

Cite this: *Chem. Sci.*, 2020, **11**, 6862

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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<sub>x</sub> cocatalyst particles on Al-doped SrTiO<sub>3</sub>, which exhibited 31× higher photocatalytic water-splitting activity than a RhO<sub>x</sub> cocatalyst. X-ray photoelectron spectroscopy proved that the dissociation of Cl<sup>−</sup> ions from preformed Rh–Cl–Zr–O solid led to formation of the active phase of RhZrO<sub>x</sub>, in which the Zr/Rh ratio was critical to high catalytic activity. Additional CoO<sub>x</sub> 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.

Received 6th March 2020

Accepted 18th June 2020

DOI: 10.1039/d0sc01363c

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## Introduction

Photocatalytic water-splitting is a promising technology for sustainable hydrogen production.<sup>1,2</sup> Various photocatalysts, such as TiO<sub>2</sub>, SrTiO<sub>3</sub>, TaON, GaN:ZnO, Ta<sub>3</sub>N<sub>5</sub> and Y<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>S<sub>2</sub>, have been developed for effective utilization of solar energy.<sup>3–8</sup> Developing cocatalysts for photocatalysis is equally indispensable for improving photocatalytic activity;<sup>9</sup> 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 H<sub>2</sub>O because of the metals' high activity and

stability.<sup>10</sup> However, noble metals also catalyze backward reactions, such as O<sub>2</sub> photoreduction and H<sub>2</sub>O formation, from evolved H<sub>2</sub> and O<sub>2</sub>.<sup>11</sup> Suppressing the backward reactions is central for developing an efficient HER cocatalyst. Based on this concept, Pt@SiO<sub>2</sub> core@shell,<sup>12</sup> Rh@Cr<sub>2</sub>O<sub>3</sub> core@shell<sup>11,13</sup> and Rh–Cr mixed oxide (RhCrO<sub>x</sub>)<sup>14</sup> cocatalysts have been developed. In these systems, H<sub>2</sub>O can access the noble metal surface, whereas oxygen access is prevented to dramatically suppress the backward reactions. Although both Rh@CrO<sub>x</sub> and RhCrO<sub>x</sub> are commonly used because of their excellent activity, long-duration photo-irradiation causes dissolution of Cr<sup>6+</sup> ions,<sup>15</sup> 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).<sup>16</sup> Similarly, alternatives to Cr are necessary for large-scale, environmentally friendly photocatalytic water-splitting systems.<sup>17</sup>

In this paper, we demonstrate that a novel Rh–Zr mixed oxide (RhZrO<sub>x</sub>) is an efficient HER cocatalyst for an Al-doped SrTiO<sub>3</sub> (SrTiO<sub>3</sub>:Al) photocatalyst. SrTiO<sub>3</sub>:Al is the best water-splitting photocatalyst under UV irradiation to date,<sup>18</sup> and can work in sunlight because of the high apparent quantum yield (AQY) in the UV region. Therefore, we chose SrTiO<sub>3</sub>:Al synthesized by the flux-mediated method<sup>15</sup> 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<sub>x</sub> phase forms by activation of the Rh–Cl–Zr–O mixed solid. A systematic study of loading conditions and

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† Electronic supplementary information (ESI) available: Experimental details, additional characterization and results. See DOI: 10.1039/d0sc01363c

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  $\text{SrTiO}_3\text{:Al}$  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.*  $\text{SrTiO}_3\text{:Al}$ ) 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  $\text{H}_2$  evolution activity, 3.6 $\times$  higher than the next most active element, Fe. The  $\text{H}_2/\text{O}_2$  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.

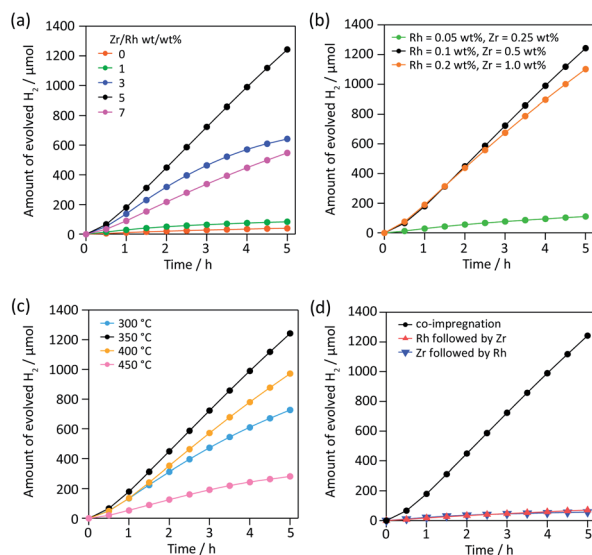
Then we optimized various parameters of  $\text{RhZrO}_x$  cocatalysts on  $\text{SrTiO}_3\text{:Al}$ . We first varied the Zr/Rh weight ratio from 0 to 7 at a constant weight percent Rh of 0.1 wt% *vs.*  $\text{SrTiO}_3\text{:Al}$  (Fig. 1a). The catalytic activity increased in accordance with increasing Zr/Rh weight ratio from 0 to 5, and showed the highest  $\text{H}_2$  evolution rate of  $249 \mu\text{mol h}^{-1}$  at Zr/Rh = 5 wt/wt%, which is 31 $\times$  higher than  $\text{RhO}_x/\text{SrTiO}_3\text{:Al}$  (Zr/Rh = 0). At Zr/Rh < 3 wt/wt%, the  $\text{H}_2$  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 ( $110 \mu\text{mol h}^{-1}$ ) 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  $\text{H}_2$  evolution activity decreased considerably ( $22 \mu\text{mol h}^{-1}$ ) 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 ( $221 \mu\text{mol h}^{-1}$ ). Based on these results, the optimum quantity of cocatalyst for  $\text{SrTiO}_3\text{:Al}$  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.  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  calcined at 350 °C showed the highest  $\text{H}_2$  evolution (Fig. 1c). A calcination temperature of 300 °C is too low to transform  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  into  $\text{ZrO}_2$  (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  $\text{ZrO}_2$ . 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.<sup>11</sup> 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  $\text{RhO}_x$  and  $\text{ZrO}_x$ . Fig. S4† summarizes all aforementioned catalytic activities including  $\text{O}_2$  evolution activity.

Next, we characterized the optimized  $\text{RhZrO}_x$  cocatalysts on  $\text{SrTiO}_3\text{:Al}$ . We conducted HRTEM to observe the hetero-interface between  $\text{RhZrO}_x$  and  $\text{SrTiO}_3\text{:Al}$  phases. We observed no appreciable spots in a FFT image from the cocatalyst region (light-blue square), whereas the  $\text{SrTiO}_3\text{:Al}$  region (orange square) exhibited spots that are attributable to crystalline  $\text{SrTiO}_3\text{:Al}$  (Fig. 2a), which indicates that the  $\text{RhZrO}_x$  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  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  as Rh and Zr precursors, respectively. Considering the exceptional stability of anhydrous  $\text{RhCl}_3$ ,<sup>19</sup> Cl may contaminate the Rh–Zr mixed oxide cocatalysts. At the impregnation conditions (350 °C for 1 h),  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was mostly converted into  $\text{ZrO}_2$  (Fig. S2†), whereas  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  released only  $\text{H}_2\text{O}$  to give anhydrous  $\text{RhCl}_3$  (Fig. S5†), which is stable until 600 °C in air.<sup>19</sup> Thus Cl should exist in the  $\text{RhZrO}_x$  cocatalyst; however, the XRD measurement for  $\text{RhZrO}_x$  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  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  synthesized in various experimental conditions. The quantity of evolved  $\text{H}_2$  of  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  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  $\text{H}_2\text{O}$ ; light source, 300 W Xe lamp ( $\lambda$  = 300–450 nm).



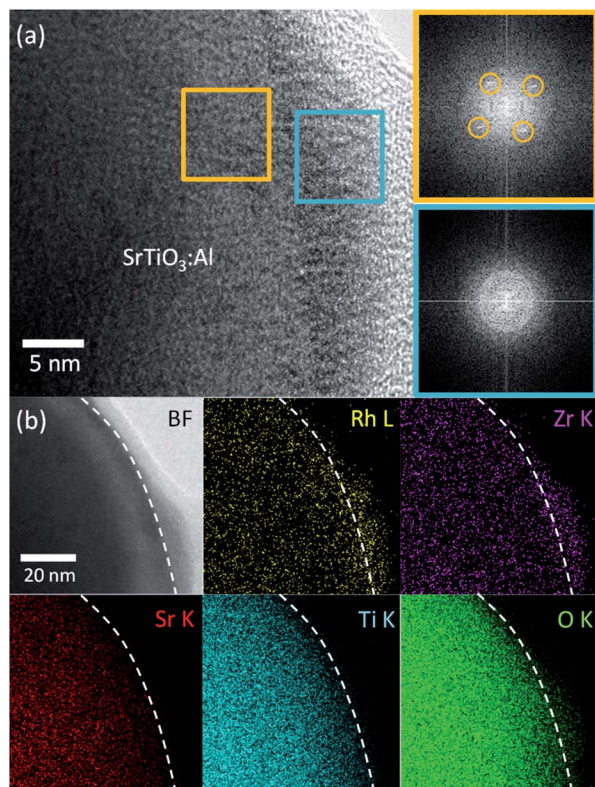


Fig. 2 Electron microscopy analyses of Rh–Zr oxide cocatalyst on SrTiO<sub>3</sub>:Al. (a) HRTEM image and FFT images of RhZrO<sub>x</sub>/SrTiO<sub>3</sub>:Al at the interface. Outer bright layer: carbon-related contamination formed during observation. Orange and light-blue squares: SrTiO<sub>3</sub>:Al and cocatalyst, respectively. (b) STEM-EDS elemental mapping images of RhZrO<sub>x</sub>/SrTiO<sub>3</sub>:Al at the interface. White broken lines: surface of SrTiO<sub>3</sub>: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<sub>x</sub>/SrTiO<sub>3</sub>: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 Rh<sub>2</sub>O<sub>3</sub> and RhCl<sub>3</sub>·3H<sub>2</sub>O, suggesting that the Rh is partially oxidized to a Rh–Cl–O species. Zr 3d and Cl 2p peaks can be assigned to Zr<sup>4+</sup> of ZrO<sub>2</sub> and Cl<sup>−</sup> of RhCl<sub>3</sub>·3H<sub>2</sub>O, respectively. These results indicate the formation of Rh–Cl and Zr–O bonds. In addition, water-washed RhZrO<sub>x</sub>/SrTiO<sub>3</sub>:Al still has clear Cl 2p peaks along with Rh 3d and Zr 3d peaks, which is consistent with the intrinsic insolubility of anhydrous RhCl<sub>3</sub> 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.<sup>20</sup> 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.

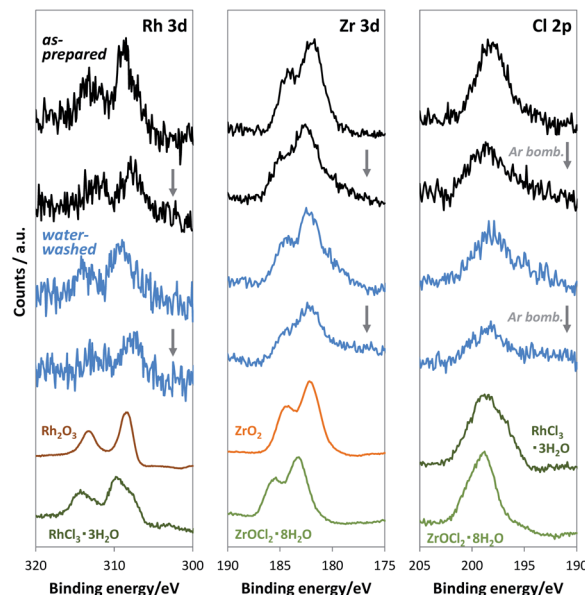


Fig. 3 XPS spectra of RhZrO<sub>x</sub>/SrTiO<sub>3</sub>:Al and reference materials at the energy ranges of (left) Rh 3d, (middle) Zr 3d and (right) Cl 2p. Black and blue spectra: as-prepared and water-washed samples, respectively, before and after Ar bombardment.

To understand why Rh–Cl–Zr–O solid-loaded SrTiO<sub>3</sub>: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 SrTiO<sub>3</sub>:Al do not reduce Rh<sup>3+</sup> into Rh<sup>0</sup>, as observed in previously reported RhCrO<sub>x</sub> cocatalysts.<sup>21</sup>

We conducted XPS measurements of RhZrO<sub>x</sub>/SrTiO<sub>3</sub>:Al after a 5 h reaction to further clarify the valence and composition

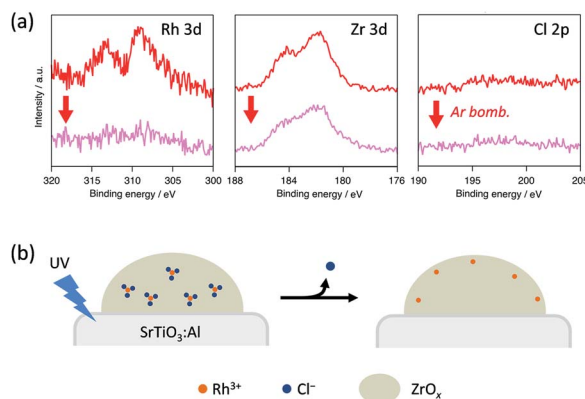


Fig. 4 (a) XPS spectra of Rh 3d, Zr 3d and Cl 2p peaks in a RhZrO<sub>x</sub> cocatalyst on SrTiO<sub>3</sub>:Al after the reaction. (b) Schematic of the atomic rearrangement in Rh–Cl–Zr–O solid during photocatalysis.





changes of the elements in the cocatalyst (Fig. 4a). The Rh 3d<sub>5/2</sub> peak at 309 eV showed no considerable shift after the reaction, which is consistent with our *in situ* XANES results. The Zr 3d<sub>5/2</sub> 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<sup>−</sup> 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 Rh<sup>3+</sup> 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 Rh<sup>3+</sup> on SrTiO<sub>3</sub>:Al; this is because *in situ* XANES and XPS measurements revealed that Rh<sup>3+</sup> was not reduced during the photocatalysis.

Considering the aforementioned results, we summarize the structural change of RhZrO<sub>x</sub> 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 RhCl<sub>3</sub> and ZrO<sub>2</sub>, respectively. As the reaction proceeds, the Cl<sup>−</sup> ions move to the surface and elute to water. The Rh<sup>3+</sup> ions also migrate together with Cl<sup>−</sup> ions to the surface because of the strong Rh–Cl bond. As a result, the Rh<sup>3+</sup> ions are condensed near the water/cocatalyst interface. However, the driving force for Cl<sup>−</sup> dissolution remains to be clarified. In the resulting structure, the insulating ZrO<sub>x</sub> layer may hinder the electron transfer from SrTiO<sub>3</sub>:Al to Rh<sup>3+</sup> reaction centres. Recently, it has been reported that the photoelectrodes coated with the insulating layers (ZrO<sub>2</sub>, SiO<sub>x</sub>, Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, etc.) exhibited enhanced photocatalytic activity, in which the photoexcited electrons can penetrate a few nanometre insulating overlayers.<sup>22–26</sup> Because our RhZrO<sub>x</sub> cocatalysts are several nanometres in size, it is reasonable that the photoexcited electrons can migrate through ZrO<sub>x</sub> layers to reach Rh<sup>3+</sup>.

The atom migration (induced by Cl<sup>−</sup>) in the cocatalysts seems to affect the catalysts' catalytic properties. To confirm this migration effect, we synthesized RhZrO<sub>x</sub>/SrTiO<sub>3</sub>:Al catalysts from Cl-free precursors, such as Rh(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, which were converted into mixed oxide cocatalysts through co-impregnation (Fig. S8†). The photocatalysts synthesized from Rh(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O have considerably lower activity than those from RhCl<sub>3</sub>·3H<sub>2</sub>O (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<sup>−</sup> elution from the Rh–Cl–Zr–O solid formed the RhZrO<sub>x</sub> active species with the optimal spatial distribution of Rh, Zr and O for the overall water-splitting reaction.

The ZrO<sub>x</sub>-loaded SrTiO<sub>3</sub>:Al showed almost no H<sub>2</sub> evolution activity (1 μmol h<sup>−1</sup>), therefore, the ZrO<sub>x</sub> 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<sub>x</sub>. We loaded the RhZrO<sub>x</sub> cocatalysts on carbon powder (XC-72) by the same

impregnation method adopted for SrTiO<sub>3</sub>:Al. We evaluated the catalytic activity of the backward reaction by measuring the current density of the oxygen reduction reaction (ORR) in O<sub>2</sub>-saturated 1 M aqueous Na<sub>2</sub>SO<sub>4</sub>. 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<sup>−2</sup> 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 Na<sub>2</sub>SO<sub>4</sub>. Overpotential of HER at −8 mA cm<sup>−2</sup> 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<sub>x</sub> on XC-72 is exactly the same as that of activated RhZrO<sub>x</sub> on SrTiO<sub>3</sub>:Al, because the amount of RhZrO<sub>x</sub> used in the electrochemical test was not enough for XPS measurement (Rh + Zr = 0.12 μg). Although the Cl<sup>−</sup> effect is unclear in electrochemical catalyses without structural characterization, the RhZrO<sub>x</sub>/XC-72 prepared from Rh(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O showed different ORR and HER activities from that prepared from RhCl<sub>3</sub>·3H<sub>2</sub>O (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<sub>x</sub> hinders both ORR and HER of Rh<sup>3+</sup> regardless of the Cl<sup>−</sup>-mediated activation.

The ORR blocking ability of ZrO<sub>x</sub> was confirmed in the photocatalysis of RhZrO<sub>x</sub>/SrTiO<sub>3</sub>:Al (Zr/Rh = 5 wt/wt%) by monitoring the concentrations of accumulated H<sub>2</sub> and O<sub>2</sub> in a reaction vessel after turning off the light irradiation (Fig. S14†). H<sub>2</sub> and O<sub>2</sub> 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<sub>x</sub>/SrTiO<sub>3</sub>: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<sub>x</sub> 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<sub>x</sub>/SrTiO<sub>3</sub>: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.<sup>27</sup> For example, co-loading of cobalt oxide (CoO<sub>x</sub>) with RhCrO<sub>x</sub> on SrTiO<sub>3</sub>:Al enhances both the catalytic activity and durability.<sup>15</sup> Encouraged by these results, we co-loaded CoO<sub>x</sub> and RhZrO<sub>x</sub> on SrTiO<sub>3</sub>:Al (CoO<sub>x</sub> + RhZrO<sub>x</sub>/SrTiO<sub>3</sub>:Al) by sequential impregnation. Initially, we loaded CoO<sub>x</sub> (Co = 0.1 wt% vs. SrTiO<sub>3</sub>:Al) on SrTiO<sub>3</sub>:Al, followed by loading RhZrO<sub>x</sub>



(Rh = 0.1 and Zr = 0.5 wt% vs.  $\text{SrTiO}_3\text{:Al}$ ). The HER activity of  $\text{CoO}_x + \text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  was  $296 \mu\text{mol h}^{-1}$ , which is  $1.2\times$  higher than that of  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  (Fig. 5a). We confirmed that 0.1 wt% vs.  $\text{SrTiO}_3\text{:Al}$  is an optimum amount of Co in the range of 0.05–0.2 wt% (Fig. S15<sup>†</sup>). Other well-known OER cocatalysts like  $\text{NiO}_x$  and  $\text{IrO}_x$  were also tested as additives on  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  but their activities did not exceed the  $\text{CoO}_x + \text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  (Fig. S16<sup>†</sup>). We calculated the AQY of  $\text{CoO}_x + \text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  to be  $33 (\pm 4)\%$  at 365 nm. The solar-to-hydrogen efficiency (STH) was estimated to be 0.21% (Fig. S17<sup>†</sup>). The stability was also improved by co-loading  $\text{CoO}_x$  with  $\text{RhZrO}_x$  (Fig. 5b). Because  $\text{CoO}_x/\text{SrTiO}_3\text{:Al}$  showed much lower activity for HER (Fig. 5a and b), we conclude that coexistence of  $\text{CoO}_x$  and  $\text{RhZrO}_x$  has a synergetic effect on the catalytic activity. In the case of the  $\text{CoO}_x + \text{RhCrO}_x$  combination,  $\text{CoO}_x$  promotes hole extraction from  $\text{SrTiO}_3\text{:Al}$ , which disrupts hole migration to  $\text{RhCrO}_x$  to suppress the degradation,<sup>21</sup> and also catalyzes water oxidation. We consider that this positive effect would also be effective for  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$ . 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  $\text{H}_2/\text{O}_2$  molar ratio of approximately 2 (Fig. 5c and d), indicating the robustness of  $\text{CoO}_x + \text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$ .

Although we have shown the superior catalytic performance of  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$ , the activity is still less than that of  $\text{RhCrO}_x/\text{SrTiO}_3\text{:Al}$ , which has a >50% AQY at 365 nm (Table S3<sup>†</sup>).<sup>15</sup> In the  $\text{Rh@Cr}_2\text{O}_3$  cocatalyst, the  $\text{Cr}_2\text{O}_3$  layer suppresses only the ORR and does not hinder the HER of Rh.<sup>11</sup> This seems to be one of the reasons why  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  has less activity than  $\text{RhCrO}_x/\text{SrTiO}_3\text{:Al}$ . To enhance the activity of  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$ , doping foreign metals into  $\text{ZrO}_2$  may increase proton conductivity.<sup>28</sup> This strategy may help proton penetration towards the Rh reaction centres to evolve a larger quantity of  $\text{H}_2$ . Robot-

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

## Conclusions

We demonstrated that a Rh–Zr mixed oxide efficiently functions as a HER cocatalyst on  $\text{SrTiO}_3\text{:Al}$ . The active phase for HER,  $\text{RhZrO}_x$ , formed by spontaneous Cl-dissolution-assisted activation of the Rh–Cl–Zr–O solid solution. Unexpected  $\text{Cl}^-$  contamination was found to sacrificially assist the formation of suitable spatial distributions of  $\text{Rh}^{3+}$  and  $\text{Zr}^{4+}$  in  $\text{RhZrO}_x$  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,  $\text{CoO}_x$ , further improved the photocatalytic activity and stability of  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$ . 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.

## Acknowledgements

We thank H. Tokudome and S. Okunaka of TOTO Ltd. for preparing  $\text{SrTiO}_3\text{:Al}$ . This work was partly supported by the Artificial Photosynthesis Project of the New Energy and Industrial Technology Development Organization (NEDO) of Japan and JSPS KAKENHI for Scientific Research S (Grant No. JP19H0563) (T. T.), and Young Scientists B (Grant No. 17K14081) (M. S.).

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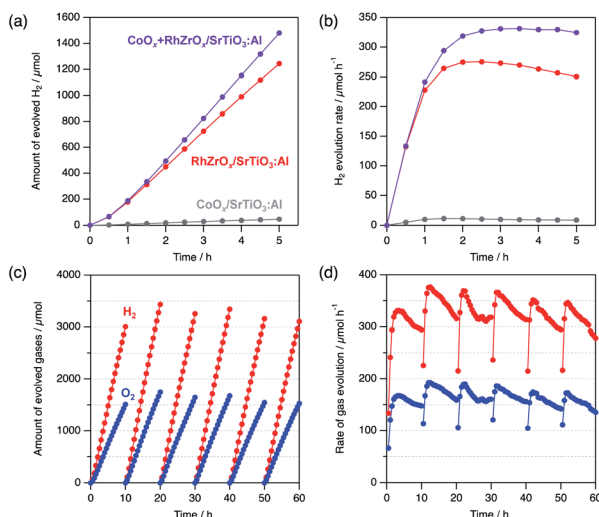


Fig. 5 (a) Quantity of evolved  $\text{H}_2$  and (b)  $\text{H}_2$  evolution rate of  $\text{CoO}_x + \text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$ ,  $\text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  and  $\text{CoO}_x/\text{SrTiO}_3\text{:Al}$ . (c) Quantity of evolved gases and (d) evolution rate of gases of  $\text{CoO}_x + \text{RhZrO}_x/\text{SrTiO}_3\text{:Al}$  in a long-term test for 60 h. Red and blue circles represent  $\text{H}_2$  and  $\text{O}_2$ , respectively. Reaction conditions: catalyst, 10 mg; solution, 20 mL of  $\text{H}_2\text{O}$ ; light source, 300 W Xe lamp ( $\lambda = 300\text{--}450$  nm).



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