

## Magnetic field effect on heterogeneous photocatalytic reactions

H. Okumura\*, S. Endo, S. Joonwichien, E. Yamasue, K. N. Ishihara  
Graduate School of Energy Science, Kyoto University, Kyoto, 606-8501, JAPAN  
\*corresponding author: okumura@energy.kyoto-u.ac.jp

### Introduction

In the research of magnetic field effects (MFEs) on non-magnetic systems, the reproducibility is often the major issue. The MFEs on homogeneous systems are, however, rather established [1]. In the electrochemistry field the magnetic field (MF) control of reactions and precipitations has been actively studied, especially for the last 20 years. The MFEs on homogeneous systems are generally explained in terms of the radical pair mechanism. By contrast, the MFE on heterogeneous photocatalysis is rather limited, where not only the mechanism but the reproducibility becomes a subject of debate. Kiwi reports [2] the MFEs on photosensitized reactions using TiO<sub>2</sub> and CdS particles under 0.4 T (tesla). The MFE on Pt/TiO<sub>2</sub> system is also studied [3,4]. The systems studied are thus lopsided to titania, and the mechanism is still controversial. In this study the MFE on the heterogeneous systems is discussed using ZnO powder, including our previous works and further evolution [5].

### Materials and Methods

Reaction systems involve (i) decoloration of MB (methylene blue) solution, and (ii) reduction precipitation of Ag from AgNO<sub>3</sub> solution. The “settling time” is defined as the time interval between preparation of MB solution and ZnO powder immersion into the solution in a cell (4mL). Concentration of dissolved oxygen (DO) is monitored by a multifunction meter with DO electrode. The cell is irradiated with UV-LED (365 nm) under MF (0-0.7 T). The MB concentration is estimated from absorbance by spectroscopy (at 664 nm), which is performed *in-situ* (1 sec interval) as well. The effect of temperatures on MFE is also investigated (6~45°C). As for bubbling systems Ar or O<sub>2</sub> gas is bubbled into a solution for 1h (0.1 L/min), followed by powder dispersion and light irradiation. Dye adsorption onto ZnO or TiO<sub>2</sub> (st41) is performed in dark (0.7 T). For reduction experiments, AgNO<sub>3</sub> solution (0.01 mol/L) is irradiated with LED for 1h under MF. Concentration of Ag<sup>+</sup> is quantified by titration of NaCl solution. Fluorescein sodium solution is used to determine the end of titration by color change.

### Results and Discussion

As shown in Figure 1 the MFE (5min settling) is dependent on the MB concentration, highly reproducible, and positive MFEs are seen. The data are taken at least 3 times and averaged, shown with an error bar. This indicates diffusion of dye molecules is involved with the MFE. From this, the MFE for 0.02 mmol/L is studied in detail. With elongated settling time (1, 3 h) the MFE decreases and disappears after 24h (not shown). The degradation behavior under 0.3 T

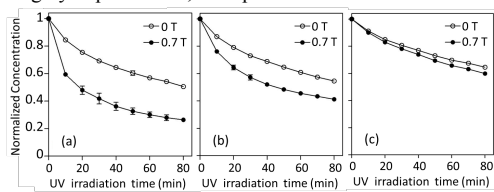


Figure 1. Photodegradation of MB solution under 0 T (○) and 0.7 T (●) for 5min settling with: (a) 0.01, (b) 0.02, (c) 0.03 [mmol/L]

is similar to 0 T, and the MFE appears only under 0.5, 0.7 T, with the largest MFE for 0.7 T. The heterogeneous system with large powder/solution interface may exhibit local fluctuations on various physical / chemical properties within the narrow volume around powders. Since the diffusion of paramagnetic DO is accelerated by a gradient static MF [6], magnetic force may act on DO molecules around the powder [5]. In addition, when the temperature is varied, an S-curve-like behavior of the MFE is observed for the first time.

After the MB solution (24h settling) is bubbled with Ar or O<sub>2</sub> gas for 1 h, the photodegradation behaviors are as in Fig.2. The slope in (a) is less steep than in Fig.1(b), and no MFE observed. By contrast, the MFE is clear in (b), where the direction of MFE is large negative, which is also observed for the TiO<sub>2</sub> system (not shown). This suggests at least the dual mechanism or different rate-determining steps for MFE. The excessive DO may aggregate on powder to reduce the active area. The magnetic adsorption (MA) of MB dye is consistent with the MFE for both ZnO and TiO<sub>2</sub>, in that positive MFE is observed for positive MA behavior, possibly related to the difference in equipotential surfaces. The local molecular transport toward the powder surface is extremely important during photocatalysis, and the MA is one of the key factors for the MFE.

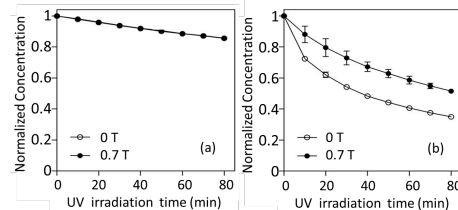


Figure 2. Photodegradation of MB after bubbling with (a) Ar, (b) O<sub>2</sub>

In order to separate the DO-involved MFE from others, the MFE on photocatalytic reductions of Ag<sup>+</sup> is studied (Redox pot. [eV]: Ag<sup>+</sup>+e<sup>-</sup>=>Ag: 0.80, and O<sub>2</sub>+e<sup>-</sup>=>O<sub>2</sub><sup>-</sup>: -0.28). The reduction rate is varied with MF, where slightly negative or no MFE exists at 0.3T and the largest MFE at 0.7 T (not shown), indicating dual mechanisms. Mogi et al. report that, during electroless deposition of Ag on a Cu chip (2Ag<sup>+</sup>+Cu=>Cu<sup>2+</sup>+2Ag), the denser and spiral dendritic Ag is deposited in vertical MF of 8T [7], while Yonemochi et al. report stripe deposition in a parallel MF [8]. The difference in Ag deposition is due to MF acting on Ag<sup>+</sup> diffusion, known as magneto-hydrodynamic (MHD) effect. Since the photocatalytic reduction is electrochemical, similar mechanism is suggested.

### Significance

MFE on heterogeneous photocatalysis is highly reproducible, which could be used for various energy environmental applications. MFE temperature dependence is also reported for the first time. The states of DO and ions in solution are involved with the MFE. Simultaneous multiple mechanisms are suggested operative, or, switch from one to another depending on MF.

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