RhZrO_x/SrTiO₃:Al. A 60 h long-term stability test in 10 h intervals revealed that the gas evolution rate was relatively constant to the end of the reaction, maintaining a H₂/O₂ molar ratio of approximately 2 (Fig. 5c and d), indicating the robustness of CoO_x + RhZrO_x/SrTiO₃:Al.

Although we have shown the superior catalytic performance of RhZrO_x/SrTiO₃:Al, the activity is still less than that of RhCrO_x/SrTiO₃:Al, which has a >50% AQY at 365 nm (Table S3[†]).¹⁵ In the Rh@Cr₂O₃ cocatalyst, the Cr₂O₃ layer suppresses only the ORR and does not hinder the HER of Rh.¹¹ This seems to be one of the reasons why RhZrO_x/SrTiO₃:Al has less activity than RhCrO_x/SrTiO₃:Al. To enhance the activity of RhZrO_x/SrTiO₃:Al, doping foreign metals into ZrO₂ may increase proton conductivity.²⁸ This strategy may help proton penetration towards the Rh reaction centres to evolve a larger quantity of H₂. Robot-

operating combinatorial experiments will help researchers discover such novel ternary or quaternary oxides cocatalyst materials from enormous numbers of candidates.²⁹

Conclusions

We demonstrated that a Rh–Zr mixed oxide efficiently functions as a HER cocatalyst on SrTiO₃:Al. The active phase for HER, RhZrO_x, formed by spontaneous Cl-dissolution-assisted activation of the Rh–Cl–Zr–O solid solution. Unexpected Cl⁻ contamination was found to sacrificially assist the formation of suitable spatial distributions of Rh³⁺ and Zr⁴⁺ in RhZrO_x cocatalyst during photocatalysis. Electrochemical measurements showed that addition of Zr suppresses not only the ORR, but also the HER of Rh. We used this fact to determine the proper weight ratio of Zr/Rh (=5) for overall water splitting. Additional deposition of an OER cocatalyst, CoO_x, further improved the photocatalytic activity and stability of RhZrO_x/SrTiO₃:Al. Our nonhazardous Zr-based cocatalyst will be useful for large-scale applications to photocatalytic water splitting.

Conflicts of interest

There are no conflicts to declare.

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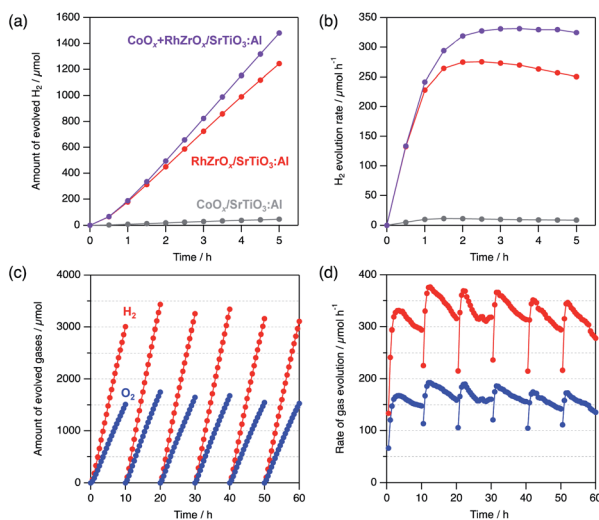


Fig. 5 (a) Quantity of evolved H₂ and (b) H₂ evolution rate of CoO_x + RhZrO_x/SrTiO₃:Al, RhZrO_x/SrTiO₃:Al and CoO_x/SrTiO₃:Al. (c) Quantity of evolved gases and (d) evolution rate of gases of CoO_x + RhZrO_x/SrTiO₃:Al in a long-term test for 60 h. Red and blue circles represent H₂ and O₂, respectively. Reaction conditions: catalyst, 10 mg; solution, 20 mL of H₂O; light source, 300 W Xe lamp (λ = 300–450 nm).



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