

## Insight into Microwave-Enhanced Heterogeneous Catalytic Reactions – Non-Equilibrium Local Heating and Acceleration of Electron Transfer

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Microwaves often exhibit enhanced reaction rate and improved product selectivity in a broad range of organic and inorganic reactions as compared to conductive heating<sup>1,2</sup>. The microwave enhanced reaction are considered due to thermal effects (super heating, selective heating, and rapid heating) as well as non-thermal effect, however, there are very few papers dealt with their detailed mechanism under precisely controlled reaction condition. This paper briefly introduces the recent advances in Wada's group in Tokyo Institute of Technology, Japan, regarding insight into the mechanisms involved in microwave-enhanced reactions at the interface of solid catalyst, especially focusing on non-equilibrium local heating and acceleration of electron transfer.

### Non-equilibrium local heating at the solid catalyst

Selective heating of solids due to microwaves generates local thermal non-equilibrium at the vicinity of solid catalyst and enhances chemical reactions. However, the local temperature of the catalyst is hardly measured by the existing thermometers. Molecular thermometer was, therefore, used to measure the local temperature of the heterogeneous catalyst under microwaves. Photoluminescent (PL) probes can be used as a molecular thermometer by detecting their temperature-dependent PL lifetime<sup>3</sup>. First, BaTiO<sub>3</sub> core was covered with SiO<sub>2</sub> shell particle and subsequently rhodamine B (RhB) was loaded into the SiO<sub>2</sub> mesopores to obtain BaTiO<sub>3</sub>-RhB@SiO<sub>2</sub> probe (Fig. 1a). In this system, BaTiO<sub>3</sub> core becomes the heat source under microwaves. The calibration line between temperature and PL lifetime of RhB on BaTiO<sub>3</sub>-RhB@SiO<sub>2</sub> was obtained in heptane using conventional heating with good validity ( $R^2 = 0.9880$ ). *In situ*

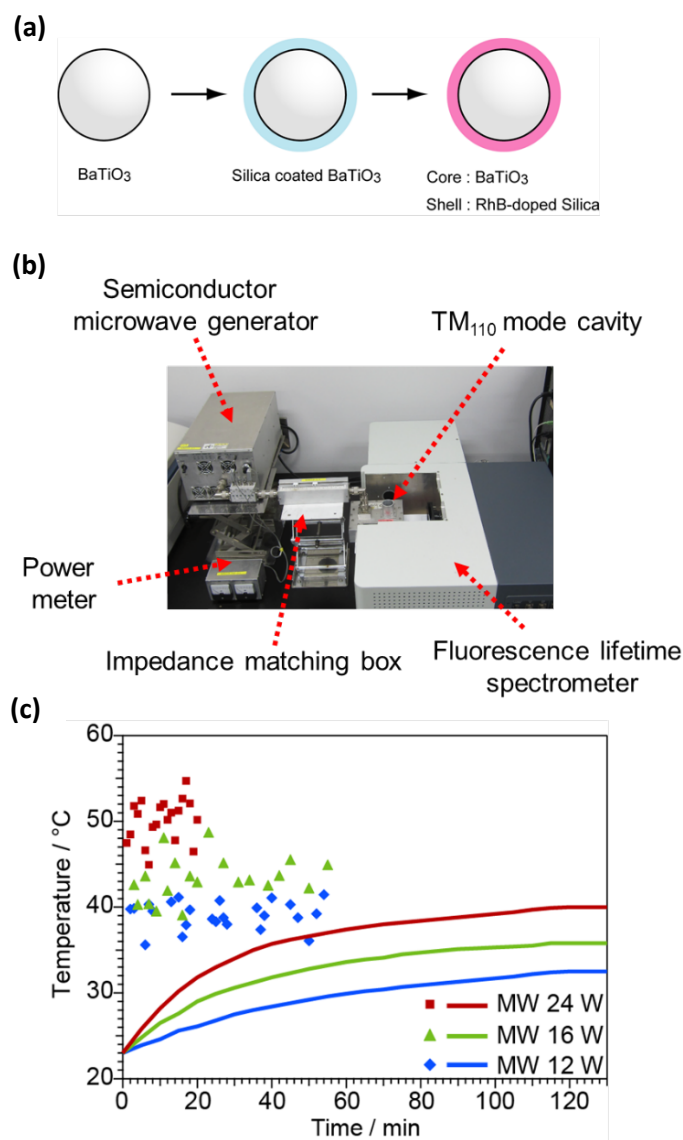
temperature measurement of BaTiO<sub>3</sub>-RhB@SiO<sub>2</sub> was, then, conducted by the fluorescence lifetime spectrometer equipped with semiconductor microwave generator and TM<sub>110</sub> mode microwave cavity (Fig. 1b). BaTiO<sub>3</sub>-RhB@SiO<sub>2</sub> gave 28°C higher than the bulk heptane temperature under microwave irradiation (at 24 W, Fig. 1c) demonstrating the existing of local thermal non-equilibrium at the particle.

The microwave-induced local thermal non-equilibrium can be effectively applied to heterogeneous catalytic systems. For instance, dehydration of alcohols was enhanced by using a core-shell, carbon filled zeolite@zeolite, which was prepared by carbon filling at the core of the Y-type zeolite (Fig. 2a). Both inter- and intra-molecular dehydration of 1-phenylethanol was enhanced by carbon filled zeolite under microwaves as compared to conventional heating due to heat generation at the carbon filled core by microwaves (Figs. 2b, c). In contrast, sole zeolite gave the same reaction behavior regardless of microwave irradiation since zeolite exhibit very low dielectric loss. The local temperatures at the reaction spaces in the shell zeolite were then estimated from the Arrhenius plot obtained by oil bath heating. The temperature rises were estimated as +6 k for intramolecular dehydration and +11 K for intermolecular dehydrations. These results strongly suggest the generation of local thermal non-equilibrium at the heterogeneous catalyst to enhance chemical reactions under microwaves.

### Electron-transfer acceleration at the solid interface

In addition to the local thermal non-equilibrium, electron transfer can be accelerated by microwave oscillating electromagnetic field. Recently, microwave-accelerated photoinduced electron transfer was

observed for photocatalytic reduction of bipyridinium ion over CdS quantum dots (QD)<sup>5</sup>. CdS QD was immobilized on SiO<sub>2</sub> thin film, and their PL life time was measured in a presence of electron acceptor under microwave irradiation. Microwaves gave shorter PL lifetimes due to enhanced electron transfer from CdS QD to the electron donor, than conventional heating. According to the Marcus theory, microwaves were found to affect electronic coupling matrix element ( $H_{AB}^2$ ) rather than reorganization energy ( $\lambda$ ).



**Figure 1.** (a) Synthesis of BaTiO<sub>3</sub>-RhB@SiO<sub>2</sub>. (b) The fluorescence lifetime spectrometer with a solid-state microwave generator and a TM<sub>110</sub> mode resonance cavity. (c) *In-situ* temperature measurement of BaTiO<sub>3</sub>-RhB@SiO<sub>2</sub> under microwaves (dots: local temperature, lines: bulk temperature measured by fiber optic thermometer). Reproduced from Ano et al.<sup>3</sup> with permission from Royal Society of Chemistry.

Microwave-accelerated electron transfer was also observed for oxygen evolution reaction over  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> deposited FTO electrode<sup>6</sup>. The pulsed microwave irradiation exhibited increased anodic current which is attributed to oxygen evolution by water splitting (Fig. 3). This process was too instantaneous so that it cannot be explained by temperature increase due to microwave heating. Then, continuous microwave irradiation for 6 seconds gave slight increase in current density due to elevation in the temperature as measured by the fiber optic thermometer. Since electron transfer process is the rate determining step in the water oxidation reaction, the increased anodic current can be attributed to enhancement in electron transfer under microwaves.

## Conclusions

In the present paper, non-equilibrium local heating and acceleration of electron transfer was proposed as the two key mechanisms involved in the microwave enhanced reaction (Fig. 4). The non-equilibrium local heating can be observed in binary mixing system where high loss-factor material and low loss-factor material exist. Local thermal non-equilibrium can be generated at higher loss-factor materials and generates temperature gradient in the reaction system which cannot be reproduced by conventional heating. In contrast, microwaves can enhance these electron-transfer processes irrespectively to alternation in the reaction temperature. The electron transfer is an important elementary step for photocatalysis, as well as oxidation-reduction reactions. The synergistic application of these two mechanisms are expected to open new ways to use microwaves as an external field to enhance heterogeneous catalytic reactions.

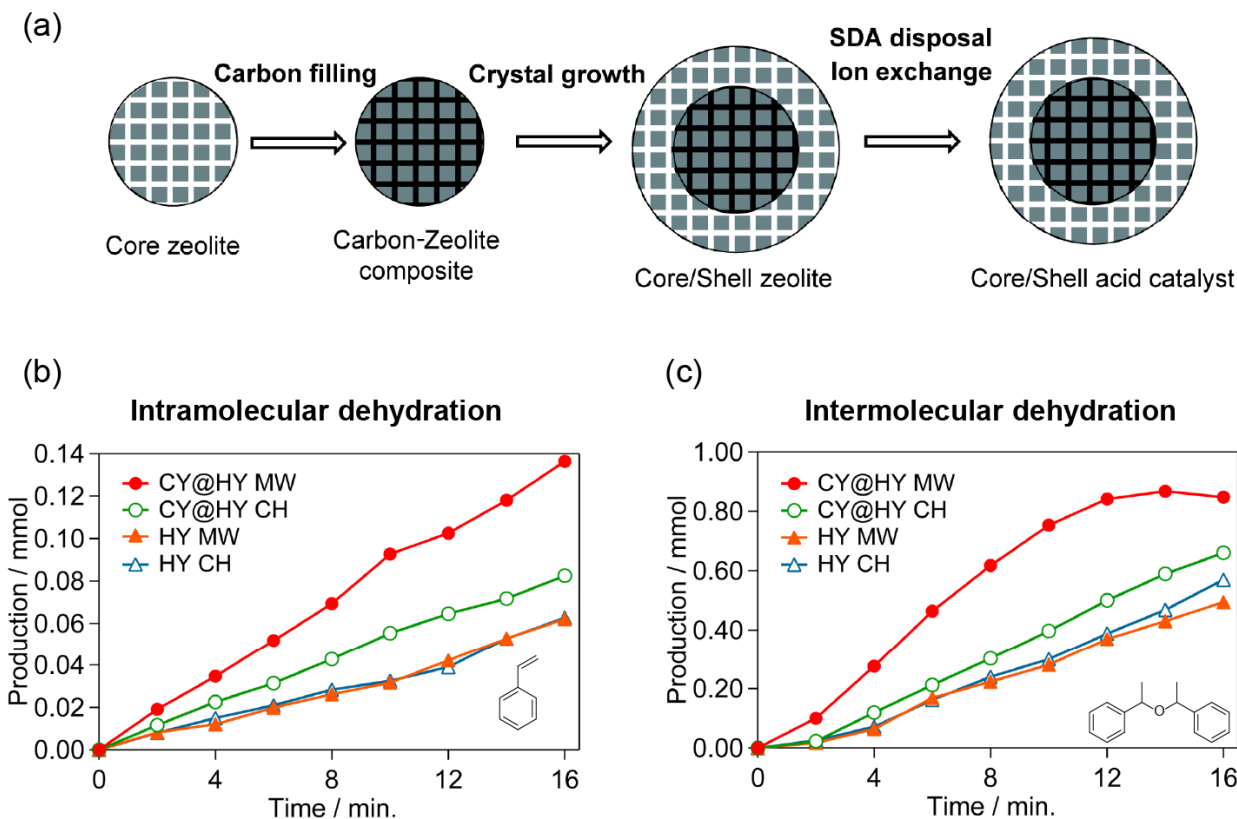
## For further reading:

1. D. M. P. Mingos, D. R. Baghurst "Applications of microwave dielectric heating effects to synthetic problems in chemistry" *Chemical Society Reviews*, **20**, pp. 1-47, 1997.
2. A. Loupy, *Microwaves in Organic Synthesis*, Wiley-VCH Verlag GmbH & Co., KGaA 2006.
3. T. Ano, F. Kishimoto, R. Sasaki, S. Tsubaki, M. M. Maitani, E. Suzuki, Y. Wada, "In situ temperature measurements of reaction spaces under microwave irradiation using photoluminescent probes" *Physical Chemistry Chemical Physics*, **18**, pp. 13173-13179, 2016.
4. D. Mochizuki, R. Sasaki, M. M. Maitani, M. Okamoto, E. Suzuki, Y. Wada, "Catalytic reaction enhanced under microwave-induced local thermal non-equilibrium in a core-shell, carbon-filled zeolite@zeolite" *Journal of Catalysis*, **323**, pp 1-9, 2015.
5. F. Kishimoto, T. Imai, S. Fujii, D. Mochizuki, M. M. Maitani, E. Suzuki, Y. Wada, "Microwave-enhanced

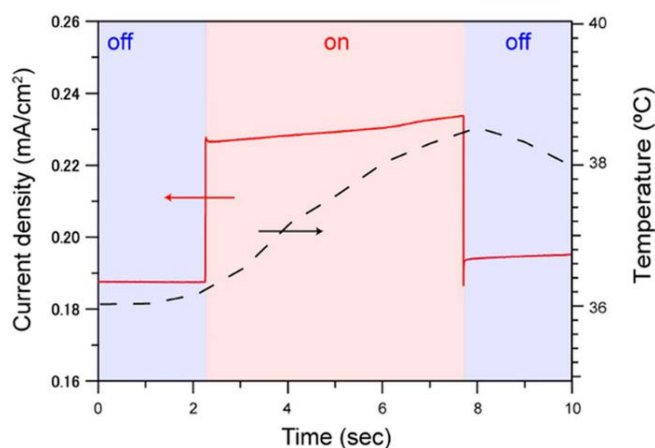
photocatalysis on CdS quantum dots – evidence of acceleration of photoinduced electron transfer” Scientific Reports, **5**, 11308, 2015.

“Enhancement of anodic current attributed to oxygen evolution on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrode by microwave oscillating electric field” Scientific Reports, **6**, 3554, 2016

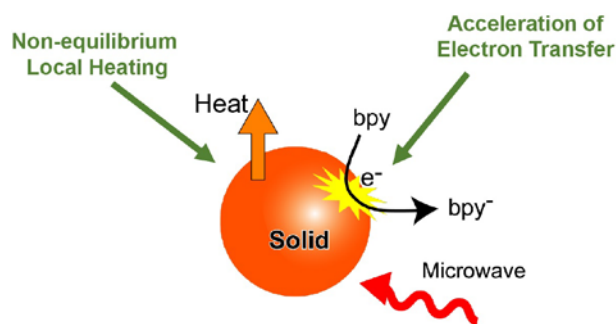
6. F. Kishimoto, M. Matsuhisa, S. Kawamura, S. Fujii, S. Tsubaki, M. M. Maitani, E. Suzuki, Y. Wada,



**Figure 2.** (a) Synthesis of carbon filled core shell zeolite. (b) Intramolecular dehydration and (c) intermolecular dehydration of 1-phenylethanol (CY: Carbon core zeolite, HY: Sole zeolite, MW: Microwave heating, CH: Conventional heating). Reproduced from Mochizuki et al<sup>4</sup> with permission from Elsevier B.V.



**Figure 3.** The potentiostatic amperometry at 1.966 V vs RHE with pulsed microwave irradiation. Reproduced from Kishimoto et al<sup>6</sup> with permission from Nature Publishing Group.



**Figure 4.** Schematic illustration of non-equilibrium local heating and acceleration of electron transfer at the interface of solids.

### About the Authors

Wada group in Tokyo Institute of Technology, Japan, is dedicated to nano-materials chemistry, photo chemistry as well as microwave chemistry. Under the leadership of Prof. Yuji Wada, we are trying to reveal the unique physical and chemical phenomenon induced by electromagnetic wave energy in a wavelength from nanometer scale (near ultraviolet, visible and near infrared region) to meter scale (including microwaves) using noble nano-hybrid systems.

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