

# Acceleration of Electron Transfer at Interfaces of Solid Semiconductors under Microwave Irradiation

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**Abstract:** Electron transfer at the interfaces of solid semiconductors is accelerated by microwave irradiation. We demonstrate data proving the acceleration here for two systems, i.e., enhanced anodic current of a hematite electrode for water oxidation under microwaves and enhancement in the reduction quenching of fluorescence of cadmium sulfide nanoparticles under microwaves, resulting in the enhanced photocatalytic reduction of methylviologen by microwaves. This acceleration of electron transfer is an origin of “microwave special effects” observed as enhancement of chemical reactions and shortening of completion time of chemical syntheses under microwave irradiation. It would lead to a new methodology for promoting redox reactions.

**Keywords:** microwaves, microwave non-thermal effects, electron transfer

## Introduction

Researchers interested in chemical reactions have been long attracted by “microwave special effects” observed as acceleration of chemical reactions, shortening of the completion time of chemical synthesis, increase in the chemoselectivity in both homogeneous and heterogeneous reaction systems<sup>1)</sup>. We find the papers insisting on the presence of “microwave special effects” for hydrodesulfurization of thiophene (exothermic) and decomposition of hydrogen sulfide (endothermic) on MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub><sup>2)</sup>, and the enhanced reactions of steam-carbon and water-gas shift reaction<sup>3)</sup> and the enhanced reduction of copper oxide under microwave magnetic-field irradiation by coupling of H-field with the Fermi level electrons of CuO, resulting in cleavage of Cu-O bond<sup>4,5)</sup>. It is a need to more carefully investigate these systems in order to understand the mechanisms of microwave special effects. Wada and Tsubaki’s research group recently has proposed two aspects of “microwave special effects” supported by the precisely designed experiments, i.e., “nonequilibrium local heating” and “acceleration of electron transfer”. Both phenomena are observed especially for heterogeneous systems containing solids, interestingly for the interface between solid-solid, and liquid-solid. The authors focus the “acceleration of electron transfer” in the present paper by demonstrating the two examples for an electrochemical water oxidation and a photoinduced electron transfer.

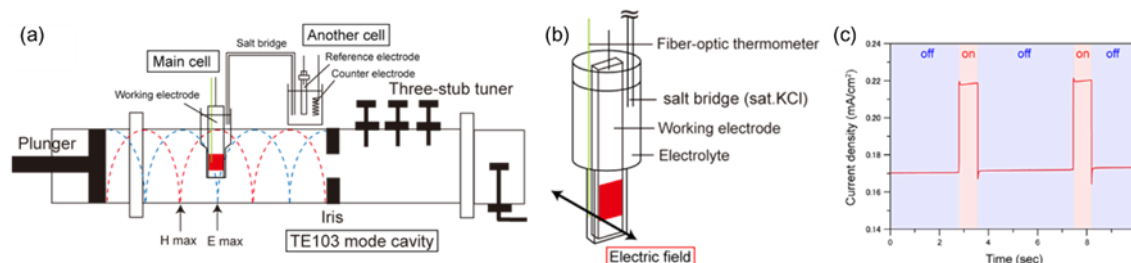
## Results and discussion

### MW-accelerated electron transfer observed for water oxidation on a hematite electrode<sup>6)</sup>

We demonstrated that a water oxidation on a hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) electrode was accelerated under microwaves using a setup of an electrochemical measurement shown in Fig. 1(a). A main cell made of quartz (Fig. 1(b)) was placed into the 2.45 GHz waveguide-type single mode microwave cavity and positioned at the antinode of the oscillating electric field where the electric field is maximum in the cavity. Then, the electrode set at 1.966 V vs. RHE was irradiated with microwaves intermittently by the period of 1 s. The rectangular waves were observed under pulsed microwave irradiation as shown in Figs. 1(c). The current density was raised from 0.17 mA cm<sup>-1</sup> to ~0.22 mA cm<sup>-1</sup> simultaneously with microwave irradiation and got back to 0.17 mA cm<sup>-1</sup> after switching off. The steady increment of the anodic current density should be attributed to the enhancement of the water oxidation reaction on the surface of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/FTO electrode by the oscillating electric field of microwaves.

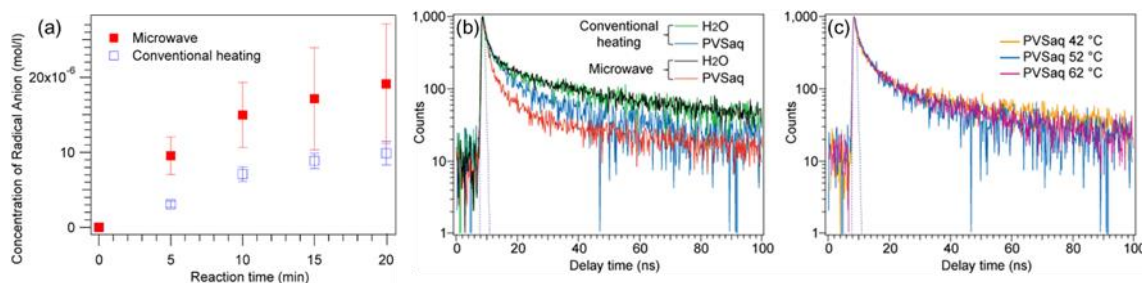
### MW-accelerated electron transfer observed for CdS nanoparticles<sup>7)</sup>

We observed the enhanced photocatalytic reduction of bipyridinium by CdS nanoparticles under microwave irradiation (Fig. 2(a)). The generation rate of the anion radicals of bipyridinium under microwaves was two times faster than that under conventional heating, exhibiting the enhancement of the photocatalytic activity of CdS nanoparticles.



**Figure 1** (a). The microwave irradiation cavity and the positions of the electrochemical cells. (b). Detailed illustration of the main cell. (c). The anodic current under intermittent microwave irradiation.

In order to determine the rate of electron transfer from the photoexcited CdS nanoparticles to the PVS, photoemission decays of CdS nanoparticles in a sub-nanosecond order have been measured under conventional heating and microwave irradiation. The time-resolved emission decay profiles of CdS nanoparticles immersed in pure water or PVS aqueous solution are shown in Fig. 2(b). The emission lifetime of CdS nanoparticles immersed in PVS solution was clearly shortened under microwave irradiation. These data demonstrated that the microwaves can accelerate the photoinduced electron transfer reaction from the CdS nanoparticles to the PVS in the liquid phase.



**Figure 2** (a). Time variation plots of the PVS radical anion concentration under microwaves and conventional heating. (b). Time-resolved emission decay profiles of CdS nanoparticles immersed in pure water or PVS aqueous solution under microwaves or conventional heating. (c). Temperature dependence of time-resolved emission decay profiles of CdS nanoparticles immersed in a PVS aqueous solution

## 4. Conclusions

A non-thermal special effects of microwaves revealed as “acceleration of electron transfer” in this paper can be extended to applications to enhancing redox reactions and photocatalysis as a novel methodology to control chemical reactions.

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