Quantitative description of photocatalysis for water splitting by transferring knowledge from electrocatalysis

Kazuhiro Takanabe[a*]

[a]*King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center and Physical Sciences and Engineering Division, 4700 KAUST, Thuwal 23955-6900, Saudi Arabia*
**Corresponding author: kazuhiro.takanabe@kaust.edu.sa*

Abstract: When photocatalysis undergoes multiple electron transfer steps via adsorbed intermediate species, e.g., hydrogen or oxygen evolution reactions, the typical timescale of surface electrocatalysis is much longer than that of the bulk photophysical process involving photon absorption and charge separation. When the kinetic bottleneck resides in such surface redox reactions, the description and ranking of electrocatalysis can be effectively transferred to such photocatalytic systems. The presentation provides some evidence of such cases and discusses the usefulness of the transfer of knowledge from electrocatalysis to photocatalysis.
Keywords: Photocatalysis, Electrocatalysis, Water splitting.

1. Introduction

For the photocatalytic water splitting reaction, the climax of the reaction sequence is the surface reduction (H_2 evolution) and oxidation (O_2 evolution) reactions using photoexcited electrons and holes, respectively.[1] Recent advancement in photocatalyst particulate materials (photon absorbers) enables the efficient generation of the useful electrons and holes at surface sites. Decoration of the surface with electrocatalysts (often called cocatalysts) is therefore essential to achieve a high efficiency for the entire process. When the surface electrocatalysis might be the kinetic bottleneck, the identity of the electrocatalyst and electrolyte conditions play a crucial role. Herein, we discuss two cases: one using UV-responsive large bandgap materials, typically $SrTiO_3$, for overall water splitting[2-5] and a second using visible-light-responsive materials, namely, Ta_3N_5, for the oxygen evolution reaction in the presence of electron accepters.

2. Experimental

$SrTiO_3$ synthesis and subsequent electrocatalyst decoration was described in the references in detail.[2-5] Ta_3N_5 synthesis and subsequent electrocatalyst decoration is described in the references.[6,7] The photocatalytic reaction is described in detail in the reference.[8] Detailed descriptions of the respective characterizations are also described in the corresponding references.[2-7]

3. Results and discussion

Successful overall water splitting using a $SrTiO_3$ photocatalyst under UV light illumination requires effective decoration with a hydrogen evolving electrocatalyst on its surface. The highly efficient hydrogen evolving electrocatalyst causes the back reaction of H_2 and O_2 to H_2O with and without photon illumination. In addition to the thermal recombination of H_2 and O_2, electrocatalytic O_2 reduction, or the water forming reaction, competitively occurs at the H_2 evolution potential. One way to prevent this back reaction is to introduce a membrane nanolayer on the H_2 electrocatalyst, which allows the evolved H_2 to escape but blocks the penetration of O_2 through to the catalyst surface. We reported that a Cr-layer,[2] Mo-layer,[3] and more recently SiO_2-layer[4] are able to function as such membranes. Discovery of these layers is facilitated by an electrochemistry study, where the membrane functions were quantitatively investigated based on the electrochemical behaviors of similarly decorated model electrodes. The concept is depicted in Figure 1 using the SiO_2-layer as an example. On the other hand, if the hydrogen evolving electrocatalyst is intrinsically selective for H_2 evolution, these membrane layers are not essential. We discovered that tungsten carbide nanoparticles are an excellent H_2 evolving catalyst but poor oxygen reduction catalyst, successfully achieving overall water splitting when they are used to decorate the surface of $SrTiO_3$.[5]

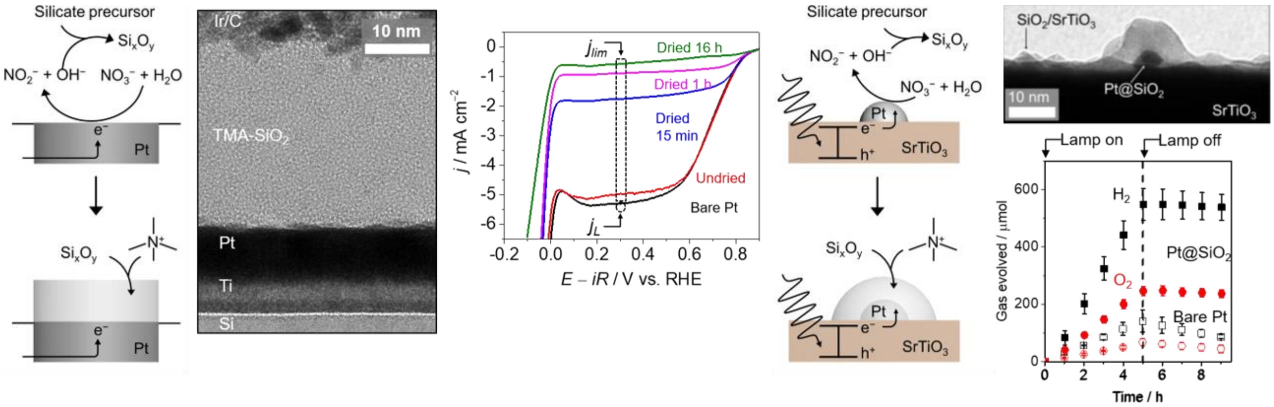

Figure 1. (From left to right) A scheme of the electrochemical deposition of SiO_x species on a Pt electrode in the presence of a structure directing agent (tetramethylammonium ions), a cross-sectional TEM image, the electrocatalytic performance, a scheme of the photodeposition of SiO_x on a Pt/$SrTiO_3$ photocatalyst, a TEM image, and the photocatalytic time on stream.[4]

Ta_3N_5 is a promising photocatalyst possessing visible-light response. Efficient photocatalytic oxygen evolution is possible, especially when a strong electron accepter is present in the system. Such reaction conditions highlight that the O_2 evolution steps are the kinetic bottleneck during the photocatalysis, and thus, the ranking of the catalyst and electrolyte conditions for O_2 evolution coincides with the electrocatalytic performances using electrodes as well as the photocatalytic performances using a powder semiconductor. This can be evaluated using a CoO_x-based electrocatalyst[6] and $NiFeO_x$-based catalyst,[7] where the latter is shown in Figure 2 as an example.

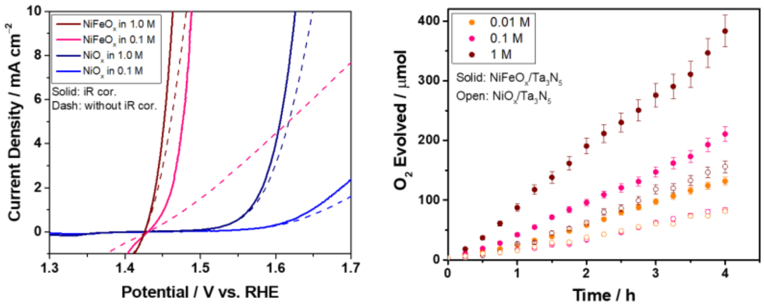

Figure 2. (Left) Electrocatalytic performance of $NiFeO_x$ or NiO_x and (right) photocatalytic performance of Ta_3N_5 decorated with $NiFeO_x$ or NiO_x in the presence of 0.1 M $Na_2S_2O_8$ in 0.1 M or 1.0 M NaOH.

4. Conclusions

As the efficiency of a photocatalyst semiconductor is improved, the electrocatalysis occurring on its surface becomes critical. We demonstrate the successful transfer of knowledge from electrocatalysis to photocatalysis, in which the potentials are well-defined (electrocatalysis) to ill-defined (photocatalysis). The integration of such knowledge is effective to further improve photocatalytic water splitting and beyond.

References

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