CHEMISTRY & SUSTAINABILITY
CHEMSUSCHEM
ENERGY & MATERIALS

Accepted Article

Title: Facile Synthesis of BiVO4 for Visible-Light-Induced C-C Bond Cleavage of Alkenes to Generate Carbonyls

Authors: Eun Jin Cho, Joon Yong Park, Hye Rin Choe, Ki Min Nam, Sung Su Han, and Ho Seong Hwang

To be cited as: *ChemSusChem* 10.1002/cssc.201900439

Link to VoR: http://dx.doi.org/10.1002/cssc.201900439

A Journal of
ChemPubSoc Europe

WILEY-VCH

www.chemsuschem.org

Facile Synthesis of $BiVO_4$ for Visible-Light-Induced C-C Bond Cleavage of Alkenes to Generate Carbonyls

Sung Su Han,[a] Joon Yong Park,[b] Ho Seong Hwang,[a] Hye Rin Choe,[b] Ki Min Nam,*,[b] and Eun Jin Cho*,[a]

Abstract: $BiVO_4$ crystals (Sono-$BiVO_4$) synthesized by an ultrasonic-assisted method showed improved efficiency as a heterogeneous photocatalyst under visible-light irradiation. Sono-$BiVO_4$ was successfully used for the C-C bond cleavage of alkenes to generate carbonyl compounds. Styrene derivatives were converted to carbonyl compounds in the presence of Sono-$BiVO_4$ under highly sustainable conditions, requiring only natural sources, i.e., molecular oxygen, visible light, and water, at room temperature. In addition, Sono-$BiVO_4$ could be easily separated from the reaction mixture and reused.

With the growing awareness for sustainable development, there has been much interest in finding greener sources and methods in the chemistry community.[1] An abundant and easily available energy source, visible light, has great potential in driving environmentally benign chemical transformations. In the last decade, visible-light photocatalysis has seen a flourishing renaissance, with various photocatalysts.[2] However, recent significant developments have focused on homogeneous catalysis, which requires the use of organic dyes or metal (such as Ru, Ir, and Cu) complexes. On the other hand, heterogeneous catalysis remains largely underdeveloped despite the notable advantages of the catalysts, such as stability and reusability by easy separation from the reaction mixture, which is an important consideration for industrial manufacturing processes.[3]

Metal oxides such as TiO_2, ZnO, and Nb_2O_5 are stable, inexpensive, and easily filtered from the mixture.[3a,4] However, because of their wide bandgap (large gap between the valance and conduction bands), these oxides function as efficient photocatalysts only under UV irradiation, and they show a narrow substrate scope under visible-light irradiation (Figure 1).[5] Given its narrower band gap energy, bismuth vanadate ($BiVO_4$) has great potential for use as a heterogeneous visible-light photocatalyst that can be easily activated in the visible-light wavelength range (~500 nm).[6,7] Surprisingly, $BiVO_4$ has rarely been used as a photocatalyst in organic transformations[8] as it shows poor photoreactivity under visible-light irradiation. Herein, we prepared $BiVO_4$ crystals in order to improve the efficiency of this oxide toward organic transformations under visible-light irradiation.

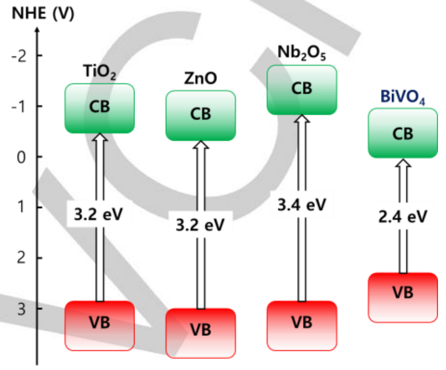


Figure 1. Redox potentials of valence (VB) and conduction (CB) bands, and bandgap energies of metal oxides.

A mixture of 0.2 M $Bi(NO_3)_3•5H_2O$ and 0.2 M VCl_3 precursor solution was prepared, and ultrasonication was performed under ambient conditions (Figure 2a). Performing the ultrasound under ambient conditions for 1 h resulted in the efficient preparation of $BiVO_4$ powders. The as-prepared $BiVO_4$ powders were annealed at 500 °C for 3 h in air to yield crystallized $BiVO_4$ (denoted as Sono-$BiVO_4$ crystals). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM, inset) images confirmed the high uniformity of the $BiVO_4$ cubes with an average grain size of 426 ± 104 nm (Figures 2b). X-ray diffraction (XRD) analysis was carried out to obtain reliable structural information about this material (Figure 2c).

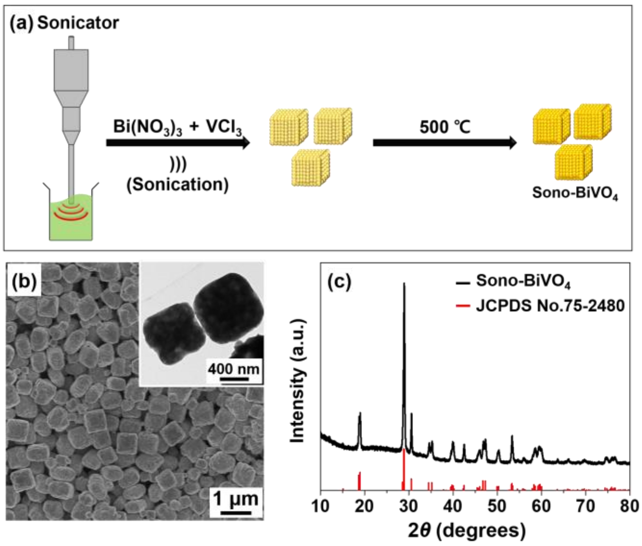


Figure 2. (a) Schematic of the preparation of Sono-$BiVO_4$ crystals. (b) SEM and TEM (inset) images of the Sono-$BiVO_4$ crystals. (c) XRD pattern of the Sono-$BiVO_4$ crystals.

---

[a] Sung Su Han, Ho Seong Hwang, and Prof. Dr. Eun Jin Cho
Department of Chemistry, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu, Seoul 06974, Republic of Korea
E-mail: ejcho@cau.ac.kr
[b] Joon Yong Park, Hye Rin Choe, and Prof. Dr. Ki Min Nam
Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 46241, Republic of Korea
E-mail: namkimin.chem@gmail.com

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

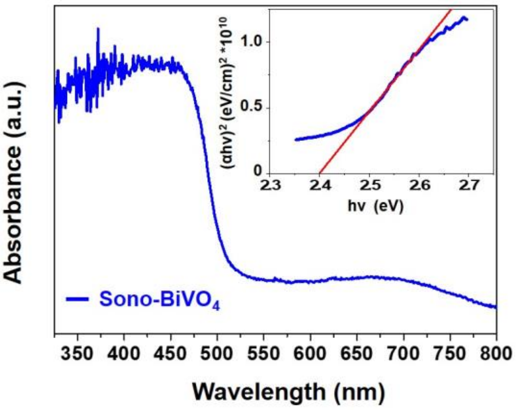


Figure 3. UV-visible absorption spectrum and Tauc plot (inset) of Sono-$BiVO_4$ crystals.

The diffraction peaks of the Sono-$BiVO_4$ crystals were indexed to the monoclinic scheelite structure (JCPDS No. 75-2480), indicative of well-crystallized $BiVO_4$. The bandgap was estimated from the onset of UV-visible absorbance (Figure 3). From the absorbance data, the Sono-$BiVO_4$ crystals showed direct transition with band gap of 2.4 eV. To compare the photocatalytic performance of the Sono-$BiVO_4$ crystals, various $BiVO_4$ materials were prepared by well-known synthetic methods such as the solid-state reaction and hydrothermal method[9] (the materials are denoted as SS-$BiVO_4$, and HT-$BiVO_4$, respectively). Figure *S2* shows the SEM images and XRD patterns of SS-$BiVO_4$, and HT-$BiVO_4$. The XRD peaks of these samples were identical to those of the monoclinic scheelite structure of $BiVO_4$.

The photocatalytic activities of the $BiVO_4$ samples were then evaluated in the degradation of methyl orange (MO) dye in water under UV-visible irradiation (1 sun, 100 mW/cm^2).

Figure 4a shows the absorption spectra of the MO solution as a function of illumination time in the presence of the Sono-$BiVO_4$ crystals. The absorption peak at 465 nm decreased gradually and finally disappeared after 180 min, indicating complete degradation of the dye. Blank test (MO without any catalyst) under UV-visible light showed the negligible self-photolysis of MO. For comparison, SS-$BiVO_4$ and HT-$BiVO_4$ were also used for photocatalytic MO degradation under the same conditions. Figure 4b shows the degradation of MO in the presence of Sono-$BiVO_4$, HT-$BiVO_4$, and SS-$BiVO_4$ samples. After irradiation for 180 min, the degradation percentages were 99%, 23%, and 11% for Sono-$BiVO_4$, HT-$BiVO_4$, and SS-$BiVO_4$, respectively. The Sono-$BiVO_4$ crystals exhibited higher photocatalytic activity for MO degradation as compared to SS-$BiVO_4$ and HT-$BiVO_4$. The improved photocatalytic activity is mainly attributed to the charge separation (hole diffusion length) and surface area. The hole diffusion length of $BiVO_4$ is about 100 nm.[10] The Sono-$BiVO_4$ crystals prepared in this study had a radius of about 200 nm (Figure 2), which is effective size of charge separation as compared to SS-$BiVO_4$ (~500 nm) and HT-$BiVO_4$ (~1000 nm) crystals. Furthermore, the Brunauer-Emmett-Teller (BET, nitrogen, 77K) surface area of the Sono-$BiVO_4$ sample (6.79m^2/g) was nearly 5 times as large as that of SS-$BiVO_4$ (1.44 m^2/g) and HT-$BiVO_4$ (0.81 m^2/g). Thus, the Sono-$BiVO_4$ is a more efficient structure for degradation of organic pollutants in water.

Having verified the improved photoreactivity of Sono-$BiVO_4$ based on the photocatalytic degradation of MO, we next investigated the reactivity of this catalyst in organic transformations. The use of molecular oxygen and water as natural reagents, in addition to this new heterogeneous visible-light photocatalyst, is expected to attract much attention in sustainable chemistry.[1]

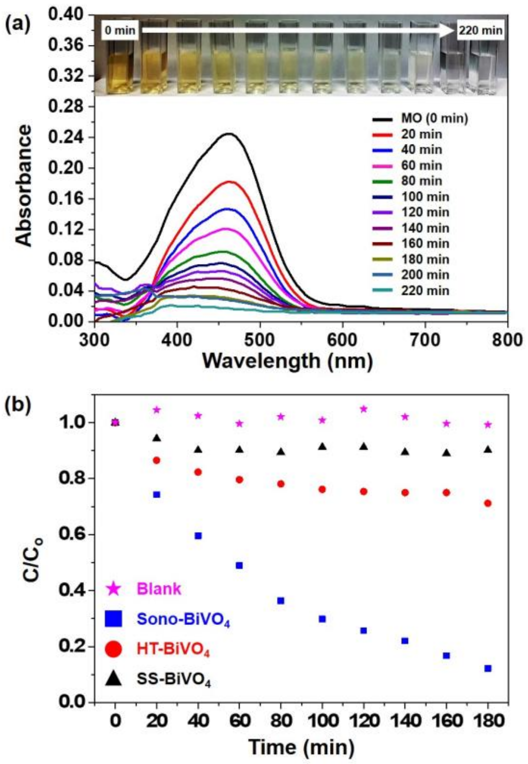
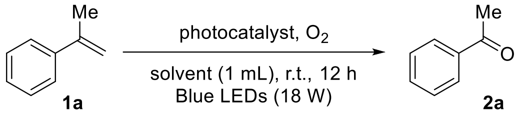


Figure 4. (a) Time-dependent UV-Vis absorption spectra of MO solution in the presence of the Sono-$BiVO_4$ crystals. (b) Photocatalytic degradation rates of MO when using Sono-$BiVO_4$ (blue squares), HT-$BiVO_4$ (red circles), SS-$BiVO_4$ (black triangles) crystals, and without $BiVO_4$ (pink stars).

Carbonyl functionalities such as aldehydes and ketones are some of the most important and versatile functional groups in organic chemistry.[11,12] Accordingly, a wide range of synthetic methods for carbonyls have been developed; in particular, oxidative cleavage of alkenes to generate carbonyls is a widely employed strategy both in academia and in the industry. A widely used traditional approach is ozonolysis.[13] However, this two-step process requires the toxic ozone as the oxidant, as well as special equipment and an additional reductant. The other representative method is Lemieux-Johnson oxidation, where OsO_4-catalyzed direct oxidation of alkenes to diols is followed by C-C bond cleavage using $NaIO_4$.[14] This two-step process also has an inherent disadvantage because of the toxicity of the reagents used. Although much effort has been made to develop environmentally benign methods for the cleavage of alkenes to carbonyls,[15] there is no established method using molecular oxygen as the oxidant in water at room temperature.

Table 1. Oxidative cleavage of alkene **1a** to acetophenone **2a**



entry	solvent	photocatalyst	variation	yield (%)[b]
1	**H_2O**	**Sono-$BiVO_4$**		**78**
2	CH_2Cl_2	Sono-$BiVO_4$		trace
3	MeCN	Sono-$BiVO_4$		trace
4	MeOH	Sono-$BiVO_4$		trace
5	DMF	Sono-$BiVO_4$		14
6	DMSO	Sono-$BiVO_4$		35
7	H_2O	Sono-$BiVO_4$	No hv	0
8	H_2O	Sono-$BiVO_4$	No O_2	trace
9	H_2O	-	No catalyst	0
10	H_2O	Sono-$BiVO_4$	Green LEDs (525 nm, 18 W)	75[c]
11	H_2O	Sono-$BiVO_4$	H_2O (0.25 mL)	19
12	H_2O	Sono-$BiVO_4$	H_2O (4.0 mL)	43
13	H_2O	**SS-$BiVO_4$**		18
14	H_2O	**HT-$BiVO_4$**		45

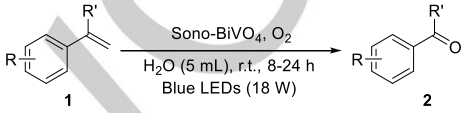
[a] Reaction conditions: 1a (0.1 mmol), Sono-BiVO4 (3 mg) [b] The yields were determined by GC-MS using n-dodecane as the internal standard. [c] Reaction time: 36 h

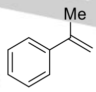
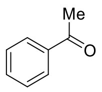
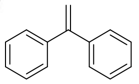
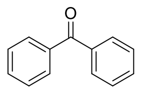
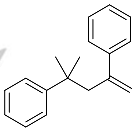
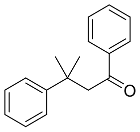
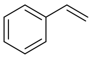
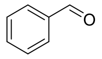
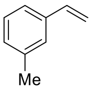
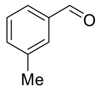
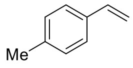
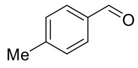
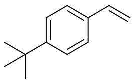
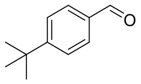
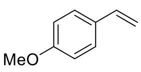
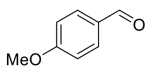
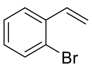
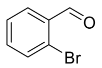
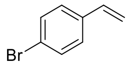
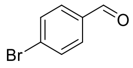
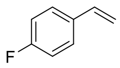
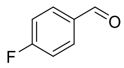
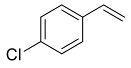
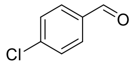
We envisioned that selective aerobic oxidation[16] of alkenes to carbonyls would proceed in the presence of Sono-$BiVO_4$ in water (solvent) under visible-light irradiation at room temperature. We started our investigation with α-methylstyrene **1a** as the model substrate (**Table 1**). To our delight, oxidative cleavage of **1a** occurred in the presence of Sono-$BiVO_4$ in water at room temperature under visible-light irradiation from 18 W blue LEDs (450 nm) to give acetophenone **2a** in 78% yield (entry 1). None of the organic solvents we employed showed better reactivity than water (entries 2-6). Control experiments revealed that the reaction requires a photocatalyst, visible light, and molecular oxygen (entries 7-9). The reaction also proceeded well under irradiation by 18 W green LEDs (entry 10), although a longer time was required in this case. This heterogeneous reaction was significantly affected by the amount of water (entries 1, 11, and 12).

We further confirmed that this newly prepared Sono-$BiVO_4$ shows better reactivity as a heterogeneous visible-light photocatalyst as compared to SS-$BiVO_4$ and HT-$BiVO_4$. Consistent with the results shown in Figure 4, the reaction yield obtained using Sono-$BiVO_4$ was higher than that in the case of HT-$BiVO_4$ and SS-$BiVO_4$ (entry 1 vs. entries 13 and 14).

Next, we investigated the substrate scope of the C-C bond cleavage to generate the carbonyl products from styrene derivatives. 1,1-Disubstituted compounds **1a**, **1b**, and **1c** were converted to the ketone products in good yields. Reactions of various styrene derivatives proceeded under the optimal conditions, regardless of the electron density, to give the corresponding aldehyde products. Substrates with electron-donating substituents such as *m*-, *p*-methyl (**1e, 1f**), *p*-*tert*-butyl (**1g**), and *p*-methoxy (**1h**) groups as well as electron-withdrawing substituents such as *o*-, *p*-bromo (**1i**, **1j**), *p*-fluoro (**1k**), and *p*-chloro (**1l**) furnished the corresponding aldehydes (**2**). In general, the carboxylic acid compound was generated as a side product through further oxidation of the aldehyde product under the conditions. In particular, more amount of carboxylic acid was generated from the styrene derivatives with electron-donating groups such as **1f** and **1g**.

Table 2. Substrate scope for the aerobic C-C bond cleavage

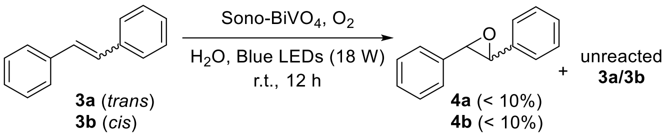


entry	styrene derivative (**1**)		product (**2**)		yield (%)[b]
1	**1a**		**2a**		78
2	**1b**		**2b**		50
3	**1c**		**2c**		80
4	**1d**		**2d**		85
5	**1e**		**2e**		73
6	**1f**		**2f**		71
7	**1g**		**2g**		69
8	**1h**		**2h**		76
9	**1i**		**2i**		82
10	**1j**		**2j**		81
11	**1k**		**2k**		68
12	**1l**		**2l**		77

[a] Reaction conditions: 1 (0.5 mmol), Sono-$BiVO_4$ (15 mg). [b] Isolated yields, GC yields using *n*-dodecane as the internal standard, or ^1H NMR yields using bromoform as the internal standard.

The synthetic utility of the transformation was examined in a gram-scale synthesis, where product **2a** was prepared on a 10 mmol scale. The yield was similar to that obtained in the 0.5 mmol scale reaction, despite the longer reaction time.

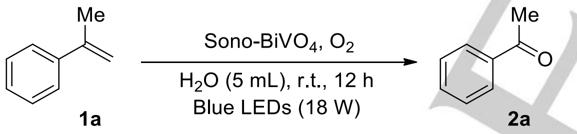
The reaction was selective as only terminal alkenes participated in the C-C bond cleavage. Internal alkenes were not suitable substrates for this transformation.[17] Interestingly, the reactions of highly conjugated stilbenes (*trans* and *cis*) provided the corresponding epoxide products despite very low conversion (Scheme 1).



Scheme 1. Reactions of stilbene. **3a**/**3b** (0.1 mmol), Sono-$BiVO_4$ (3 mg), H_2O (1 mL). The yields were determined by GC-MS using *n*-dodecane as the internal standard.

Note that the heterogeneous Sono-$BiVO_4$ could be easily separated from the reaction mixture and reused (**Table 3**). The recovered photocatalyst was subjected to the same reaction more than 5 times. In all cases, the catalyst provided **2a**, without notable loss of reactivity, demonstrating the most significant advantage for a heterogeneous catalyst. Furthermore, the turnover number (TON) of 2100 was obtained in the presence of 0.01% Sono-$BiVO_4$.

Table 3. Reusability of Sono-$BiVO_4$ crystals[a]



Number of recycling runs	1	2	3	4	5
yield (%)[b]	78	77	75	76	73

[a] Reaction conditions: 1a (0.5 mmol), Sono-$BiVO_4$ (15 mg). [b] The yields were determined by GC-MS using n-dodecane as the internal standard.

Next, to ascertain mechanistic insight into the source of oxygen, isotopic labeling experiment was conducted with water-^{18}O in the reaction of **1a**. The ^{18}O-labelled product was not formed from the reaction, indirectly confirming that molecular oxygen is the oxygen source for the carbonyl products. Additionally, several experiments were conducted to propose a mechanism for the oxidative cleavage of alkenes (Table *S2*). The reaction of **1a** was conducted in the presence of various additives such as TEMPO, 1,4-dinitrobenzene, benzoquinone, and DABCO. TEMPO (free radical quencher) and 1,4-dinitrobenzene (single electron transfer inhibitor) completely inhibited the transformation. The use of benzoquinone (superoxide quencher) also prevented the reaction to give less amount of **2a** in 17% yield, indicating the involvement of superoxide as the reactive oxygen species. However, it is not possible to rule out a mechanism where singlet oxygen involve because the use of DABCO (singlet oxygen quencher) also decreased the reaction yield to 32%. The proposed mechanism is shown in Scheme *S1* of the supporting information.

In conclusion, an efficient heterogeneous catalyst, $BiVO_4$ was synthesized by an ultrasonic-assisted method and successfully applied for the C-C bond cleavage of alkenes. Complementary to the traditional two-step processes such as ozonolysis and Lemieux-Johnson oxidation, this method is expected to be a practically viable alternative. Remarkably, the transformation in the presence of our newly synthesized $BiVO_4$ is highly sustainable, requiring only natural sources, i.e., molecular oxygen, visible light, and water. The $BiVO_4$ crystals can be easily separated from the reaction mixture and reused with the same efficiency.

Experimental Section

An oven-dried resealable tube equipped with a magnetic stir bar was charged with Sono-$BiVO_4$ (15 mg) in H_2O (5 mL) and the tube was sealed with a silicone septum screw cap. Molecular oxygen was bubbled through the reaction mixture for 5 min; then, styrene derivatives (0.5 mmol) were added. (Please add styrenes after oxygen bubbling due to the volatility of some styrenes.) An oxygen-filled balloon was fixed to the tube, which was then placed under 18 W 450 nm blue LEDs (420-480 nm) at room temperature, with stirring for 8-24 h. The reaction progress was monitored by gas chromatography or ^1H NMR spectroscopy. After completion of the reaction, dichloromethane or ethyl ether was added to the mixture, and the organic phase was extracted and concentrated on a rotary evaporator (carefully evaporated using a vacuum controller owing to the volatility of some carbonyl products). The carbonyl products was purified by silica gel flash column chromatography, using hexanes and ethyl ether as the eluent.

Acknowledgements

This research was supported by the Chung-Ang University Graduate Research Scholarship in 2018 for S. S. Han. We gratefully acknowledge the National Research Foundation of Korea [NRF-2012M3A7B4049657, NRF-2014-011165, NRF-2017R1E1A1A01074224 and NRF-2017R1A2B2004082].

Keywords: Heterogeneous catalysis • Bismuth Vanadates • Oxygen • Photocatalysis • C-C bond cleavage

[1] a) P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, **1998**; b) M. Poliakoff, J. M. Fitzpatrick, T. R. Farren, P. T. Anastas, *Science* **2002**, *297*, 807-810; c) C. -J. Li and M. Trost, *Proc. Natl. Acad. Sci. U. S. A.*, **2008**, *105*, 13197-13202.

[2] Some recent reviews on visible-light photocatalysis, see: a) Visible Light Photocatalysis in Organic Chemistry, ed. C. R. J. Stephenson, T. R. Yoon and D. W. C. MacMillan, John Wiley & Sons, **2018**; b) D. Cambi, C. Bottecchia, N. J. W. Straathof, V. Hessel, T. Noël, *Chem. Rev.* **2016**, *116*, 10276–10341; c) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075–10166; d) T. Chatterjee, N. Iqbal, Y. You, E. J. Cho, *Acc. Chem. Res.* **2016**, *49*, 2284-2294.

[3] Some reviews on heterogeneous photocatalysis, see: a) X. Lang, X. Chen, J. Zhao, *Chem. Soc. Rev.* **2014**, *43*, 473-486; b) S. Dong, J. Feng, M. Fan, Y. Pi, L. Hu, X. Han, M. Liu, J. Sun, J. Sun, *RSC. Adv.* **2015**, *5*, 14610-14630

[4] Some examples on metal oxides, see: a) S. Furukawa, T. Shishido, K. Teramura, T. Tanaka, *ACS. Catalysis.* **2011**, *2*, 175-179; b) X. Lang, W. Ma, Y. Zhao, C. Chen, H. Ji, J. Zhao, *Chem. Eur. J.* **2012**, *18*, 2624-2631; c) M. Rueping, J. Zoller, D. C. Fabry, K. Poscharny, R. M. Koenigs, T. E. Weirich, J. Mayer, *Chem. Eur. J.* **2012**, *18*, 3478-3481.

[5] a) A. G. S. Prado, L. B. Bolzon, C. P. Pedroso, A. O. Moura, L. L. Costa, *Appl. Catal. B-Environ.* **2008**, *82*, 219-224; b) S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, *Angew. Chem. Int. Ed.* **2013**, *52*, 7372-7408; c) K. Pingmuang, J. Chen, W. Kangwansupamonkon, G. G. Wallace, S. Phanichphant, A. Nattestad, *Sci. Rep.* **2017**, *7*

[6] $BiVO_4$ has recently attracted as a photoanode for solar water oxidation, see: Y. Park, K. J. McDonald, K. S. Choi, *Chem. Soc. Rev.* **2013**, *42*, 2321-2337.

[7] a) T. Saison, N. Chemin, C. Chanéac, O. Durupthy, L. Mariey, F. Maugé, V. Brezová, J. P. Jolivet, *J. Phys. Chem. C* **2015**, 119, 12967−12977; b) M. V. Malashchonak, E. A. Streltsov, D. A. Kuliomin, A. I. Kulak, A. V. Mazanik, *Materials Chemistry and Physics* **2017**, *201*, 189-193; c) H. L. Tan, R. Amal, Y. H. Ng, *J. Mater. Chem. A* **2017**, 5, 16498–16521.

[8] a) B. Yuan, R. Chong, B. Zhang, J. Li, Y. Liu, C. Li, *Chem. Commun.* **2014**, *50*, 15593-15596; b) S. M. López, K. Villa, T. Andreu, J. R. Morate, *ACS Catal*. **2014**, 4, 3013-3019; c) S. Samanta, S. Khilari, D. Pradhan, R. Srivastava, *ACS Sustain. Chem. Eng.* **2017**, 5, 2562-2577; d) L. K. S. Ng, E. J. C. Tan, T. W. Goh, X. Zhao, Z. Chen, T. C. Sum, H. S. Soo, *Appl. Mater. Today*, **2019**, 15, 192-202.

[9] a) G. Park, J. Y. Park, J. H. Seo, K. H. Oh, A. Ma and K. M. Nam, *Chem. Commun.* **2018**, *54*, 5570-5573; b) A. D. Proctor, S. Panuganti and B. M. Bartlett, *Chem. Commun.* **2018**, *54*, 1101-1104.

[10] A. J. E. Rettie, H. C. Lee, L. G. Marshall, J.-F. Lin, C. Capan, J. Lindemuth, J. S. McCloy, J. Zhou, A. J. Bard and C. B. Mullins, *J. Am. Chem. Soc.*, **2013**, *135*, 11389-11396.

[11] Some reviews on oxidation reactions, see: a) T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329-2363; b) Z. Shi, C. Zhang, C. Tang, N. Jiao, *Chem. Soc. Rev*. **2012**, *41*, 3381-3430.

[12] A. Kleemann, J. Engel, B. Kutscher, D. Reichert, *Pharmaceutical Substances, 4th ed.*; Georg Thieme: Stuttgart, Germany, **2001**.

[13] S. G. V. Ornum, R. M. Champeau, R. Pariza, *Chem. Rev.* **2006**, *106*, 2990−3001.

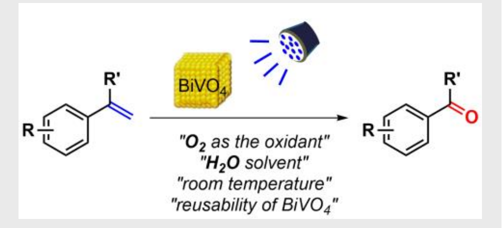
[14] a) R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.* **1956**, *21*, 478–479; b) K. B. Sharpless, K. J. Akashi, *J. Am. Chem. Soc.* **1976**, *98*, 1986− 1987; c) B. R. Travis, R. S. Narayan, B. J. Borhan, *J. Am. Chem. Soc.* **2002**, *124*, 3824−3825.

[15] Some examples, see: a) K. Ohkubo, T. Nanjo, S. Fukuzumi, *Org. Lett.*, **2005**, *7*, 4265-4268; b) P. Daw, R. Petakamsetty, A. Sarbajna, S. Laha, R. Ramapanicker, J. K. Bera, *J. Am. Chem. Soc.* **2014**, *136*, 13987-13990; c) A. Gonzalez-de-Castro, J. Xiao, *J. Am. Chem. Soc.* **2015**, *137*, 8206-8218.

[16] A. A. Ghogare, A. Greer, *Chem. Rev.* **2016**, *116*, 9994-10034.

[17] Please see Table *S1* of the supporting information where unsuccessful examples are shown.

COMMUNICATION



As an efficient heterogeneous catalyst, $BiVO_4$ crystals were synthesized by an ultrasonic-assisted method and successfully applied for the C-C bond cleavage of alkenes.

Sung Su Han, Joon Yong Park, Ho Seong Hwang, Hye Rin Choe, Ki Min Nam, and Eun Jin Cho**

Page No. – Page No.

Facile Synthesis of $BiVO_4$ for Visible-Light-Induced C-C Bond Cleavage of Alkenes to Generate Carbonyls