

Electronic Supplementary Information for

**PINO/NHPI-mediated selective oxidation of cycloalkene to cycloalkenone via a
photo-electrochemical method**

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1. Instrumentation

Photo-electrochemical measurements were performed using a computer controlled bi-potentiostat (BAS. Inc., ALS Model 660E) and a solar simulator (SAN-EI ELECTRIC CO., Model XES-40S1) calibrated to AM 1.5 (1 sun, 100 mW cm⁻²) with a spectroradiometer (SOMA Optics, Model S-2440).

2. Materials

All reagents were purchased from commercial suppliers and used without further purification. Cyclohexene, cyclopentene, cycloheptene, *N*-hydroxyphthalimide (NHPI), *N*-hydroxy-4-nitrophthalimide (NO₂NHPI), *N*-hydroxysuccinimide (NHSI), 2,2,6,6-tetramethylpiperidine 1-oxyl free radical (TEMPO), and furan were purchased from the Tokyo Chemical Industry. Acetonitrile (super dehydrated) and lithium perchlorate (LiClO₄) were purchased from FUJIFILM Wako Pure Chemical Industries. *N*-Hydroxytetrachlorophthalimide (Cl₄NHPI) and Nafion membrane (NRE-212) were purchased from SIGMA-ALDRICH.

3. Preparation of Photoelectrodes

The BiVO₄/WO₃^[1], WO₃^[2], and Fe₂O₃^[3] photoelectrodes were prepared according to the literature. The BiVO₄/WO₃ photoelectrode was prepared on an F-doped SnO₂ conductive glass (FTO) substrate (Nippon Sheet Glass Co., Ltd.). Tungsten hexachloride (WCl₆) adjusted to 504 mM was coated on the FTO by spin coating (1000 rpm, 15 s) before the film was calcined at 500°C for 30 min. The coating of the WO₃ layer was again performed using WCl₆ adjusted to 252 mM, resulting in the formation of a WO₃ underlayer with a rough porous surface. A solution (Bi/V = 1:1) of bismuth oxide and vanadium oxide of EMOD (Enhanced Metal Organic Decomposition) materials (Synmetrix Co., USA) was dissolved in butyl acetate containing ethylcellulose as a thickener. An aggregation inhibition agent was then coated on the WO₃ underlayer by spin coating (500 rpm, 15 s) followed by calcined at 550°C for 30 min to form the BiVO₄/WO₃ photoelectrodes.

Porous WO₃ film was coated on the FTO substrate by spin coating using an aqueous solution of H₂WO₄ containing PEG (average molecular weight = 300, PEG-300). Typically, the aqueous solution of H₂WO₄ is prepared by passing an aqueous solution of Na₂WO₄ (0.5 M) through a proton-exchange resin (Dowex 50WX2, 100-200 mesh). Using a

dropper, ethanol (20 mL) was added to the solution to neutralise the pH. After PEG-300 (12.5 mL) was added to the aqueous solution, the solvent was evaporated at 65°C until the volume of the mixture was reduced to approximately 20 mL. The solution of H₂WO₄-containing PEG (400 µL) was coated on the FTO by spin coating (2000 rpm, 15 s) before the film was calcined at 550°C for 30 min. Coating the WO₃ layer was repeated ten times, which resulted in the formation of a porous WO₃ photoelectrode with high photoelectrochemical properties.

The Fe₂O₃ layer was prepared on an FTO substrate via a hydrothermal method at 140°C for 1 h using an aqueous solution of FeCl₃ (150 mM), ZrCl₂O (4.5 mM) and NaNO₃ (100 mM). After washing with ion exchange water, the substrate was calcined at 800°C for 5 min.

The photoelectrodes were characterized using X-ray diffraction spectroscopy (XRD, PANalytical, Empyrean) using Cu K α radiation ($\lambda = 0.154$ nm) and scanning electron microscopy (SEM, Hitachi, Ltd., S-4800). In Figure S1, XRD spectra for the prepared BiVO₄/WO₃ composite photoelectrode were confirmed to have BiVO₄ (monoclinic, PDF number: 01-083-1699) and WO₃ (monoclinic, PDF number: 01-083-0950). The cross-section view of BiVO₄/WO₃ composite photoelectrode was shown in previous literature.^[4] The thickness of BiVO₄ and WO₃ layers are 100-150 nm and 100-120 nm, respectively. In Figure S3, the BiVO₄/WO₃ composite photoelectrode was also characterized using X-ray photoelectron spectroscopy (XPS, ULVAC-PHI) using Al-K α radiation. The estimated surface mole ratio of Bi : V : W was 34 : 42 : 24.

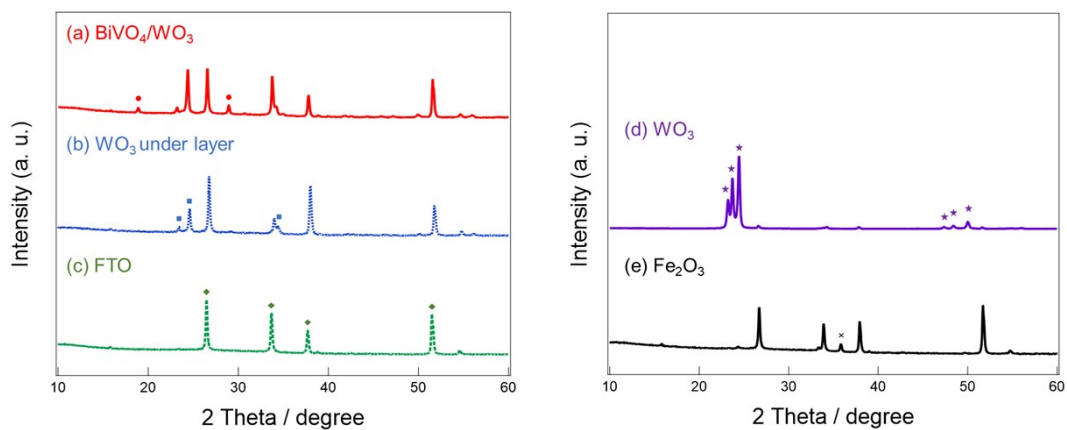


Figure S1. The XRD pattern of (a) the BiVO₄/WO₃ photoelectrode, (b) the WO₃ underlayer of the BiVO₄/WO₃ photoelectrode, (c) the FTO substrate, (d) the WO₃ photoelectrode and (e) the Fe₂O₃ photoelectrode.

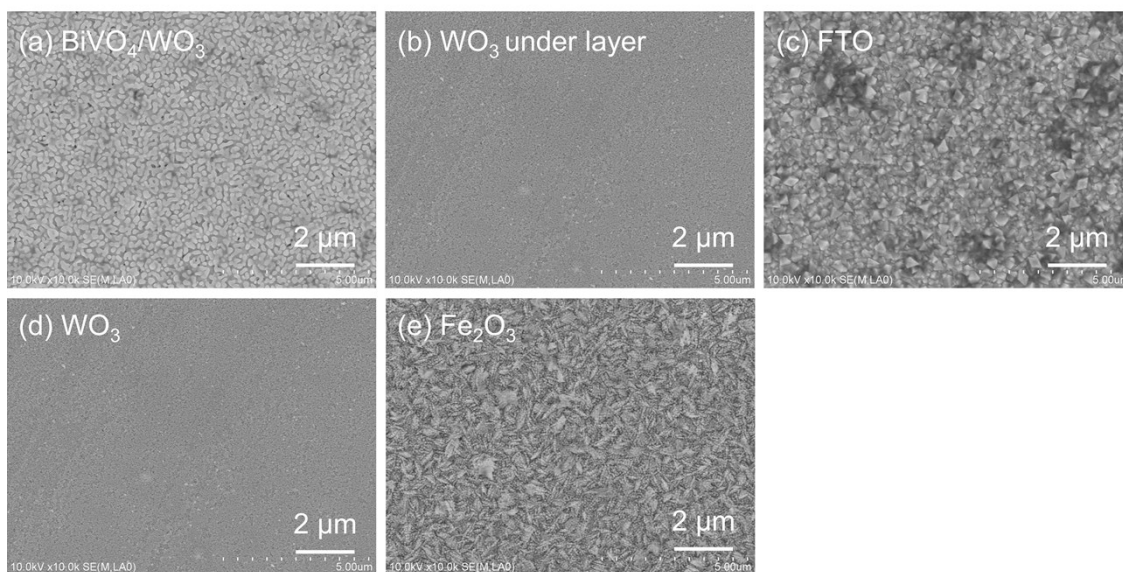


Figure S2. The SEM images of (a) the BiVO₄/WO₃ photoelectrode, (b) the WO₃ underlayer of the BiVO₄/WO₃ photoelectrode, (c) the FTO substrate, (d) the WO₃ photoelectrode, and (e) the Fe₂O₃ photoelectrode.

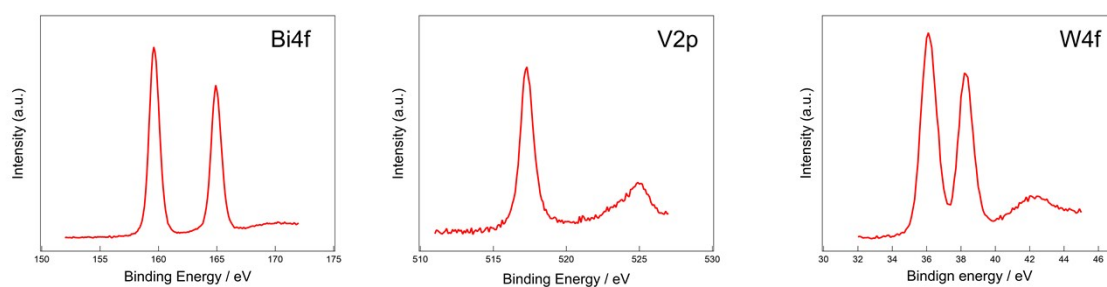


Figure S3. The XPS spectrum of Bi4f, V2p, and W4f from the BiVO₄/WO₃ composite photoelectrode.

4. Electrochemical Measurements

Linear sweep voltammograms were measured with a three-electrode system using a BiVO₄/WO₃ photoelectrode (working electrode, $\varphi = 5$ mm), graphite disk electrode ($\varphi = 3$ mm), a Pt wire (counter electrode), and an Ag/AgNO₃ reference electrode. The cyclic voltammograms obtained for NHPI using graphite disk electrode are shown in Figure S4.

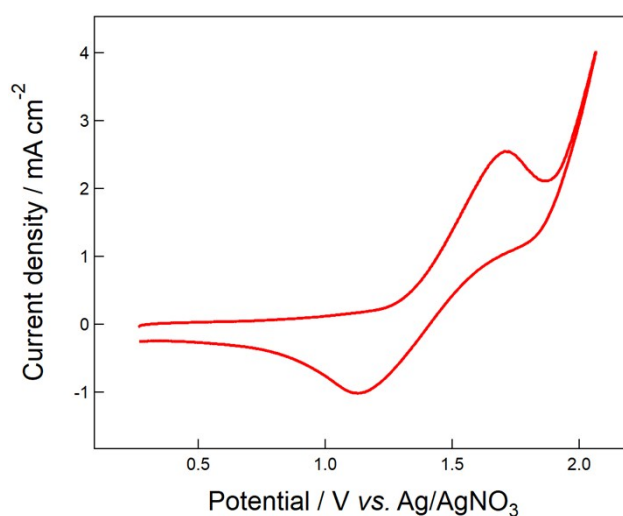


Figure S4. Cyclic voltammograms of 10 mM NHPI in 100 mM LiClO₄/MeCN (30 mL) using a graphite disk ($\varphi = 3$ mm) as a working electrode. Scan rate was 100 mV s⁻¹.

5. General Procedure for Photo-electrochemical Oxidation of NHPI Using a BiVO₄/WO₃ Photoelectrode

Constant current photo-electrolysis was conducted using a two-compartment cell

divided by a Nafion membrane. Photo-electrochemical oxidation of NHPI was performed on the surface of the $\text{BiVO}_4/\text{WO}_3$ photoanode (working electrode, $2 \times 2 \text{ cm}^2$) and a Pt mesh cathode (counter electrode, 80 mesh) under solar simulated light irradiation from the back of the photoelectrode. The anolyte and catholyte each consisted of NHPI (0.3 mmol, 10 mM) and LiClO_4 (3 mmol, 100 mM) in MeCN (30 mL). After the charge was passed through the system, the anolyte solution was analysed using UV spectrometry at 384 nm (Figure S5).

An incident photon to current efficiency (IPCE, the apparent quantum efficiency to photocurrent) spectra of 10 mM NHPI in 100 mM $\text{LiClO}_4/\text{MeCN}$ was measured using a $\text{BiVO}_4/\text{WO}_3$ photoelectrode (working electrode, 4 cm^2), a Pt wire (counter electrode), and an Ag/AgNO_3 reference electrode (Figure S6). The IPCE measurement was conducted with monochromatic light irradiation from the back of the $\text{BiVO}_4/\text{WO}_3$ photoelectrode at 0.8 V vs. Ag/AgNO_3 .

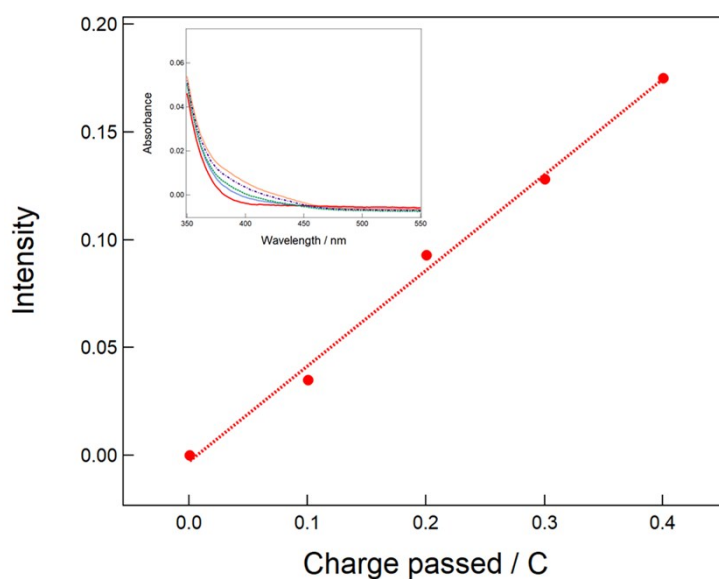


Figure S5. The absorption – charge passed curve for the generation of PINO at 384 nm.

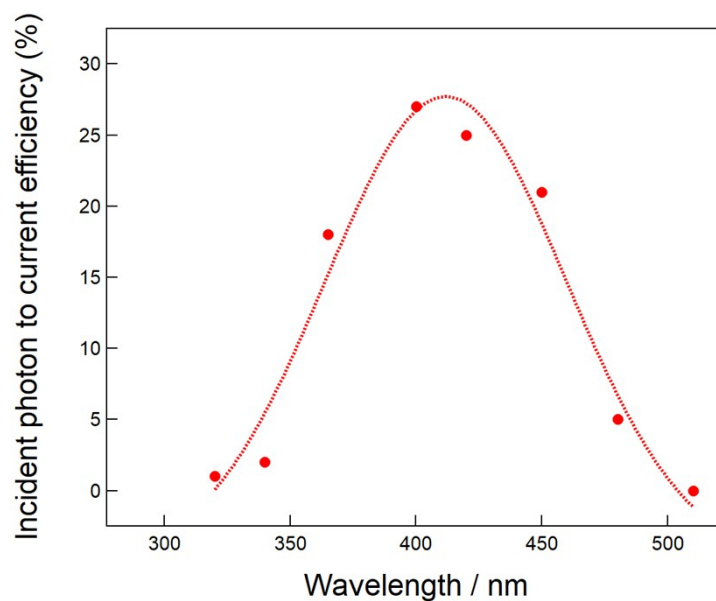


Figure S6. IPCE spectra of 10 mM NHPI in 100 mM LiClO₄/MeCN (30 mL) under monochromatic light irradiation using a BiVO₄/WO₃ photoelectrode.

6. General Procedure for *N*-oxyl Radicals Mediated Photo-electrochemical Oxidation of Cycloalkene to Cycloalkenone Using Photoelectrodes

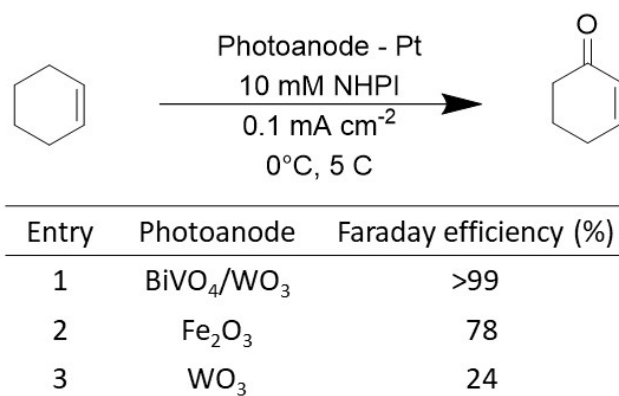
Photo-electrochemical oxidation of cycloalkene was performed in constant current mode (0.1 mA cm⁻²) using a two-compartment cell divided by a Nafion membrane. The cell contained a BiVO₄/WO₃ photoanode (working electrode, 2 × 2 cm²) and a Pt mesh cathode (counter electrode, 80 mesh) in 100 mM LiClO₄/MeCN under solar simulated light irradiation from the back of the photoelectrode. The anolyte and catholyte each consisted of cycloalkene (0.3 mmol, 10 mM), *N*-oxyl radical as a mediator (0.3 mmol, 10 mM) and LiClO₄ (3 mmol, 100 mM) in MeCN (30 mL). After the charge (5 C) was passed through the system, the anolyte solution (200 μL) was diluted with MeCN (total amount was 1000 μL) then analysed via high-performance liquid chromatography (HPLC; Shimazu, LC-20AD and SPD-20A, Luna Omega PS C18 column, sampling error; ±3% faraday efficiency) to detect 2-cyclohexene-1-one. The anolyte solution was also analysed via gas chromatography (GC; Shimazu, GC-2014 and column) to detect 2-cyclohexene-1-ol and 2-cyclohexene-1-hydroperoxide. As a result, a slight amount of 2-cyclohexene-1-ol was only detected in this case. Faraday efficiency was determined from plausible mechanism in Scheme 1 in the manuscript. At first step, the NHPI mediated oxidation of

cyclohexene proceeds via single-electron transfer to provide the same amount of 2-cyclohexene-1-ol and 2-cyclohexene-1-one. At second step, 2-cyclohexene-1-ol is suffered further two-electron oxidation to produce 2-cyclohexene-1-one. Totally, 2 electrons per mol were consumed to produce 2-cyclohexene-1-one. Then, the calculation of faraday efficiency was defined as below.

$$[(\text{Amount of product}) / (\text{Charge passed}/2F)] \times 100$$

A study of the effects of the photoanode material (Fe_2O_3 and WO_3) was also conducted in the same manner as described above (Table S1).

Table S1. Photo-electrochemical oxidation of cyclohexene mediated by PINO/NHPI using various photoanodes^a



^aThe electrolyte solution is 30 mL of 100 mM $\text{LiClO}_4/\text{MeCN}$ (each component); substrate concentration is 10 mM (Entries 1-6) and 100 mM (Entries 7 and 8); working electrodes are photoanodes ($2 \times 2 \text{ cm}^2$); counter electrode is a Pt mesh (80 mesh); cell type is a two-compartment cell divided by a Nafion membrane; light source is a solar simulator (calibrated to AM 1.5, 100 mW cm^{-2}); and charge passed through the system is 5 C.

7. References

- [1] K. Fuku and K. Sayama, *Chem. Commun.*, 2016, **52**, 5406-5409.
 [2] B. D. Alexander, P. J. Kulesza, I. Rutkowska, R. Solarska and J. Augustynski, *J. Mater. Chem.*, 2008, **18**, 2298-2303.

[3] Li Fu, H. Yu, C. Zhang, Z. Shao and B. Yi, *Electrochem. Acta*, 2014, **136**, 363-369.

[4] Y. Miyase, S. Takasugi, S. Iguchi, Y. Miseki, T. Gunji, K. Sasaki, E. Fujita and K. Sayama, *Sustainable Energy Fuels*, 2018, **2**, 1621-1629.