

# Supporting Information

## Compositional Screening of the Pb-Bi-Mo-O System. Spontaneous Formation of a Composite of p-PbMoO<sub>4</sub> and n-Bi<sub>2</sub>O<sub>3</sub> with Improved Photoelectrochemical Efficiency and Stability

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### Experimental Section

**Materials.** Fluorine-doped tin oxide (FTO, TEC 15, Pilkington, Toledo, OH) coated glass was used as the substrate for both the spot array electrodes and the bulk film electrodes. Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (99.999%), Pb(NO<sub>3</sub>)<sub>2</sub> (99.99%), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (99.98%), were obtained from Strem Chemicals (Newburyport, MA). Na<sub>2</sub>HPO<sub>4</sub> (99.9%), NaH<sub>2</sub>PO<sub>4</sub> (99.5%), CH<sub>3</sub>OH (99.8 %), and ethylene glycol were purchased from Fisher Scientific (Pittsburgh, PA), and used as received. Deionized Milli-Q water was used as the solvent in electrochemical experiments.

**Preparation of Photocatalyst Array.** Spot array electrodes were created using a CH Instruments model 1550 dispenser (Austin, TX) with a piezoelectric dispensing tip (MicroJet AB-01-60, MicroFab, Plano, TX) connected to an XYZ stage driven by a computer-controlled stepper-motor system (Newport).<sup>1</sup> The FTO substrate electrode was cleaned with Milli-Q water, and ethanol and then sonicated in ethanol for at least 30 minutes. Before dispensing, FTO substrates were allowed to dry at room temperature in air for at least 48 hours. Metal precursor solutions (20 mM in ethylene glycol) were dispensed on the FTO substrate to create the spot array electrode. This was done by moving the piezo-dispensing tip to a programmed position over the FTO substrate and dispensing drops (~100 pL/drop) of the precursor solution by applying a potential of 80 V for 200 μs to the piezo-dispensing tip. The lead precursor solution (Pb(NO<sub>3</sub>)<sub>2</sub>) was dispensed first in a preprogrammed pattern onto the FTO substrate, followed by

a second ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) and third ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) metal precursor solution dispensed onto the FTO in an overlay pattern. The distance between photocatalyst spots on the array was about 600  $\mu\text{m}$  with a spot diameter of approximately 300  $\mu\text{m}$ . Each spot had a total of 9 drops and the spot composition was determined by the relative number of drops of each precursor solution. The prepared arrays were annealed at 600  $^\circ\text{C}$  for 3 h (with a 9 hour ramp time) in air to form the metal oxide composite materials.

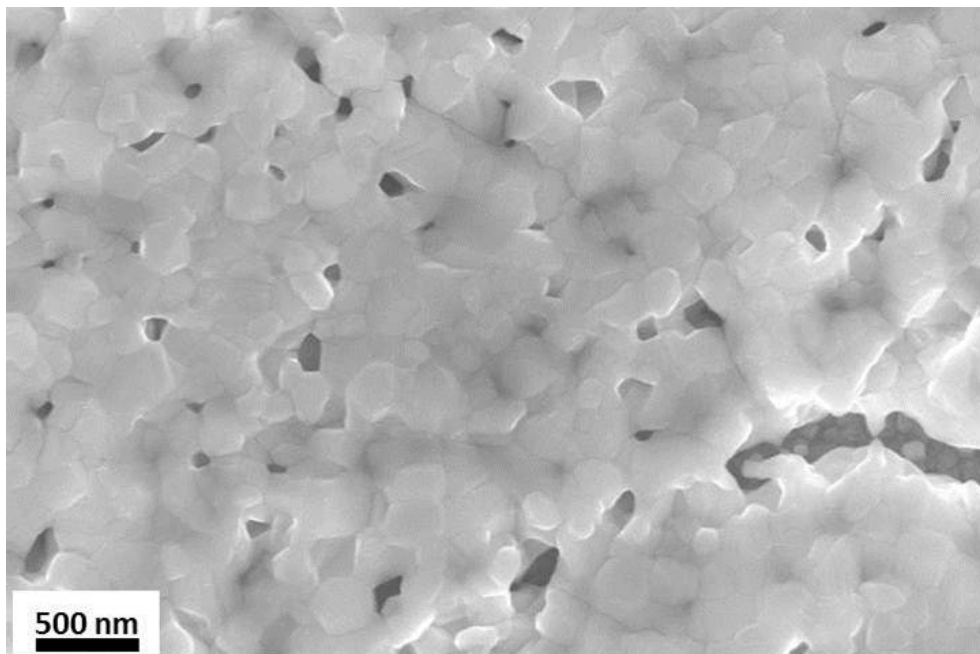
**Screening of the Spot Arrays.** A schematic of a scanning photoelectrochemical microscopy (SPECM) setup has been described previously.<sup>1</sup> Briefly, a 400  $\mu\text{m}$  diameter optical fiber was connected to a 150 W Xenon lamp (Oriental) and was attached to the tip holder of a CHI 900B SECM. The photocatalyst array was used as the working electrode and was placed in the bottom of a specially designed Teflon SECM cell with an O-ring (exposed area:  $\sim 1.0 \text{ cm}^2$ ). A Pt wire was used as the counter electrode and a KCl-saturated Ag/AgCl electrode was used as the reference electrode. The electrolyte consisted of 0.1 M  $\text{Na}_2\text{SO}_4$  and 0.2 M sodium phosphate buffer (pH 7, Air). Light from the Xenon lamp was passed through the optical fiber, positioned perpendicular to the working electrode approximately 200  $\mu\text{m}$  above the surface, to illuminate the working electrode. The optical fiber tip was scanned across the spot array electrode with a scan rate of 500  $\mu\text{m}/\text{s}$ , while a potential of 0 V vs. Ag/AgCl was applied to the working electrode through the SECM potentiostat. Scanning over the spot arrays revealed two-dimensional images indicative of the generation of photocurrent on each spot.

**Preparation of  $\text{PbMoO}_4/\text{Bi}_2\text{O}_3$  Bulk Film Electrodes.** FTO substrates were first cleaned using the method described above. A drop-casting technique was used to create the bulk film electrodes. A 200  $\mu\text{L}$  of a Pb, Bi, and Mo precursor (20 mM each) in ethylene glycol was dropped onto the FTO substrate ( $\sim 1.5 \text{ cm} \times 1.5 \text{ cm}$ ). After drop-casting, the bulk film electrode was annealed using the same conditions as the spot array electrode. The synthetic procedures of  $\text{PbMoO}_4$  and  $\text{Bi}_2\text{O}_3$  film were identical to the ones used to prepare  $\text{PbMoO}_4/\text{Bi}_2\text{O}_3$  bulk film.

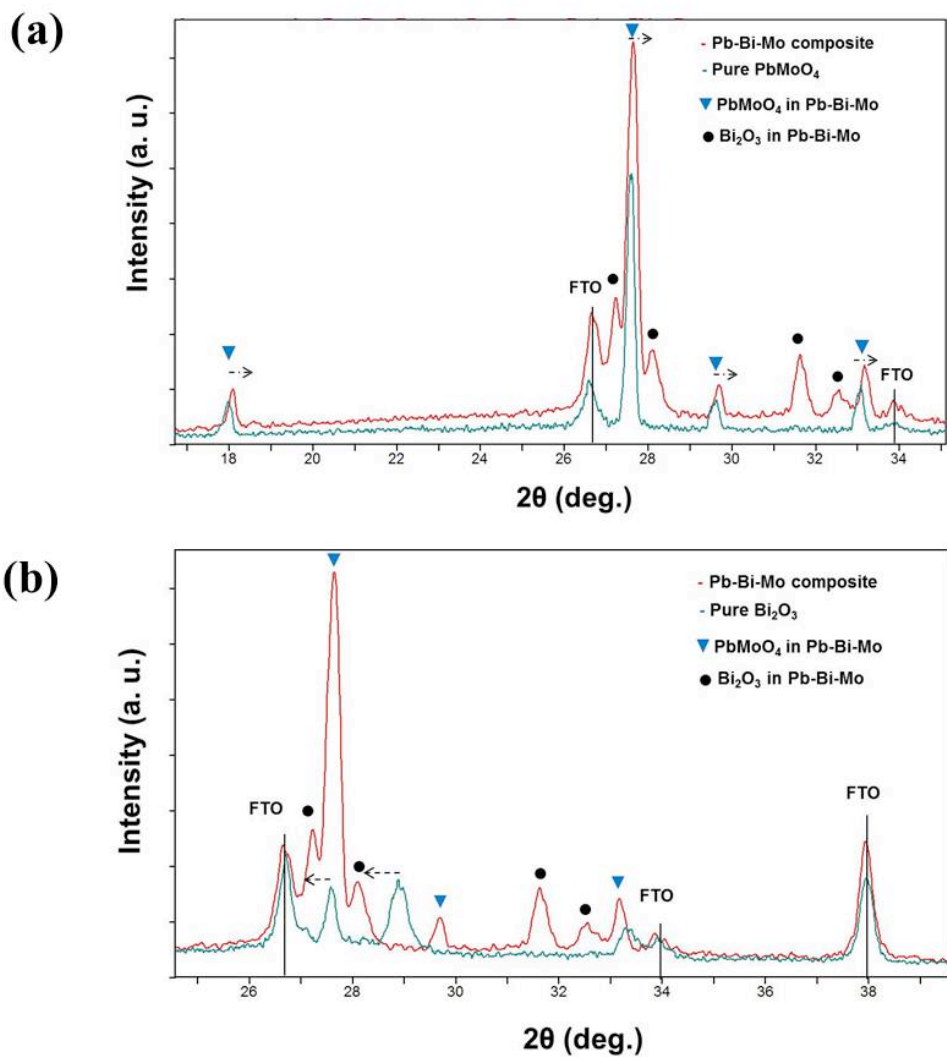
**Photoelectrochemical Characterization of Bulk Film Electrodes.** Photoelectrochemical characterization was performed in a specially designed borosilicate glass U-type cell in a 3-electrode configuration with the bulk film as the working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. The working electrode area exposed to the electrolyte was 0.27  $\text{cm}^2$ . The same 150 W Xe lamp (Oriental) was used as the light source in the PEC characterization. The PEC measurements were performed in aqueous solutions of 0.1 M  $\text{Na}_2\text{SO}_4$  for  $\text{H}^+$  reduction (argon bubbling) and  $\text{O}_2$  reduction (air bubbling) at pH 7 with 0.2 M phosphate buffer. In all tests, the intensity of the lamp on the sample was measured to be 100  $\text{mW}/\text{cm}^2$

using an optical power meter (1830-C, Newport) with a silicon detector (818-UV, Newport) and an attenuator (OD3, Newport). All samples were measured under front illumination. A monochromator (Photon Technology International, Birmingham, NJ) was used to obtain incident photon to current conversion efficiencies (IPCE (%) =  $1240 (i_{\text{ph}}/\lambda P_{\text{in}}) \times 100$ ). Chopped light linear sweep voltammetry was performed to obtain the photocurrent response of the bulk films using a CH Instruments Model 630 potentiostat (Austin, TX).

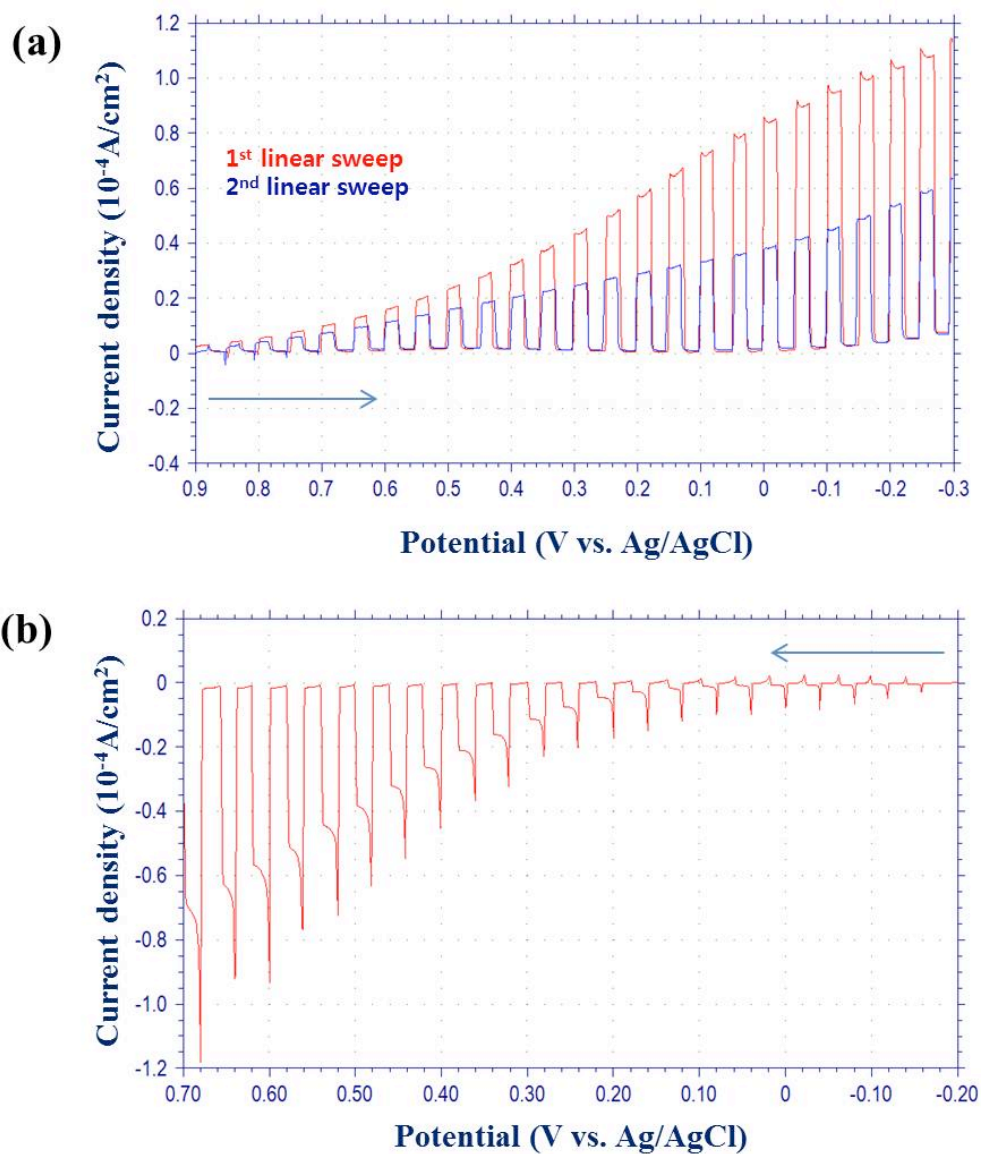
**Characterization.** X-ray diffraction (XRD) measurements were performed using a Bruker-Nonius D8 advanced powder diffractometer (Madison, WI) operated at 40 kV and 40 mA with Cu K $\alpha$  radiation. UV/visible absorption spectra were acquired with a Milton Roy Spectronic 3000 array spectrophotometer (New Rochelle, NY) for wavelengths from 300 to 900 nm. The evolved H<sub>2</sub> gas on the electrode was gathered using a gas tight syringe and qualitatively analyzed using gas chromatography-mass spectroscopy (GC-2014, Shimadzu Scientific Instruments, Columbia, MD) equipment. There is no hydrogen peak in the gas chromatography-mass spectroscopy from the blank test.



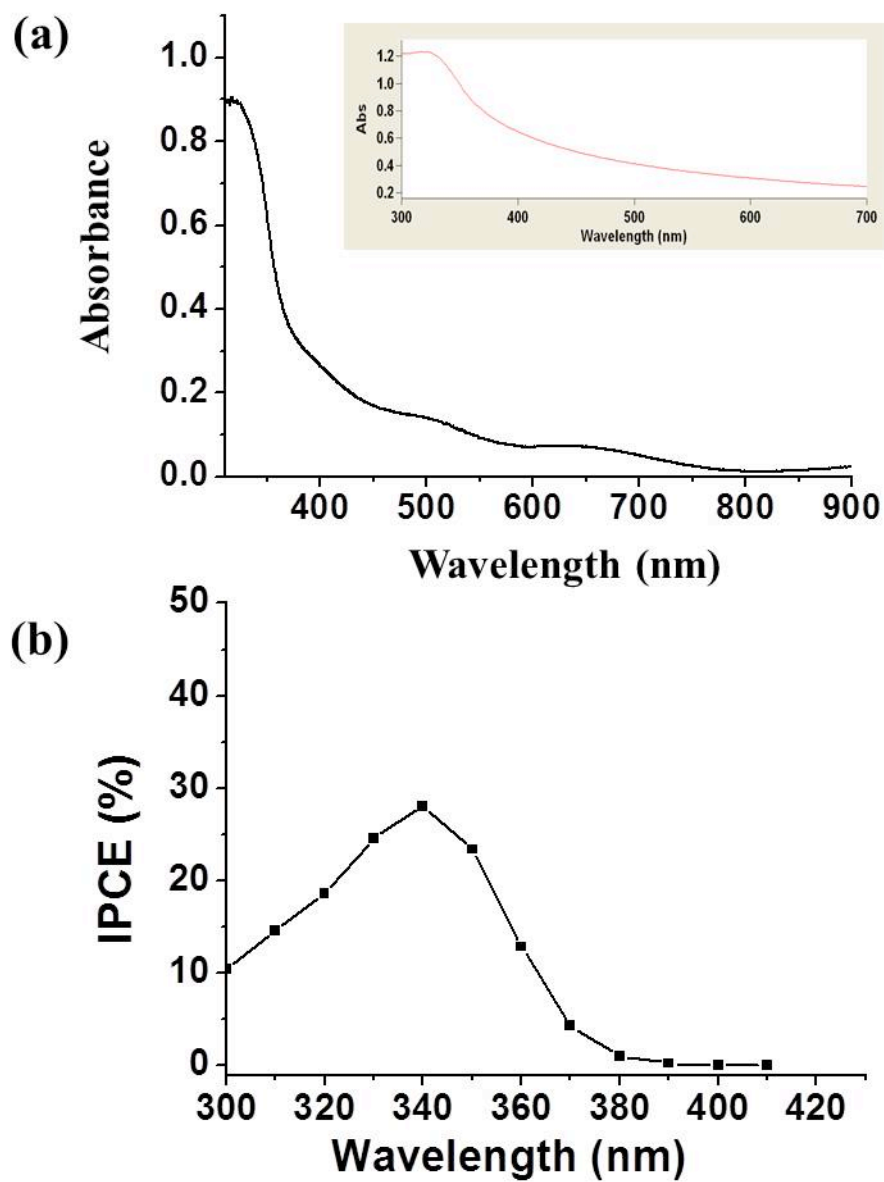
**Figure S1.** SEM image of p-PbMoO<sub>4</sub>/n-Bi<sub>2</sub>O<sub>3</sub> composite film.



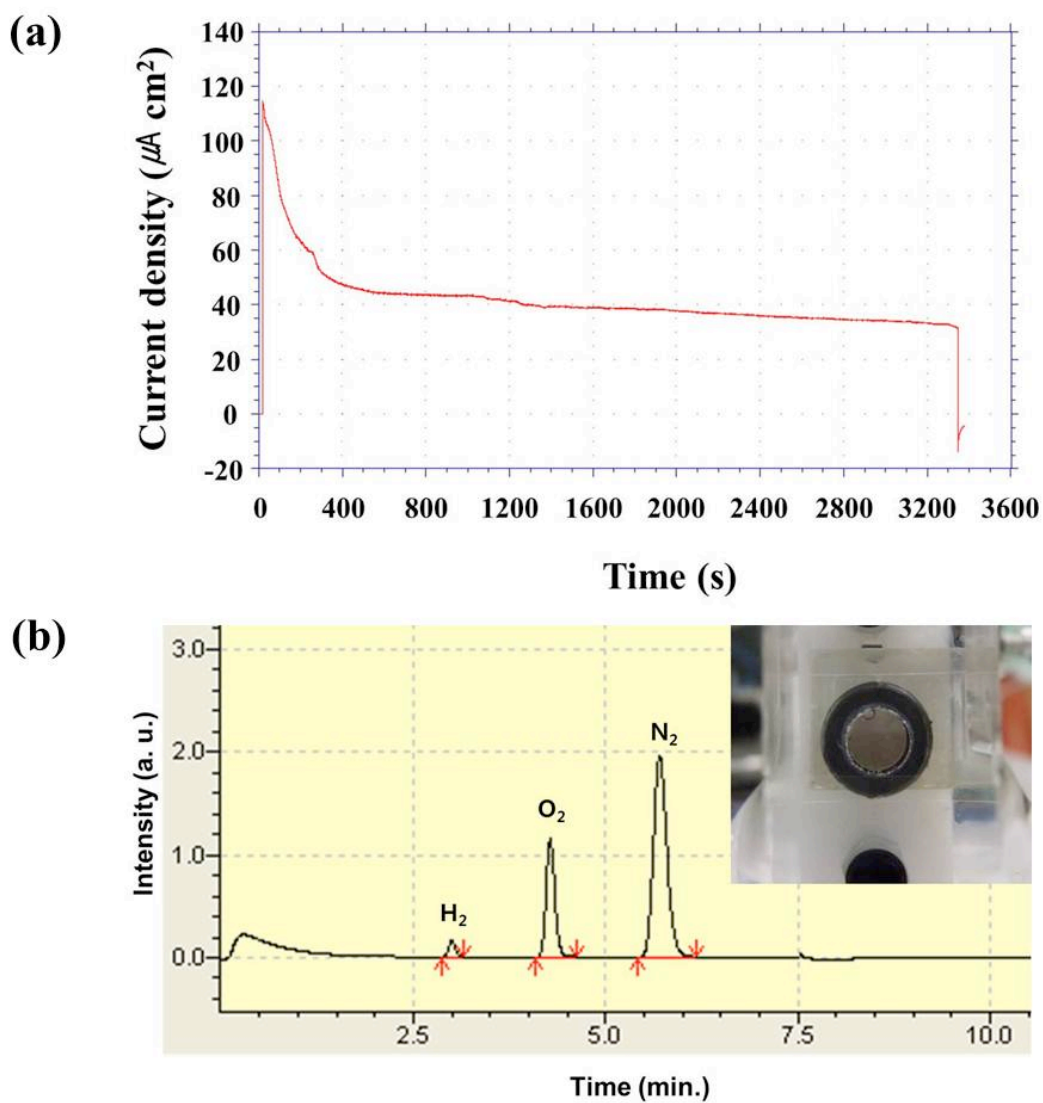
**Figure S2.** XRD patterns of Pb-Bi-Mo (1 : 1 : 1) oxide,  $\text{PbMoO}_4$ , and  $\text{Bi}_2\text{O}_3$  thin film annealed at 600 °C for 3 h in air atmosphere. Black line peaks are from the FTO substrate.



**Figure S3.** (a) Linear sweep voltammograms (LSV) of PbMoO<sub>4</sub> film in 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 0.2 M sodium phosphate buffer (pH 7, deaerated by argon bubbling) under UV-vis irradiation, and (b) LSV of Bi<sub>2</sub>O<sub>3</sub> thin film. Scan rate: 15 mV/s. Light intensity: 100 mW/cm<sup>2</sup>.

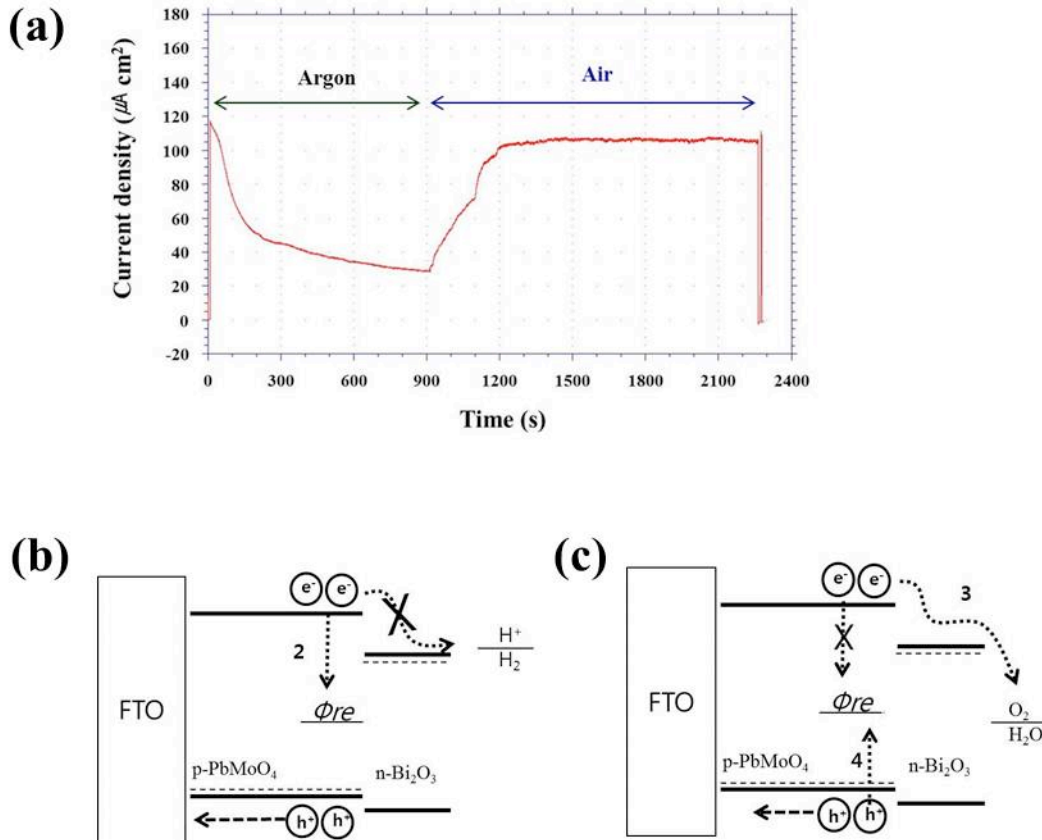


**Figure S4.** (a) UV-vis absorption spectrum of p-PbMoO<sub>4</sub>/n-Bi<sub>2</sub>O<sub>3</sub> composite electrode and p-PbMoO<sub>4</sub> electrode (inset). (b) IPCE plot of p-PbMoO<sub>4</sub>/n-Bi<sub>2</sub>O<sub>3</sub> composite electrode calculated from the photocurrents at applied potential of 0 V vs. Ag/AgCl in 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 0.2 M sodium phosphate buffer (pH 7, deaerated by argon bubbling).



**Figure S5.** (a) Current-time response curve of p-PbMoO<sub>4</sub>/n-Bi<sub>2</sub>O<sub>3</sub> composite electrode at applied potential of 0 V vs. Ag/AgCl in 0.1 M Na<sub>2</sub>SO<sub>4</sub> with 0.2 M phosphate buffer solution (pH 7) deaerated by argon bubbling conditions. (b) Gas chromatography-mass spectroscopy data and photographic images of bubbles (hydrogen) generated on p-PbMoO<sub>4</sub>/n-Bi<sub>2</sub>O<sub>3</sub> under irradiation.





**Figure S6.** (a) Current-time response curve of p-PbMoO<sub>4</sub>/n-Bi<sub>2</sub>O<sub>3</sub> composite electrode at applied potential of 0 V vs. Ag/AgCl in 0.1 M Na<sub>2</sub>SO<sub>4</sub> with 0.2 M phosphate buffer solution (pH 7) under argon and air bubbling conditions. The energy band diagram for p-PbMoO<sub>4</sub>/n-Bi<sub>2</sub>O<sub>3</sub> composite electrode in argon bubbling (b), and air bubbling (c). Pathway 2: semiconductor (PbMoO<sub>4</sub>) reduction, 3: O<sub>2</sub> reduction at the n-Bi<sub>2</sub>O<sub>3</sub> surface, 4: semiconductor (PbMoO<sub>4</sub>) oxidation.

<sup>1</sup> Lee, J.; Ye, H.; Pan, S.; Bard, A. J. *Anal. Chem.*, **2008**, *80*, 7445.