## Supplementary Information

## Improved water oxidation activity of a Sillén SrBi<sub>3</sub>O<sub>4</sub>Cl<sub>3</sub> photocatalyst prepared by flux method with an appropriate binary-component molten salt

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Fig. S1 XRD patterns of the samples prepared *via* flux method with NaCl (at 1123 K), KCl (at 1073 K), RbCl (at 1023 K), CsCl (at 923 K), SrCl<sub>2</sub> (at 1173 K).



Fig. S2 Structural model of  $NaBi_3O_4Cl_2$ 



Fig. S3 Thermodynamic phase diagrams of MCI/SrCl<sub>2</sub> (M = (a) Na, (b) K, (c) Rb, (d) Cs) (reproduced from FACT salt database).<sup>1</sup> The grey dash lines represent the mixture molar-ratio of MCl and SrCl<sub>2</sub> (0.5:0.5) in the synthetic condition shown in Fig. 1.



Fig. S4 XRD patterns of the samples prepared *via* flux method with  $CsCl/SrCl_2$  at 973 and 1123 K. 1123 K is higher than melting point of  $CsCl/SrCl_2$  (1115 K).



Fig. S5 XRD patterns of the samples prepared *via* flux method with (a) NaCl (at 1123 K) and NaCl/SrCl<sub>2</sub> (at 973 K), (b) KCl (at 1073 K) and KCl/SrCl<sub>2</sub> (973 K). The calculated XRD patterns for Sr<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> (M = Na, K) were obtained from computer program VESTA. Crystal structure of Sr<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> (M = Na, K) has cubic symmetry with I4/mmm space group and lattice constant of a = b = 3.9323(2) Å, c = 19.345(2) Å (M = Na) and a = b = 3.9235(5) Å, c = 22.081(3) Å (M = K), which are deteremined by Le Bail refinements. This crystal structure is similar to that of Pb<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> (M = Cs).<sup>2</sup> We calculated the XRD patterns of Sr<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> by replacing Pb and Cs with Sr, Na and K in the Pb<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> unit cell and appropriately changing the lattice constant. The calculated XRD patterns match exactly with the experimental and reference XRD patterns, thus confirming the crystal structure.



Fig. S6 XRD patterns of the samples prepared *via* flux method with (a) RbCl (at 1023 K) and NaCl/SrCl<sub>2</sub> (at 973 K), (b) CsCl (at 923 K) and CsCl/SrCl<sub>2</sub> (973 K). The calculated XRD patterns for Sr<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> (M = Rb, Cs) were obtained from computer program VESTA. Crystal structure of Sr<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> (M = Rb, Cs) has cubic symmetry with I4/mmm space group and lattice constant of a = b = 3.8980(3) Å, c = 19.9012(16) Å (M = Rb) and a = b = 3.90725(15) Å, c = 20.5745(11) Å (M = Cs), which are deteremined by Le Bail refinements. This crystal structure is similar to that of Pb<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> (M = Rb, Cs).<sup>2,3</sup> We calculated the XRD patterns of Sr<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> by replacing Pb with Sr in the Pb<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> unit cell and appropriately changing the lattice constant. The calculated XRD patterns match exactly with the experimental and reference XRD patterns, thus confirming the crystal structure.



Fig. S7 XRD patterns of the samples prepared *via* flux method with  $KCl/SrCl_2$  at different temperatures (823 – 1023 K).



Fig. S8 XRD patterns of the samples prepared *via* solid-state reaction (SSR) method at different temperatures (at 873-973 K).



Fig. S9 SEM images of the SrBi $_3O_4Cl_3$  samples prepared *via* (a-c) flux method with KCl/SrCl $_2$  and (d–f) SSR method (at 873, 923, 973 K).



Fig. S10 XP spectrum of the  $SrBi_3O_4Cl_3$  sample prepared *via* flux method (at 973 K) in the K 2p regions. The binding energy of elemental K was referred to form reference handbook.<sup>4</sup>



Fig. S11 EUPS spectra of  $SrBi_3O_4Cl_3$  samples prepared *via* flux method (KCl/SrCl<sub>2</sub>) and solid-state reaction (at 973 K) in (a) the Cl 2p and (b) Bi 4f regions.

-state rection (at	873, 923, 973 K).		
	Temperature / K	flux	SSR
	072	0.0	0.0

Table S1 Cl/Bi atomic ratios (EDX) of  $SrBi_3O_4Cl_3$  samples prepared *via* flux method (KCl/SrCl<sub>2</sub>) and solid-state rection (at 873, 923, 973 K).

Temperature / K	TIUX	22K
873	0.9	0.8
923	0.9	0.8
973	1.0	0.8



Fig. S12 (a) Schematic illustration of the experimental setup for the anisotropic TRMC measurement. (b-d) Anisotropic TRMC transients of SrBi<sub>3</sub>O<sub>4</sub>Cl<sub>3</sub> samples prepared *via* the flux method (KCl/SrCl<sub>2</sub> flux) and solid-state reaction method at (b) 873 K, (c) 923 K, (d) 973 K in the incident microwave's directions horizontal and vertical to a quartz substrate. The incident direction affects TRMC signal probably due to orientation of particles possessing layered structure with anisotropic carrier mobilities.<sup>5,6</sup> However, TRMC signals for both directions by flux synthesis are higher than SSR although the orientations of the flux samples are different from those of the SSR samples (Fig. S9). This shows SrBi<sub>3</sub>O<sub>4</sub>Cl<sub>3</sub> samples produced by flux method have excellent carrier transport properties compared to SSR.



Fig. S13 Fitting of the TRMC kinetics of SrBi<sub>3</sub>O<sub>4</sub>Cl<sub>3</sub> prepared by (a) flux method at 973 K and SSR method at (b) 973 and (c) 1023 K using biexponential function  $(A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t))$  (the solid black line). The SSR sample at 1023 K was synthesized to investigate the Cl defects on the effective lifetime of  $(\tau_{eff} = (A_1 + A_2)(A_1k_1 + A_2k_2)^{-1})$  of the TRMC signals for the SrBi<sub>3</sub>O<sub>4</sub>Cl<sub>3</sub> samples. The lifetime (9.1 × 10<sup>-6</sup> s) of the SSR sample at 1023 K with higher Cl defects (i.e., Cl/Bi = 0.87 determined by XPS measurement) was shorter than that  $(1.3 \times 10^{-5} s)$  of the SSR sample at 973 K with lower Cl defects (i.e., Cl/Bi = 0.91). This result suggested the Cl defects contributed to the lifetimes.



Fig. S14 (a) XRD patterns of the samples prepared *via* flux method (with KCl/SrCl<sub>2</sub>) at 873, 923, 948, 973 K. (b) their FWHM of the (107) diffraction peak of the XRD patterns and (c) their initial rates of the O<sub>2</sub> evolution in an aqueous AgNO<sub>3</sub> solution (5 mM, 180 mL) under visible light irradiation ( $\lambda$  > 400 nm). To optimize the photocatalytic activity in the flux sample, we synthesized the flux sample at 948 K between at 923 and 973 K, which showed an intermediate photocatalytic activity.



Fig. S15 Time course of O<sub>2</sub> evolution over a SrBi<sub>3</sub>O<sub>4</sub>Cl<sub>3</sub> sample prepared *via* flux method (KCl/SrCl<sub>2</sub>) at 973 K in an aqueous Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution (5 mM, 180 mL, at pH = 2.4) under visible light irradiation ( $\lambda > 400$  nm). The photocatalytic activity in second run remains 86 % of that in first run. This result supported the reusability of the photocatalyst.



Fig. S16 XRD patterns of the SrBi<sub>3</sub>O<sub>4</sub>Cl<sub>3</sub> samples prepared *via* flux method (KCl/SrCl<sub>2</sub>) at 973 K before and after the O<sub>2</sub> evolution reaction from Fe<sup>3+</sup> electron acceptor shown in Fig. S15. The XRD patterns of SrBi<sub>3</sub>O<sub>4</sub>Cl<sub>3</sub> after the reaction was no changed, which supported the stability.



Fig. S17 Time course of H<sub>2</sub> and O<sub>2</sub> evolution using a mixture of RuO<sub>x</sub>-loaded SrBi<sub>3</sub>O<sub>4</sub>Cl<sub>3</sub> sample (50 mg) prepared *via* flux method (KCl/SrCl<sub>2</sub>) at 973 K and Ru/SrTiO<sub>3</sub>:Rh (50 mg) in an aqueous Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution (1 mM, 120 mL, at pH = 2.4) under visible light irradiation ( $\lambda$  > 400 nm). The RuO<sub>x</sub> was loaded *via* impregnation method with Ru(acac)<sub>3</sub>.<sup>7</sup> The gas phase was evacuated after the initial 5 h operation. The molar ratio of H<sub>2</sub> to O<sub>2</sub> produced during the 20 h operation was approximately 2:1.



Sr<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> (M = Na, K, Rb, Cs)

Fig. S18 Structural model of Sr<sub>0.6</sub>Bi<sub>1.4</sub>M<sub>0.6</sub>O<sub>2</sub>Cl<sub>2</sub> (M = Na, K, Rb, Cs), which is viewed from different direction in Fig. 1b.



Fig. S19 UV-vis diffuse reflectance spectra of  $SrBi_3O_4Cl_3$ , BiOCl, and  $Sr_{0.6}Bi_{1.4}M_{0.6}O_2Cl_2$ (M = K, Rb, Cs).

## **Reference for Supplementary Information**

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