Oxidation

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Photo-Electrochemical C−H Bond Activation of Cyclohexane Using a WO_3 Photoanode and Visible Light

*Hiroyuki Tateno, Shoji Iguchi, Yugo Miseki, and Kazuhiro Sayama**

Abstract: *The photo-electrochemical C−H bond activation of cyclohexane to produce cyclohexanol and cyclohexanone (KA oil) with high partial oxidation selectivity (99 %) and high current utilization ratio (76 %) was achieved in air at room temperature at atmospheric pressure. The production rate of KA oil was accelerated by applying a bias. The incident photon to current efficiencies at 365 and 420 nm were 57 % and 24 %, respectively.*

Direct activation of the C−H bond has attracted widespread attention with respect to improving the atom- and step-economies of organic synthesis when considering green chemistry. In particular, C−H bond activation of simple alkanes to produce basic materials remains an important subject. It is well known that an inert C−H bond has a high dissociation energy (439 kJ mol^{-1}) compared with functionalized regions such as a C−X bond (X = I, 238 kJ mol^{-1}; Br, 294 kJ mol^{-1}; Cl, 350 kJ mol^{-1}).[1] For instance, the oxidative activation of cyclohexane to cyclohexanol (C-ol) and cyclohexanone (C-one), the mixture of which is often called KA oil, and they are important intermediates for manufacturing textiles such as nylon-6 and nylon-6,6 polymers, generally requires high temperature and pressure.[2] Therefore, much effort has been devoted to achieving KA oil production with high selectivity under ambient conditions.

Photo-electrochemical reactions such as powder photocatalyst and photoelectrode systems have been intensively investigated under ambient conditions not only for solar energy conversion such as water splitting, but also for organic synthesis of various valuable chemicals. There are many reports[3] on the C−H bond activation of cyclohexane to produce KA oil with oxide photocatalysts, mainly using TiO_2-based photocatalysts under UV light. Modification of TiO_2 by doping and loading with transition metals was investigated to utilize visible light,[4] but the photocatalytic activities in the visible-light region were insufficient. WO_3 is a visible-light-active semiconductor which absorbs light up to 480 nm, and its absorption coefficient is high because of the direct photon transition. The oxidation ability of h^+ at the valence band potential of WO_3 is almost identical to that of TiO_2. The e^- in the WO_3 conduction band (ca. +0.5 V vs. RHE) has the potential to reduce O_2. Shiraishi et al. reported that the partial oxidation selectivity of KA oil among KA oil and CO_2 reached about 93 % using a Pt-WO_3 powder photocatalyst under ambient conditions.[5] The photocatalytic reaction system is simple, however, the reaction activity was generally limited by the poor charge separation ability of the particles. In contrast, with the photoelectrode reaction system, the quantum efficiency was higher than that for the powder photocatalyst because the charge separation could be significantly accelerated by applying an external bias.[6] Therefore, it is expected that photoelectrode systems would also be useful for the oxidative transformation of organic compounds into valuable chemicals. However, only a few reactions have been reported. Choi et al. reported the photo-electrochemical oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid using a $BiVO_4$ photoanode.[7] We have successfully achieved dimethoxylation of furan and oxidative acetophenone production with excellent faradaic efficiencies using a $BiVO_4/WO_3$ photoanode.[8]The next step towards further developing an organic synthesis method using an oxide semiconductor photoelectrode under visible light and its application for barely oxidizable materials, such as the C−H activation of cyclohexane, is urgently needed.

Herein we investigated the production of KA oil by oxidative C−H bond activation of cyclohexane using a porous WO_3 photoanode in air at room temperature and atmospheric pressure (Figure 1). The production rate was easily acceler-

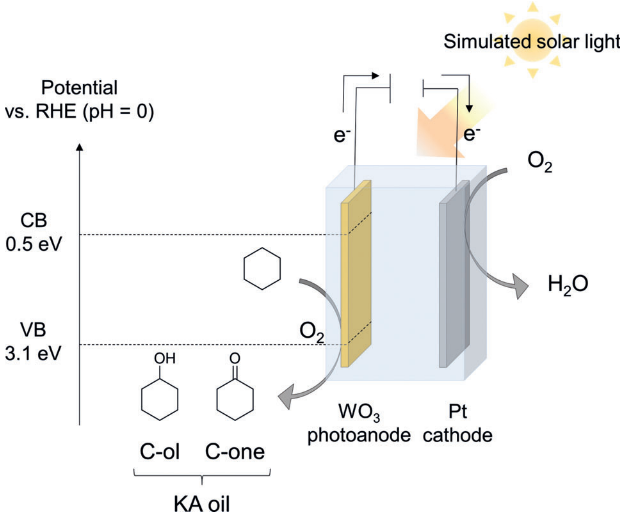

Figure 1. Schematic illustration of a photo-electrochemical system for cyclohexane oxidation to produce KA oil. CB = Conduction band, RHE = reversible hydrogen electrode, VB = valence band.

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ated, even at low external bias, with high partial oxidation selectivity (99 %) and a high current utilization ratio (apparent faradaic efficiency, 76 %) of KA oil. The incident photon to current efficiencies (IPCE) at 365 and 420 nm were 57 % and 24 %, respectively.

A porous WO_3 photoanode was prepared on a conducting glass support according to the literature,[9] and characterized as fine particles of a monoclinic crystal using X-ray diffraction spectroscopy and scanning electron microscopy (see Figures S1 and S2 in the Supporting Information). Detailed experimental conditions are given in the Supporting Information.

Linear sweep voltammograms in a cyclohexane-containing electrolyte were measured using a WO_3 photoelectrode in the dark and under simulated solar-light irradiation as shown in Figure 2. The oxidation current was above +1.2 V vs. the counter electrode (CE) in the dark, and it clearly shifted to −0.7 V vs. CE. under photoirradiation. The applied bias of above 2.0 V could be reduced by light energy at a current density of 0.5 mA cm^{-2}. The oxidation current reached around 2.0 mA cm^{-2} at a cell voltage above 0.5 V vs. CE. According to the negative potential of the WO_3 conduction band compared with that of O_2 reduction, it is reasonable that a small photocurrent was observed even at 0 V vs. the Pt counter electrode (no applied bias), as shown in Figure 2. However, the photocurrent gradually decreased with time with the constant potential method (see Figure S3). It was found that the potential of the WO_3 photoanode relative to the reference electrode under light irradiation was unchanged, and that the potential of the Pt cathode to the reference electrode was negatively shifted (see Figure S4), suggesting that the initial decrease in the photocurrent-potential property in the two-electrode system was caused by the limitation of O_2 reduction on the Pt cathode, rather than by the photoanodic reaction.

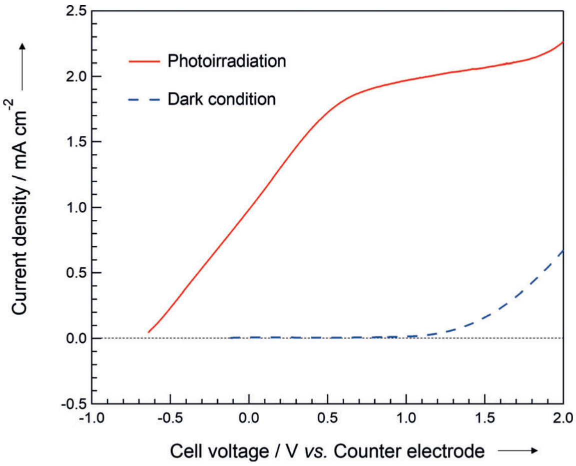


Figure 2. Linear sweep voltammograms of a cyclohexane-based electrolyte solution using a WO_3 photoelectrode in the dark and under simulated solar-light irradiation (100 mW cm^{-2}) under air. Composition of the electrolyte: 18 mL cyclohexane, 12 mL *t*BuOH, and 2 mL HNO_3; working electrode: WO_3 disk electrode ($\Phi = 5$ mm); counter electrode: Pt mesh; scan rate: 10 mV s^{-1}.

The oxidation current and accumulation of products in the dark and under simulated solar-light irradiation in the constant potential method (cell voltage of 0.5 V vs. Pt) were determined as shown in Figure 3. The oxidation current of cyclohexane was negligible in the dark. In contrast, KA oil was clearly observed upon photoirradiation, and no by-products, such as bicyclohexyls, were detected during this period. Figure 4 shows the applied bias dependence of the generation rate of KA oil under ambient conditions and simulated solar-light irradiation. KA oil was produced even at 0 V vs. CE, but the production rate was relatively low

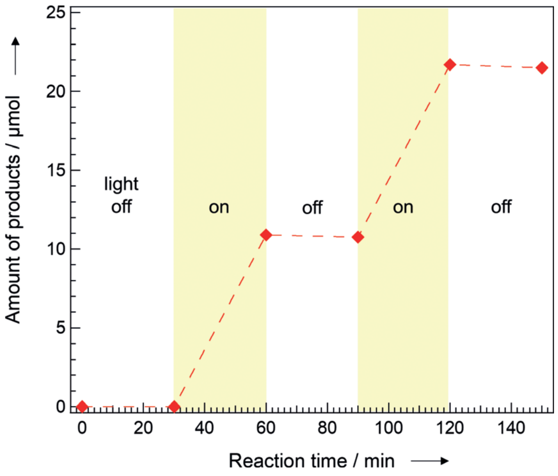


Figure 3. The effect of light irradiation on photo-electrochemical oxidation of cyclohexane to KA oil (total amount of C-ol + C-one) using a WO_3 electrode under air. Composition of the electrolyte: 18 mL cyclohexane, 12 mL *t*BuOH, and 2 mL HNO_3; working electrode: WO_3 electrode (2×2 cm^2); counter electrode: Pt mesh; light source: simulated solar light (100 mW cm^{-2}). Electrolysis was conducted in constant potential mode at a cell voltage of 0.5 V vs. counter electrode.

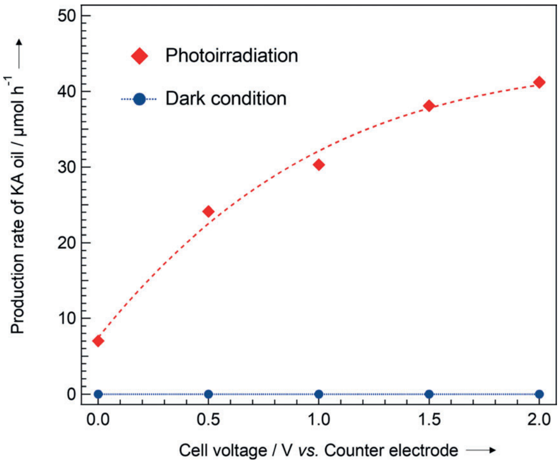
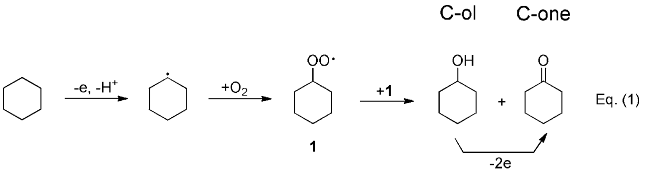


Figure 4. Applied bias dependence of the electrochemical oxidation of cyclohexane to KA oil (total amount of C-ol + C-one) using a WO_3 electrode with simulated solar-light irradiation (100 mW cm^{-2}) under air. Composition of electrolyte: 18 mL cyclohexane, 12 mL *t*-BuOH, and 2 mL HNO_3; working electrode: WO_3 electrode (2×2 cm^2); counter electrode: Pt mesh. Electrolysis was conducted in constant potential mode (0 to 2.0 V vs. counter electrode).

($< 8\ \mu mol\,h^{-1}$). The production rate of KA oil increased with the applied bias and became saturated at cell voltages above 1.5 V. The generation rate of KA oil then reached 41.2 $\mu mol\,h^{-1}$ at a cell voltage of 2.0 V, although KA oil was scarcely observed below 2.0 V in the dark. It should be noted that no oxidation products derived from cyclohexane were obtained by the conventional electrochemical oxidation system in the dark using either the Pt, glassy carbon, or graphite electrodes, even when the anodic current was observed at high anodic potential. These results indicate that the selective oxidation of cyclohexane to KA oil was performed on a WO_3 photoanode at a low cell voltage using simulated solar-light assistance.

The presence of O_2 is important for KA oil production on the photoanode as well as for O_2 reduction on the Pt CE. The oxidative transformation of cyclohexane to KA oil generally required O_2. It was reported that the selectivity for producing KA oil decreased with the O_2 concentration, and bicyclohexyl was mainly formed at low oxygen concentrations by thermal catalytic reactions over solid supported Cu^{II}, Fe^{III}, Cr^{III}, and Co^{III} salts.[2] The reaction mechanism shown in Equation (1) was proposed.[10] The oxidation of cyclohexane proceeds via a cyclohexyl radical by a single-electron transfer process, and it reacts with O_2 to form the cyclohexylperoxyl radical. Bicyclohexyl was often detected by coupling of a cyclohexyl radical when O_2 was absent. Subsequently, the generated pair of cyclohexyperoxyl radicals are disproportionated to form the same amount of C-ol and C-one. C-ol possibly underwent an additional two-electron oxidation to C-one.



Eq. (1)

Figure 5 shows the time dependence of C-ol and C-one production by oxidation of cyclohexane on a WO_3 photoanode under O_2 and N_2 atmospheres with simulated solar-light irradiation. Under an N_2 atmosphere, a negligible amount of KA oil was detected and a small amount of bicyclohexyl (10.6 μmol) was formed, although the photocurrent was almost identical to that under the O_2 atmosphere. In the presence of O_2, both C-ol and C-one were produced effectively. The ratio of produced C-one to C-ol increased with the reaction time. We confirmed that C-ol was oxidized to C-one in the *t*BuOH/HNO_3 electrolyte (without cyclohexane) on the WO_3 photoanode, suggesting that excess C-one is obtained by the oxidation of produced C-ol [Eq. (1)].

The production of CO_2 gas was reported by the complete oxidation of cyclohexane with O_2.[3,4,11] Under our experimental conditions (charge passed: 21 C, cell voltage: 0.5 V, reaction time: 5 h), the amount of CO_2 produced was small (7 μmol) compared with that of C-ol (34 μmol) and C-one (67 μmol). The partial oxidation selectivity, which is defined by Equation (2),[3e,5,12] was 99 %. This value is high compared with that for the photocatalytic reaction on Pt-WO_3 (93 %).[5]

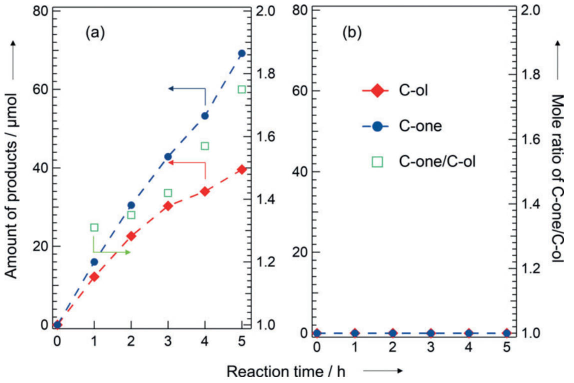


Figure 5. Reaction time dependence of the accumulation of cyclohexanol (diamonds), cyclohexanone (circles), and the mole ratio of cyclohexanone/cyclohexanol (open squares) using a WO_3 electrode under an O_2 (a) and N_2 (b) atmosphere with simulated solar-light irradiation (100 $mW\,cm^{-2}$). Composition of the electrolyte: 18 mL cyclohexane, 12 mL *t*BuOH, and 2 mL HNO_3; working electrode: WO_3 electrode ($2\times2\ cm^2$); counter electrode: Pt mesh. Electrolysis was conducted in constant potential mode at 0.5 V vs. counter electrode.

$$\text{Partial oxidation selectivity} = [(\text{C-ol} + \text{C-one})/(\text{C-ol} + \text{C-one} + (1/6)\,CO_2)]\,100 \tag{2}$$

Evaluation of the faradaic efficiency of this reaction is difficult when the reaction mechanism is not clear, because there is a possibility that reaction of a radical intermediate with O_2 will take place through chain reactions. The apparent faradaic efficiency was defined as the current utilization ratio of KA oil to the charge passed [Eq. (3); see the Supporting Information], and this was calculated as appproximately 76 %. All these results indicate that the hole in the valence band of WO_3 selectively oxidized the cyclohexane to KA oil, while the solvent might be partially oxidized. The prepared WO_3 photoanode was suitable and was reused at least five times without necessitating a regeneration process. A turnover number (moles of cylohexanol and cyclohexanone per moles of WO_3) of 57 was obtained.

$$\text{Current utilization ratio of KA oil (apparent faradaic efficiency)} = [(3\text{C-one}-\text{C-ol})/(\text{Charge passed}/96485)]\,100 \tag{3}$$

Finally, the incident photon to current efficiency (IPCE, the apparent quantum efficiency to photocurrent) of this photoanode reaction method was measured under monochromatic light using a band pass filter (Figure 6, diamonds). The IPCE spectrum was similar to the absorption spectrum of the WO_3 photoelectrode in the visible-light region (see Figure S5). The IPCE at 400 and 420 nm were 40 % and 24 %, respectively. The maximum IPCE of 57 % was obtained at a wavelength of 365 nm. These high values indicate the advantages of the efficient photo-electrochemical reaction for KA oil production. The IPCE in the shorter wavelength region at less than 365 nm was low mainly because of the absorption of the electrolyte solution (see Figure S6). For comparison, the IPCE spectrum in 1.0 M aqueous $HClO_4$ without any organic substrate for O_2 evolution from H_2O is

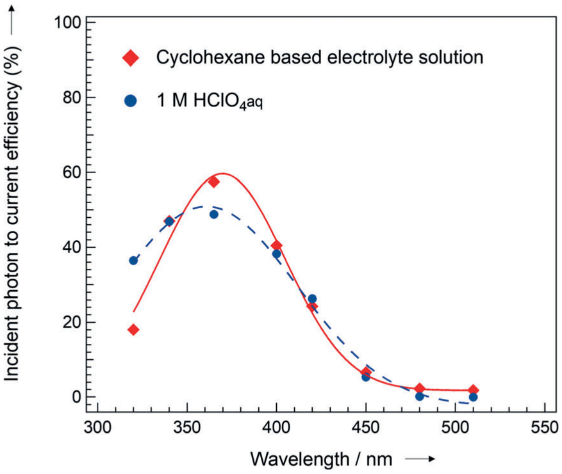


Figure 6. IPCE spectra of cyclohexane-based electrolyte solution and 1 M $HClO_4(aq)$ under monochromatic light irradiation from the front side of the WO_3 electrode at 2.0 V vs. $Ag/AgNO_3$. Composition of the electrolyte: 18 mL cyclohexane, 12 mL *t*-BuOH, and 2 mL HNO_3; working electrode: WO_3 electrode (2×2 cm^2); counter electrode: Pt mesh, reference electrode: $Ag/AgNO_3$.

also shown in Figure 6 (circles). The spectral shape for water oxidation was similar to that for cyclohexane oxidation, and the IPCE at 400 and 420 nm was 38% and 26%, respectively. These results indicate that the oxidation reaction of cyclohexane was as fast as water oxidation on the WO_3 photoanode under the reaction conditions.

In conclusion, efficient photo-electrochemical production of KA oil from cyclohexane was demonstrated for the first time. Excellent partial oxidation selectivity (99%) and apparent faradaic efficiency (76%) were achieved using a porous WO_3 photoanode in air at room temperature and atmospheric pressure. The IPCE at 365 and 420 nm were 57% and 24%, respectively. All results indicated that photo-electrochemical processes had significant potential for various organic syntheses including C−H activation.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkanes · C−H activation · electrochemistry · oxidation · photocatalysis

[1] Y. R. Luo, *Handbook of bond dissociation energies in organic compounds*, CRC, Boca Raton, **2007**.
[2] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. da Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinacé, E. L. Pires, *Appl. Catal. A* **2001**, *211*, 1–17.
[3] a) I. Izumi, W. W. Dunn, K. O. Wllbourn, F. F. Fan, A. J. Bird, *J. Phys. Chem.* **1980**, *84*, 3207–3210; b) C. Giannotti, S. Le Greneur, O. Watts, *Tetrahedron Lett.* **1983**, *24*, 5071–5072; c) W. Mu, J. M. Herrmann, P. Pichat, *Catal. Lett.* **1989**, *3*, 73–84; d) G. Lu, H. Gao, J. Suo, S. Li, *J. Chem. Soc. Chem. Commun.* **1994**, 2423–2424; e) A. Sclafani, J. M. Herrmann, *J. Phys. Chem.* **1996**, *100*, 13655–13661; f) P. Boarini, V. Carassiti, A. Maldotti, R. Amadelli, *Langmuir* **1998**, *14*, 2080–2085; g) M. A. Gonzalez, S. G. Howell, S. K. Sikdar, *J. Catal.* **1999**, *183*, 159–162; h) C. B. Almquist, P. Biswas, *Appl. Catal. A* **2001**, *214*, 259–271; i) H. Einaga, S. Futamura, T. Ibusuki, *Appl. Catal. B* **2002**, *38*, 215–225; j) P. Du, J. A. Moulijn, G. Mul, *J. Catal.* **2006**, *238*, 342–352; k) A. R. Almeida, J. A. Mouijn, G. Mul, *J. Phys. Chem. C* **2008**, *112*, 1552–1561; l) A. R. Almeida, J. A. Mouijn, G. Mul, *J. Phys. Chem. C* **2011**, *115*, 1330–1338.
[4] a) R. Amadelli, M. Bregola, E. Polo, V. Carassiti, A. Maldoti, *J. Chem. Soc. Chem. Commun.* **1992**, 1355–1357; b) A. Molinari, R. Amadelli, L. Antolini, A. Maldotti, P. Battioni, D. Mansuy, *J. Mol. Catal. A* **2000**, *158*, 521–531; c) K. Teramura, T. Tanaka, T. Yamamoto, T. Funabiki, *J. Mol. Catal. A* **2001**, *165*, 299–301; d) D. Tsukamoto, A. Shiro, Y. Shiraishi, T. Hirai, *J. Phys. Chem. C* **2011**, *115*, 19782–19788; e) J. T. Carneiro, C. C. Yang, J. A. Moulijn, G. Mul, *J. Catal.* **2011**, *277*, 129–133; f) H. Hattori, Y. Ide, S. Ogo, K. Inumaru, M. Sadakane, T. Sano, *ACS Catal.* **2012**, *2*, 1910–1915; g) Y. Ide, H. Hattori, S. Ogo, M. Sadakane, T. Sano, *Green Chem.* **2012**, *14*, 1264–1267; h) W. Zhong, T. Qiao, J. Dai, L. Mao, Q. Xu, G. Zou, X. Liu, D. Yin, F. Zhao, *J. Catal.* **2015**, *330*, 208–221; i) D. Yang, T. Wu, C. Chen, W. Guo, H. Liu, B. Han, *Green Chem.* **2017**, *19*, 311.
[5] Y. Shirakawa, Y. Sugano, S. Ichikawa, T. Hirai, *Catal. Sci. Technol.* **2012**, *2*, 400–405.
[6] a) A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37–38; b) T. Hisatomi, J. Kubota, K. Domen, *Chem. Soc. Rev.* **2014**, *43*, 7520–7535; c) C. Jiang, S. J. A. Moniz, A. Wang, T. Zhang, J. Tang, *Chem. Soc. Rev.* **2017**, *46*, 4645.
[7] H. G. Cha, K. S. Choi, *Nat. Chem.* **2015**, *7*, 328–333.
[8] a) H. Tateno, Y. Miseki, K. Sayama, *Chem. Commun.* **2017**, *53*, 4378–4381; b) H. Tateno, Y. Miseki, K. Sayama, *ChemElectroChem* **2017**, *4*, 3283–3287.
[9] C. Santato, M. Odziemkowski, M. Ulmann, J. Augustynski, *J. Am. Chem. Soc.* **2001**, *123*, 10639–10649.
[10] I. Hermans, P. A. Jacobs, J. Peeters, *Chem. Eur. J.* **2006**, *12*, 4229–4240.
[11] G. Palmisano, V. Augugliaro, M. Pagliaro, L. Palmisano, *Chem. Commun.* **2007**, 3425–3437.
[12] K. Teramura, T. Tanaka, M. Kani, T. Hosokawa, T. Funabiki, *J. Mol. Catal. A* **2004**, *208*, 299–305.

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Communications

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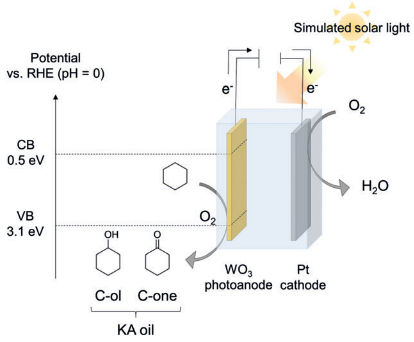

Light and electricity: The photo-electrochemical C−H bond activation of cyclohexane to produce cyclohexanol and cyclohexanone (KA oil) with high partial oxidation selectivity (99%) was achieved in air at room temperature and at atmospheric pressure. The production rate of KA oil was accelerated by applying a bias. The incident photon to current efficiencies at 365 and 420 nm were 57% and 24%, respectively.