**Electronic Supplementary Information (ESI)**

# Understanding and improving photoelectrochemical performance of Bi₂O₃/Bi₂S₃ composite

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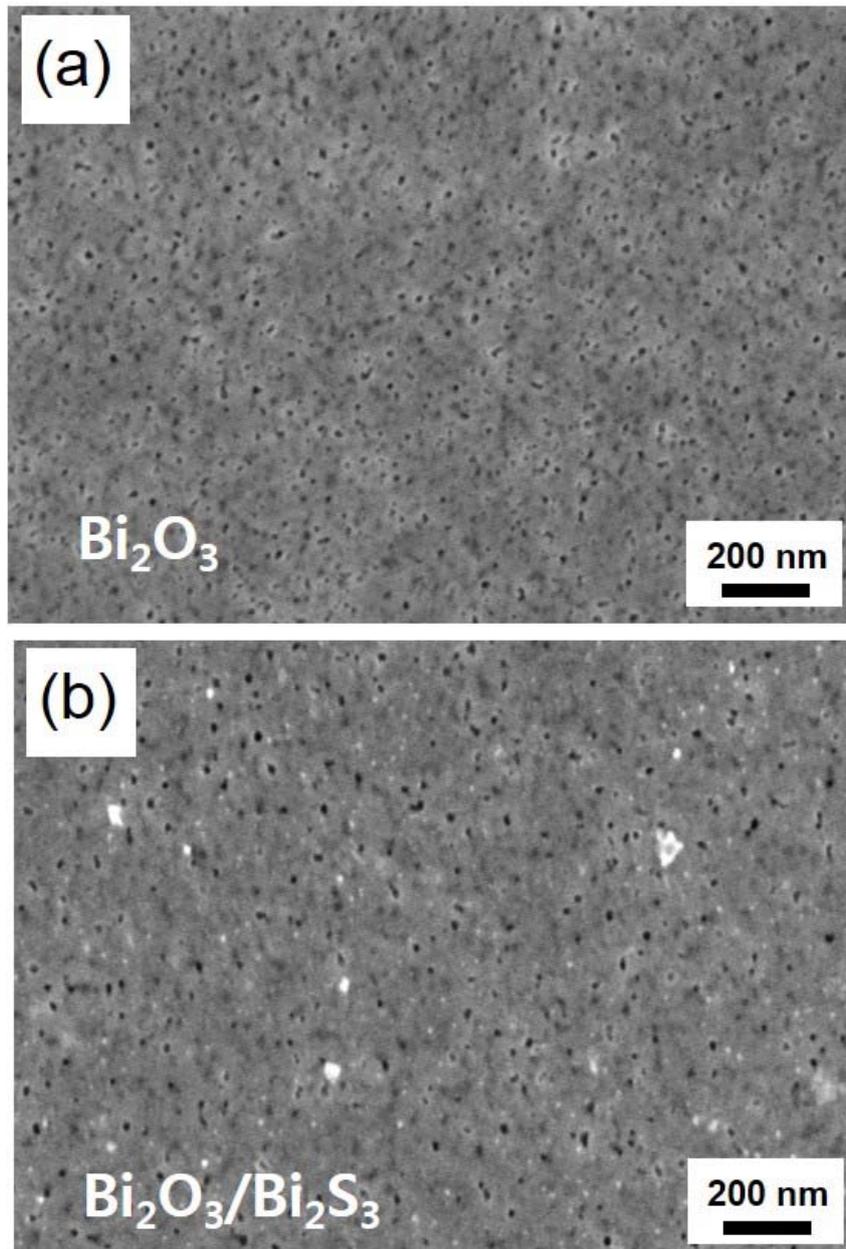[c] Korea Institute of Energy Research (KIER), Daejeon 34129, Republic of Korea.

**Fig. S1** SEM images of (a) $Bi_2O_3$, and (b) $Bi_2O_3/Bi_2S_3$ composite films on the FTO substrate.

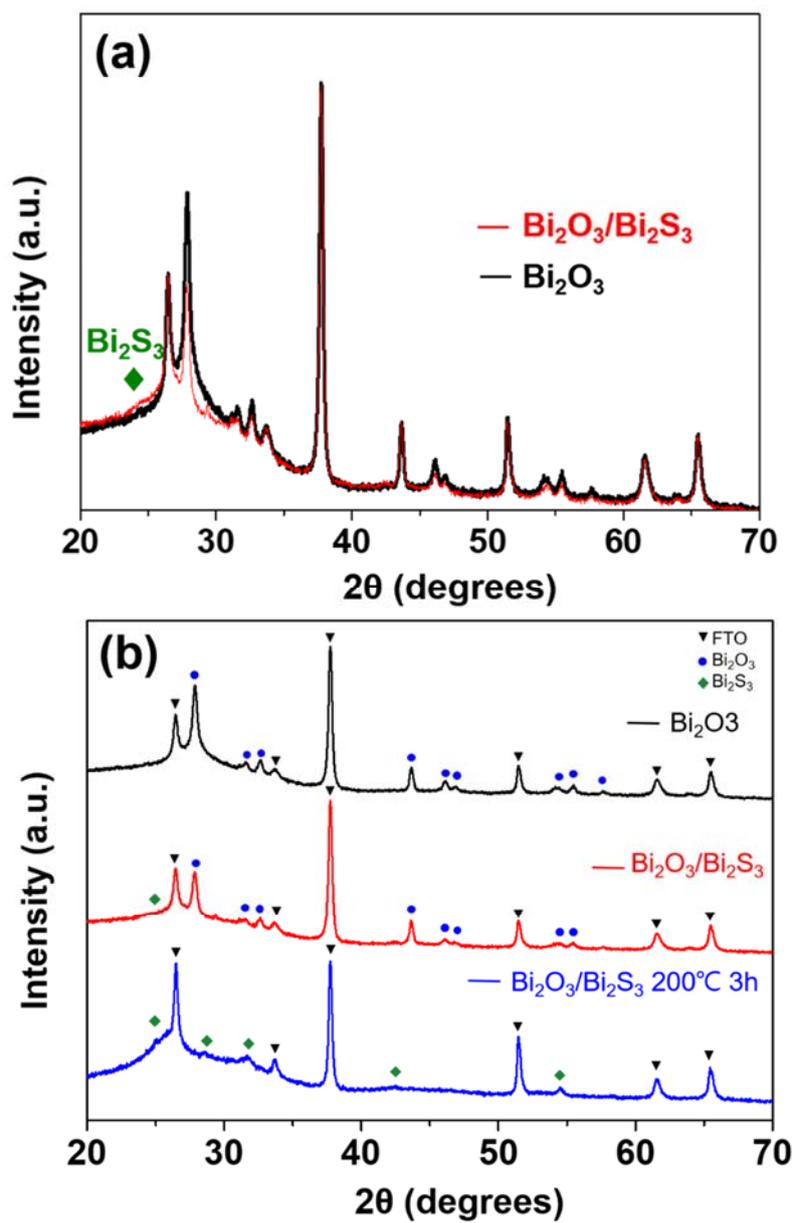**Fig. S2** (a) XRD patterns of $Bi_2O_3/Bi_2S_3$ (red line), and $Bi_2O_3$ (black line) films on the FTO substrate. (b) XRD patterns of $Bi_2O_3$ (black line), $Bi_2O_3/Bi_2S_3$ before (red line) and after (blue line) annealing process at 200 °C for 3h in air.
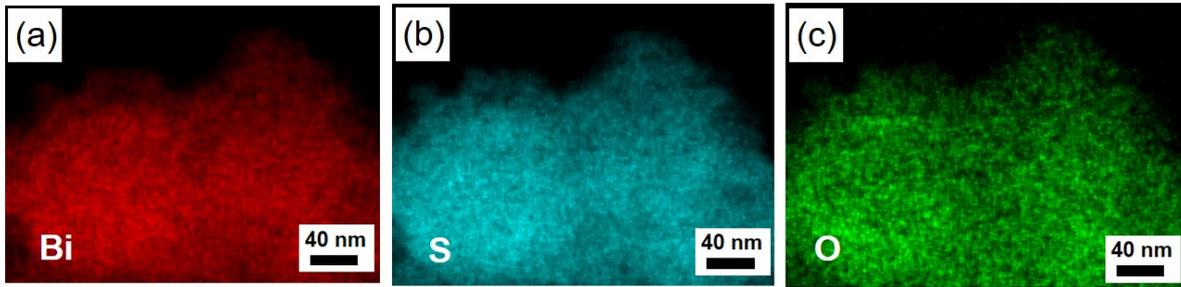
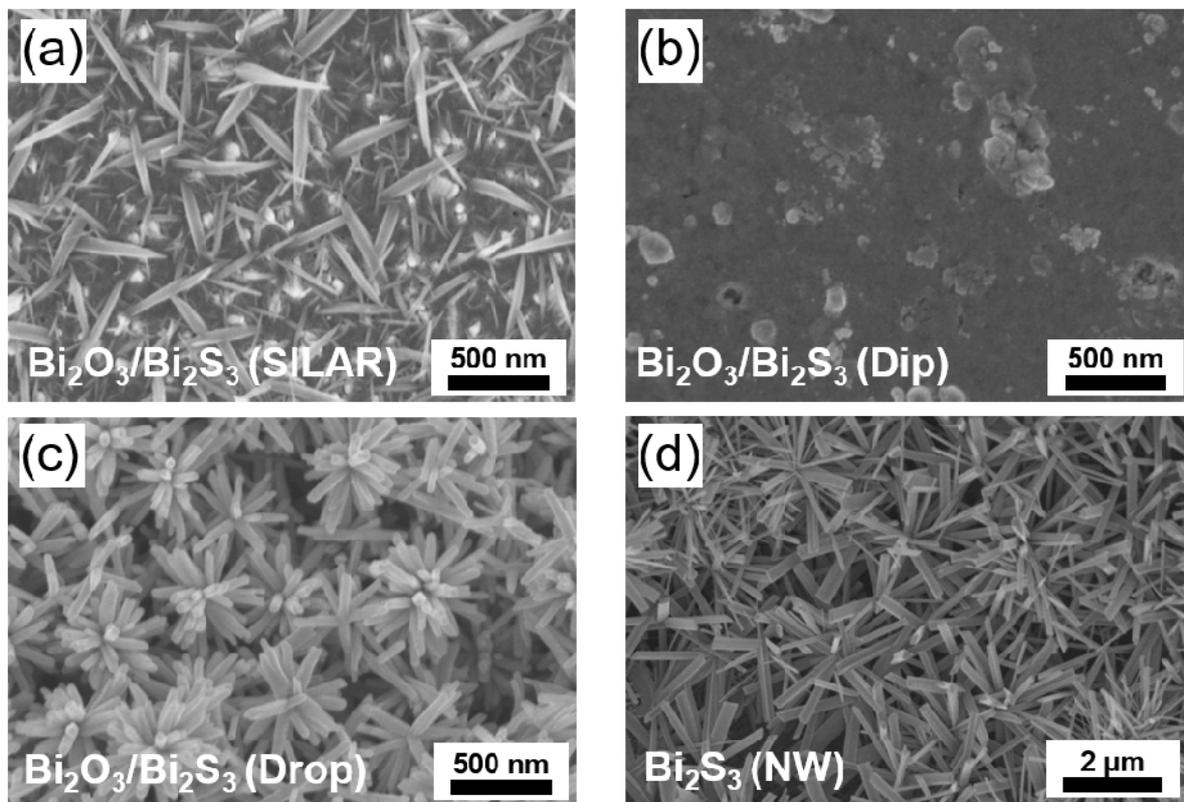**Fig. S3** Element distribution maps of (a) Bi, (b) S, and (c) O on the $Bi_2O_3/Bi_2S_3$(Sono) composite.

**Fig. S4** SEM images of (a) $Bi_2O_3/Bi_2S_3$(SILAR), (b) $Bi_2O_3/Bi_2S_3$(Dip), (c) $Bi_2O_3/Bi_2S_3$(drop), and (d) $Bi_2S_3$NW.
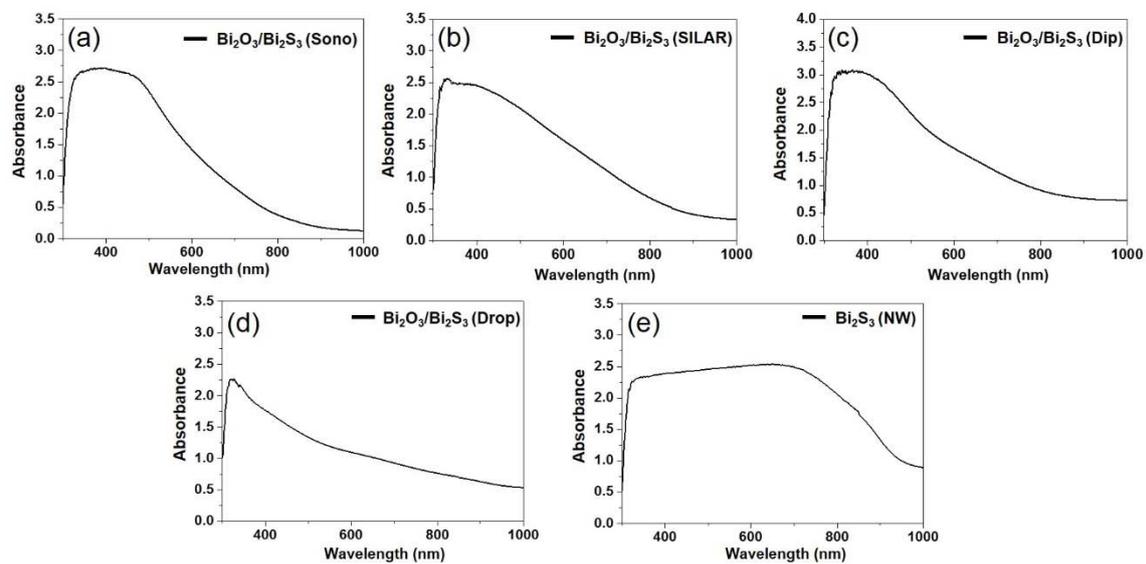
**Fig. S5** UV-visible absorption spectrums of (a) $Bi_2O_3/Bi_2S_3$(Sono), (b) $Bi_2O_3/Bi_2S_3$(SILAR), (c) $Bi_2O_3/Bi_2S_3$(Dip), (d) $Bi_2O_3/Bi_2S_3$(drop), and (e) $Bi_2S_3$NW.
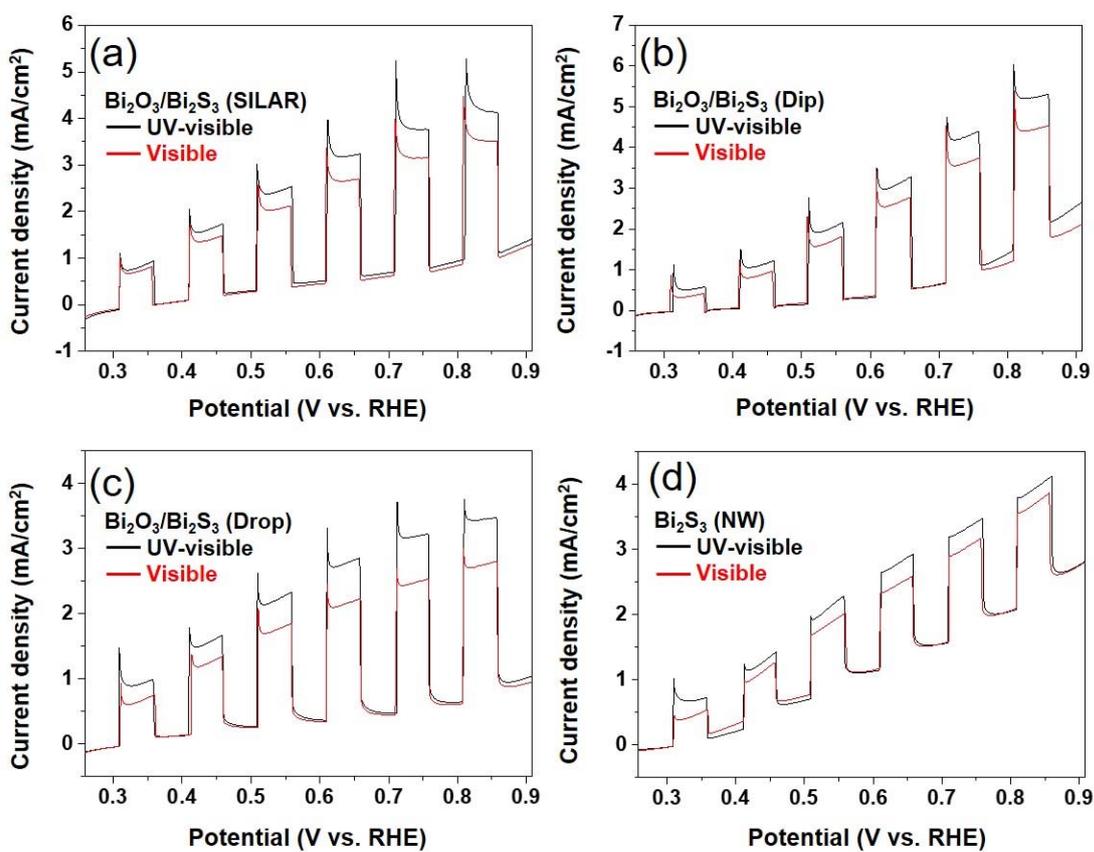
**Fig. S6** LSVs of (a) $Bi_2O_3/Bi_2S_3$(SILAR), (b) $Bi_2O_3/Bi_2S_3$(Dip), (c) $Bi_2O_3/Bi_2S_3$(drop), and (d) $Bi_2S_3$NW electrodes under UV-visible illumination and visible illumination (> 425 nm) in a 0.1 M $Na_2SO_3$ and 0.1 M $Na_2S$ solution. Scan rate: 20 mV/s. Light intensity: 100 mW/cm$^2$.
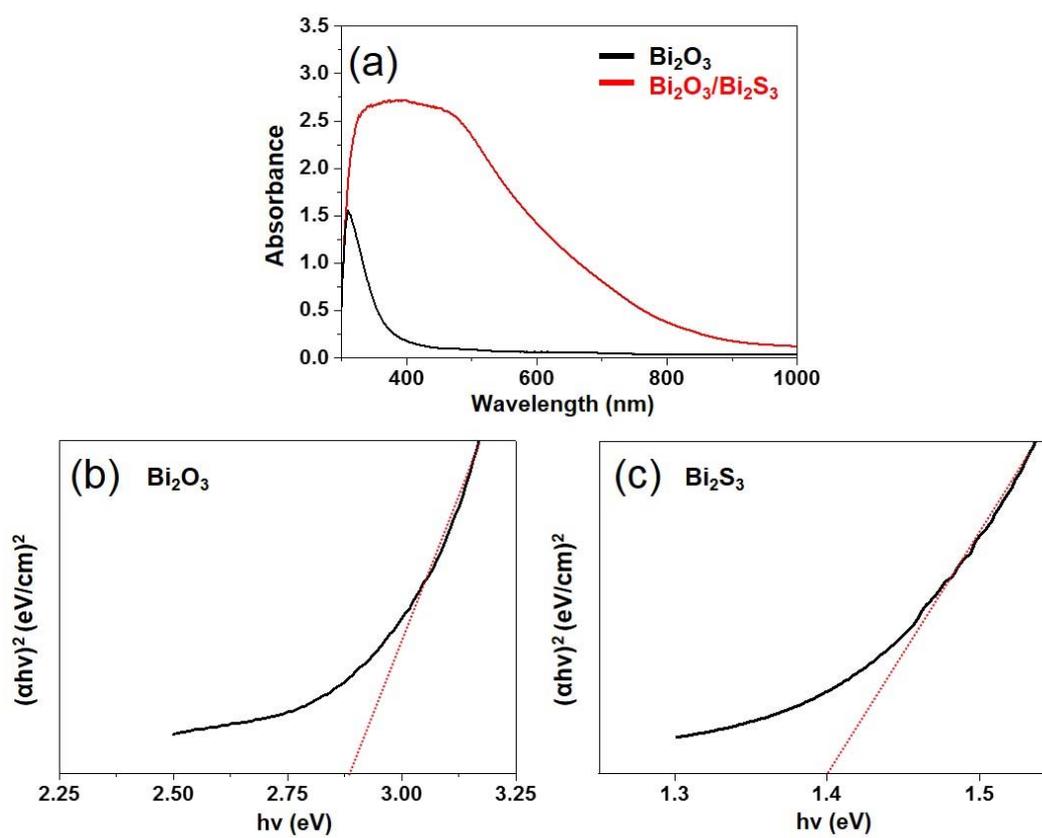
**Fig. S7** (a) UV-visible absorption spectrums of $Bi_2O_3/Bi_2S_3$ (red line), and $Bi_2O_3$ (black line) films. Tauc plots of (b) $Bi_2O_3$, and (c) $Bi_2O_3/Bi_2S_3$ electrodes.
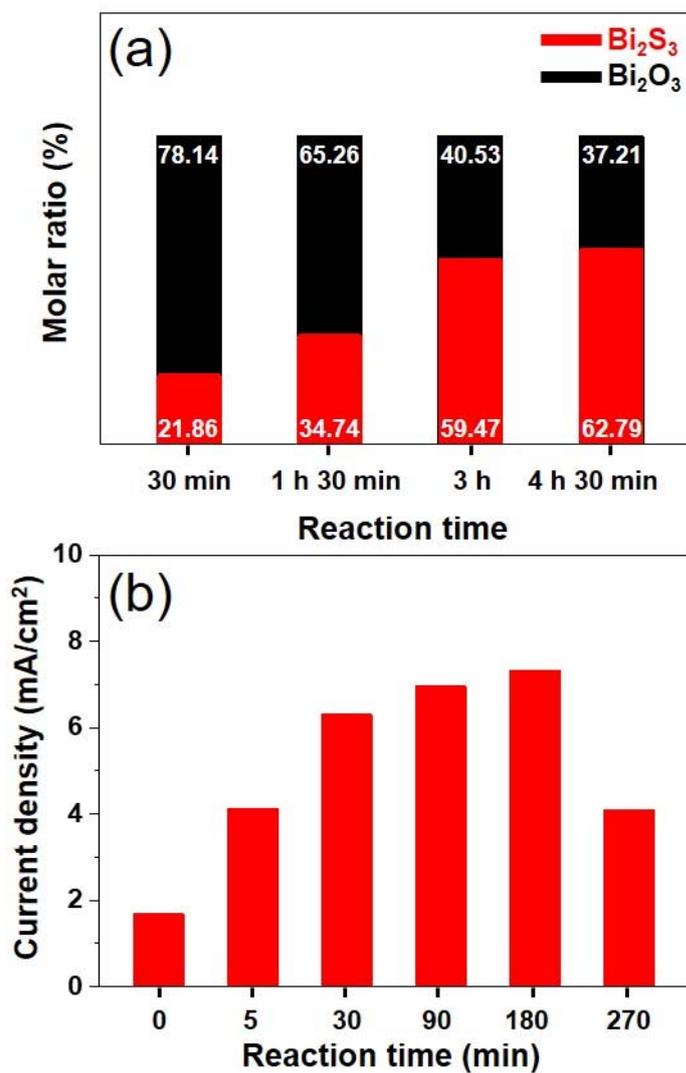
**Fig. S8** (a) The $Bi_2S_3$ to $Bi_2O_3$ molar ratios measured by the energy-dispersive X-ray (EDX) spectroscopy. (b) Photocurrent density as a function of film thickness and reaction period ($Bi_2S_3$ loading amount) at 0.75V vs. RHE.
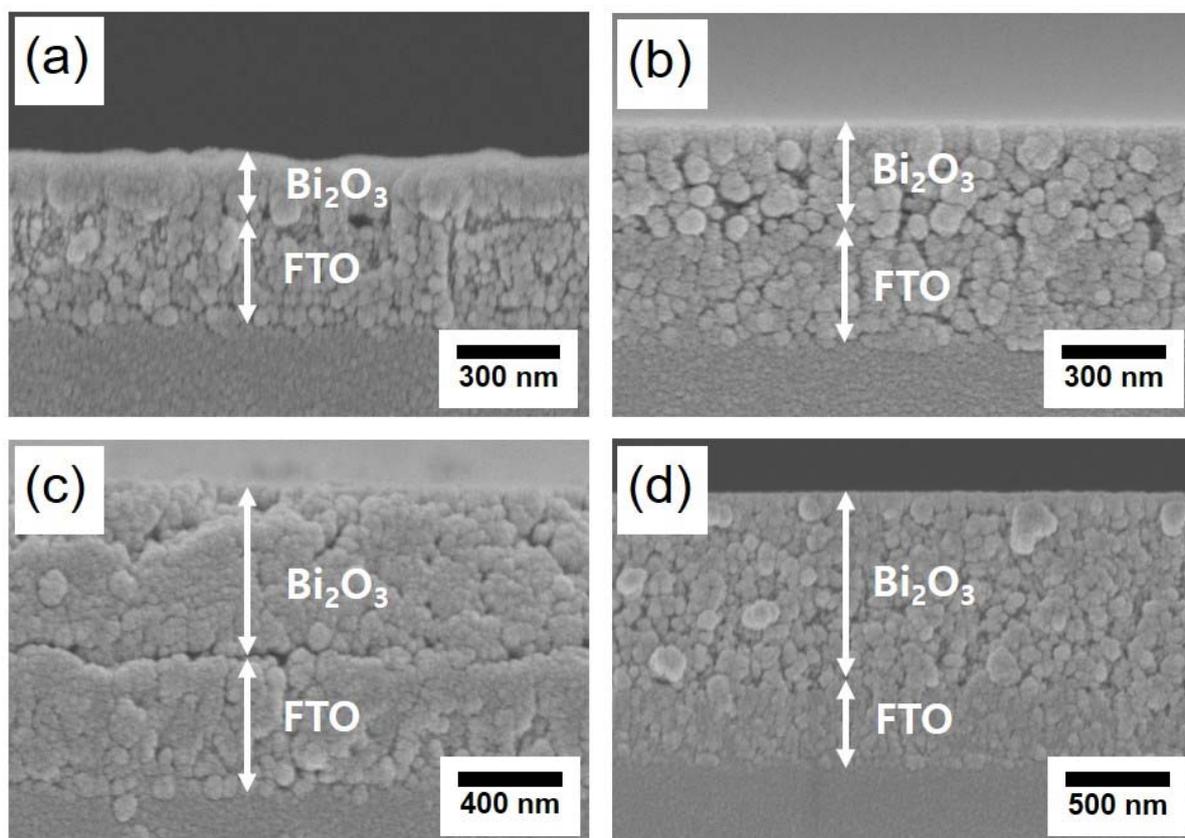
**Fig. S9** SEM cross-section images of the $Bi_2O_3/Bi_2S_3$(Sono) composites depending on the precursor concentrations of (a) 10, (b) 20, (c) 30, and (d) 40 mM.
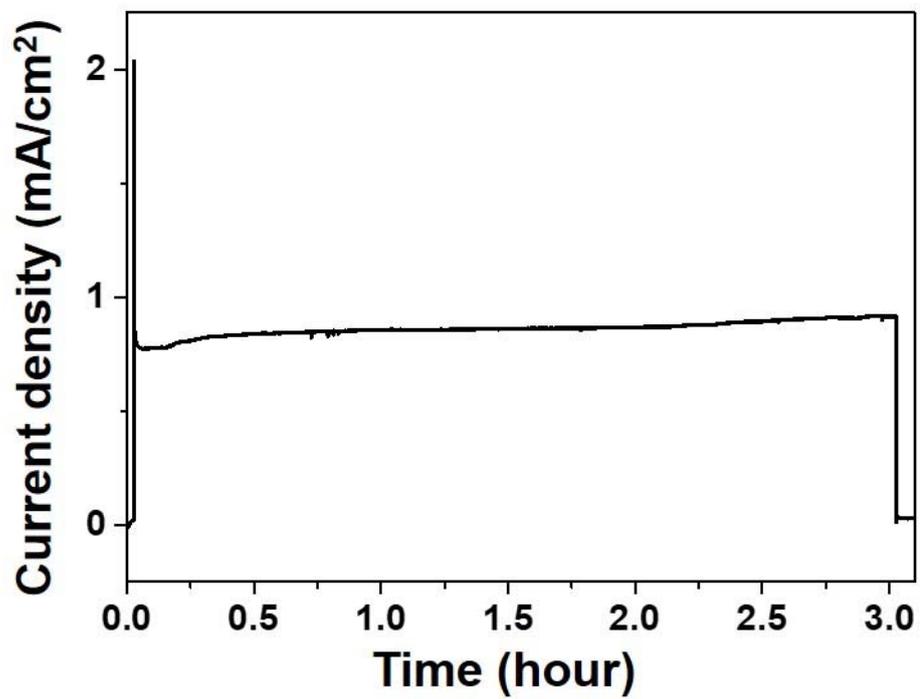
**Fig. S10** Current-time response curve of $Bi_2O_3/Bi_2S_3$(Sono) electrode under UV-visible illumination in 0.4 V vs. RHE in a 0.1 M $Na_2SO_3$ and 0.1 M $Na_2S$ solution. Light intensity: 100 mW/cm$^2$.
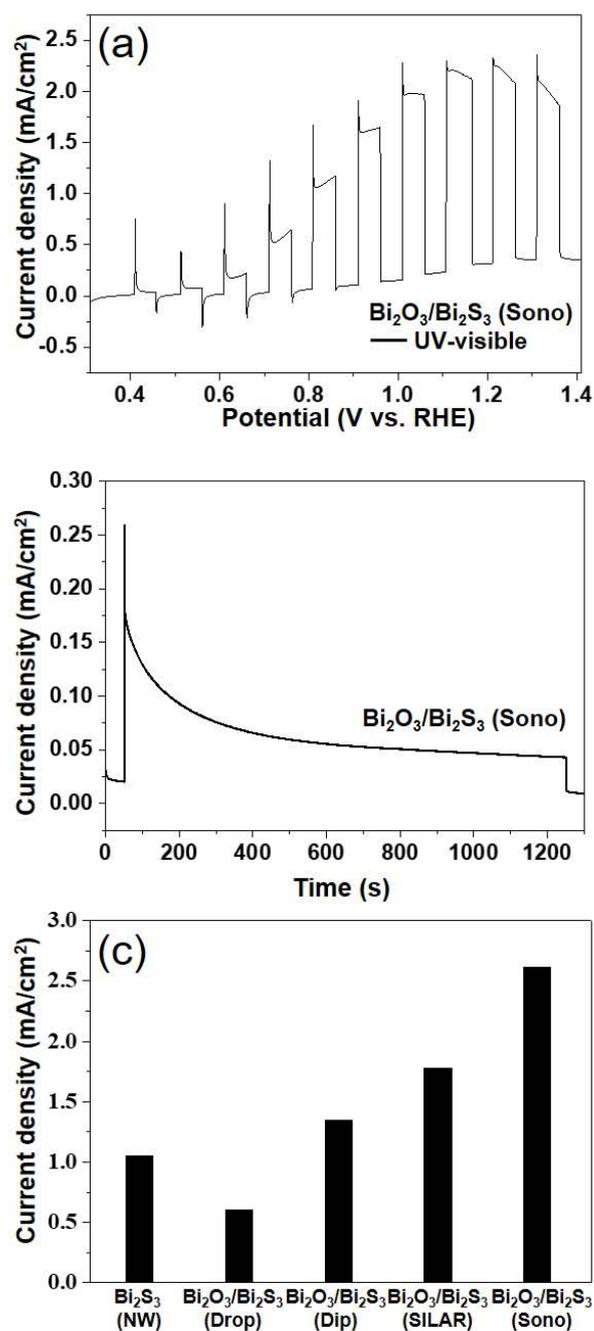
**Fig. S11** (a) LSV, and (b) Current-time response curve (0.1 V vs. Ag/AgCl) of $Bi_2O_3/Bi_2S_3$(Sono) composite under UV-visible illumination in a 0.1 M phosphate buffer (pH 7). Light intensity: 100 mW/cm$^2$. (c) Photocurrent density of electrodes under UV-visible illumination at an applied potential of 1.2 V vs. RHE in a 0.1 M phosphate buffer (pH 7).
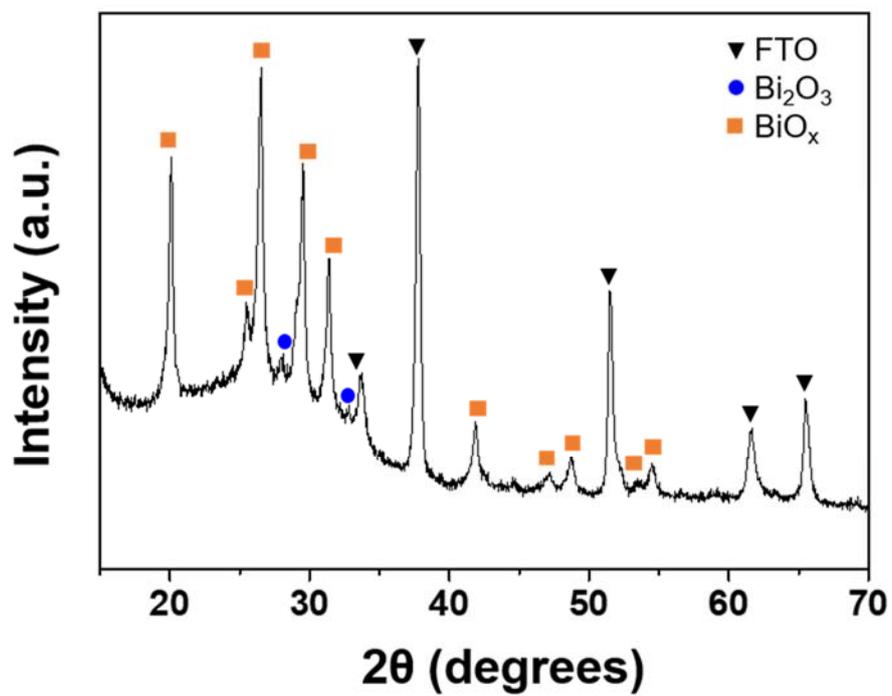
**Fig. S12** XRD patterns of $Bi_2O_3/Bi_2S_3$(Sono) composite after water oxidation indicating that the decomposition of $Bi_2S_3$ in the solution.
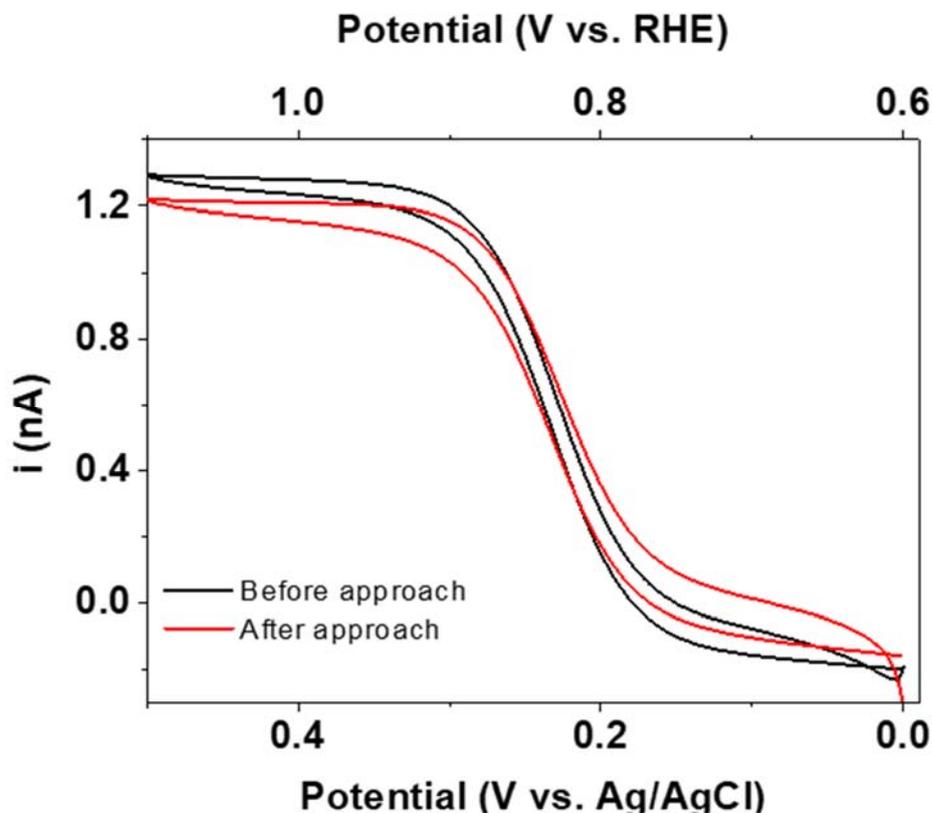
**Fig. S13** Cyclic voltammograms of Pt UME tip measured in 1 mM ferrocene methanol (D = $6.7 \times 10^{-6}$ $cm^2$/s)/0.1 M $Na_2SO_4$ solution before and after approach to the substrate. Assuming that $Bi_2O_3$/$Bi_2S_3$(Sono) substrate is almost insulating at the open circuit under dark, the normalized current ($I_T$) for the negative feedback $Bi_2O_3$/$Bi_2S_3$(Sono) substrate can be defined as;[1]

$$I_T(L) = \frac{i_T}{i_{T,\infty}} = \left[0.292 + \frac{1.515}{(d/a)} + 0.6553\exp(-2.4035/(d/a))\right]^{-1}$$

where $i_T$ and $i_{T,\infty}$ are the steady-state tip current when the tip is close to the substrate, and far from the substrate, respectively, and $d$ is distance from substrate. For cyclic voltammogram, the measured $i_T$ and $i_{T,\infty}$ were $1.2 \times 10^{-9}$ A and $1.3 \times 10^{-9}$ A, respectively. Consequently, d is obtained as 15 μm according to the above equation.

[1] A. J. Bard, L. R. Faulkner, John Wiley & Sons, Inc., (2001) 34.