

## A bridge with our customers **USER'S VOICE** Insights into Decomposition Pathways and Fate of $\text{Ru}(\text{bpy})_3^{2+}$ during Photocatalytic Water Oxidation with $\text{S}_2\text{O}_8^{2-}$ as Sacrificial Electron Acceptor

Sogang University in Korea  
Tracera, QYM-01



Professor Kyung Byung Yoon  
Sogang University in Korea

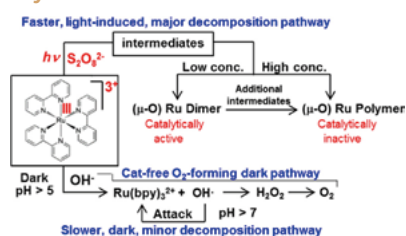
We visited Professor Kyung Byung Yoon at Sogang University in Korea. He is one of the leading researchers in the field of artificial synthesis. His laboratory features many analytical instruments, including the Tracera GC-BID system and the QYM-01 photoreaction quantum yield evaluation system\*, which permits accurate and easy simple quantitation measurements of absorbed photons.

\* The QYM-01 system is not available in Europe and may not be available in some other countries. Please contact your local Shimadzu representative for availability.

### Would you please introduce your research?

The most widely accepted system for homogeneous photocatalytic water oxidation process consists of a water oxidation catalyst,  $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$  as a photopump, and  $\text{S}_2\text{O}_8^{2-}$  as the sacrificial electron acceptor. However,

this system is far less than ideal because  $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$  undergoes very rapid decomposition and as a result the process stops before all of the  $\text{S}_2\text{O}_8^{2-}$  is consumed. In this regard its decomposition pathways and the fate of  $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$  should be elucidated to design more efficient photocatalytic water oxidation systems. We found that two pathways exist for decomposition of  $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$  in the light- $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system. The first is the formation of  $\text{OH}^\bullet$  radicals at  $\text{pH} > 6$  through oxidation of  $\text{OH}^-$  by  $\text{Ru}^{\text{III}}(\text{bpy})_3^{3+}$  in the dark, which attack the bpy ligand of  $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ . This is a minor, dark decomposition pathway. During irradiation not only  $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$  but also  $\text{Ru}^{\text{III}}(\text{bpy})_3^{3+}$  becomes photoexcited and the photoexcited  $\text{Ru}^{\text{III}}(\text{bpy})_3^{3+}$  reacts with  $\text{S}_2\text{O}_8^{2-}$  to produce an intermediate which decomposes into catalytically active Ru  $\mu$ -oxo dimers when the intermediate concentration is low or into catalytically inactive oligomeric Ru  $\mu$ -oxo species when the intermediate concentration is high. This is the major, light-induced decomposition pathway. When the  $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$  concentration is low, the light- $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ - $\text{S}_2\text{O}_8^{2-}$  system produces  $\text{O}_2$  even in the absence of any added catalysts through the  $\text{O}_2$ -producing dark pathway. When the  $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$  concentration is high, the system does not



produce  $\text{O}_2$  because the overall rate for the light-induced decomposition pathway is much faster than that of the  $\text{O}_2$ -producing dark pathway (*ACS Catal.* 2016, 6, 8361–8369).

### Are "QYM-01" and "Tracera (GC+PID Detector)" being efficiently used for your research? How are they useful?

QYM-01 can take a UV-Vis spectrum every minute or shorter than that. This allows us to monitor how fast a material reacts during photoreaction. Also, it can measure the number of photons that a photosensitizer absorbs. When we detect products, the quantum yield of the reaction is calculated by plotting the number of absorbed photons versus generated products.

Tracera is efficient for checking liquid products. The detection sensitivity was also good. Almost all materials were detected in the column.

### What do you think about the advantages and benefits of "QYM-01" and "Tracera (GC+PID Detector)"?

We can take a UV-Vis spectrum during photolysis without changing any other reaction system. We can measure the power of light we are using. This is the advantage of QYM-01. As for Tracera, the detection limit is good.



### Nexis GC-2030



The new GC System is now ready to solve your trace analysis needs. This system utilizes the new Barrier Discharge Ionization Detector technology coupled with a GC-2030 capillary gas chromatograph to create a GC system that makes it possible to reveal trace components that are difficult to see by other GC detectors.

For more details



#### Do you have any suggestions about improving or enhancing the features/functionality of the "QYM-01" and "Tracera (GC+PID Detector)"?

Firstly, the intensity of light that reaches the reaction site needs to be higher. At a wavelength, the power of light was 1 to 2 mW/cm<sup>2</sup>. Secondly, the gas inlet and outlet from the QYM-01 needs to be installed like ports for water circulation. Lastly, to check the power of light, we have to remove the lid of the machine and move the detector.

As for Tracera, the detection of formic acid needs many steps.

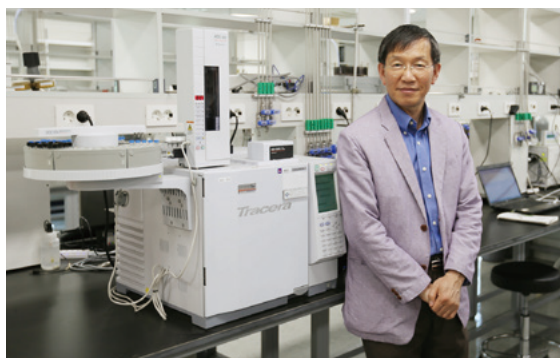
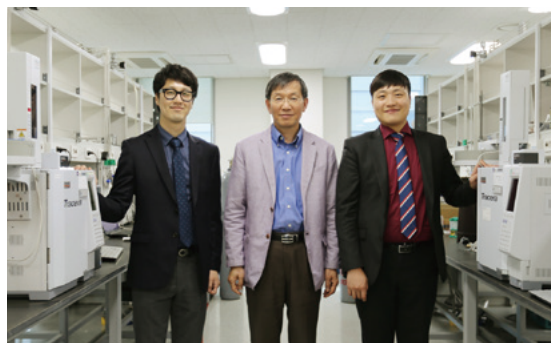
#### Do you have any requests or expectations for Shimadzu technology, products and service?

The stirring system has a lifetime. So, I hope to replace it immediately when it stops.

#### Please let us know your image of "Shimadzu Corporation"

You are providing an unprecedented product and good service.

It was great time to talk to you and to know what you think about our instruments and our attitudes. We must try to keep getting better. Thank you very much.



#### Comments About the Interview

After the interview, Professor Yoon said, "Because of few examples of its installation, QYM has a lot to be improved, such as stability or usability. On the other hand, I am impressed that Shimadzu has an original unique technology without precedent, such as QYM, and look forward to its future advancement." What pleased us more was that he added, "We can cooperate together to be the bridge of Korea and Japan, and to make both countries more affluent through Shimadzu instruments and solutions."



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<http://www.shimadzu.com/an/bridge/bridge42.html>

## Tracera, QYM-01



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