Microwave Assisted Rapid Photocatalytic Degradation of Malachite Green in TiO_2 Suspensions: Mechanism and Pathways

Yongming Ju, Shaogui Yang, Youchao Ding, Cheng Sun*, Aiqian Zhang, Lianhong Wang

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, P.R. China

Corresponding author phone: +86-25- 83593239, Fax: +86-25-83593239.

E-mail: envidean@nju.edu.cn (C. Sun) yangdlut@126.com (S.G. Yang).

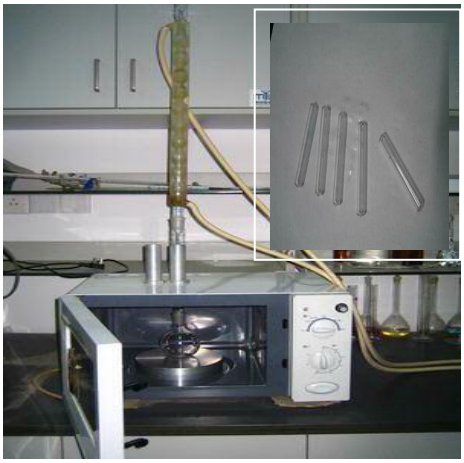

Fig.1（**S**）The whole apparatus used in the MPC condition. EDLs were displayed in the inset

All MW degradation experiments were conducted in the above-mentioned reactor, which consisted of a MW oven, Pyrex vessel, EDL, glass tube connector and water-cooling condenser. A domestic MW oven (Midea, PJ23C-SCI, China) was modified as follows: drilled a hole in the upper oven wall and an aluminum tube of the same diameter was attached to the hole in order to eliminate possible MW leaking. In the aluminum tube, a glass tube was attached connecting a water-cool condenser and a Pyrex vessel on its both sides.The EDL was placed into the vessel which was then put into the MW oven cavity. Once the MW oven begins to work, the EDL is excited to irradiate UV–vis spectra, which could be utilized by catalyst to induce the degradation

of MG, or be absorbed by the MG solution. The EDL was made of Pyrex with desired length, filled with argon and a few drops of mercury and as well as sealed under vacuum. The MW power was adjusted to a maximal value (900W), which guaranteed continuous MW radiation. The reactor was modified with a hole drilled in the upper oven wall. When the vessel was filled with 50ml MG aqueous solution, connected to the water-cooling condenser systems with the glass tube connector and EDL was placed into the MW oven cavity, the reactor began to work and the solution for measurement of MG was obtained in time. The basic degradation experiments were carried out with above mentioned MW-EDL reactor. All the processes and the results described below were performed with this reactor.

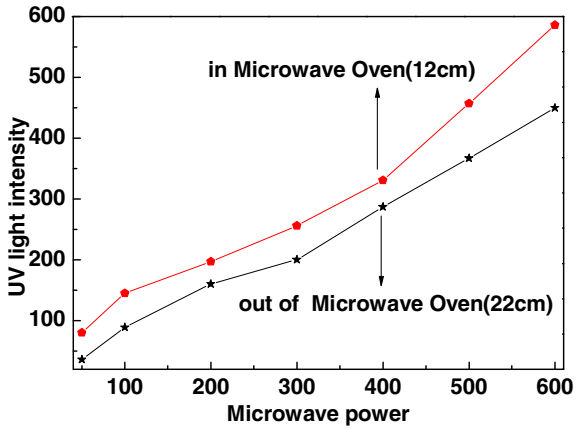

Fig.2（S）The ultraviolet light intensity of EDL-1 without solvent at 254nm in and out of microwave oven on fixed position

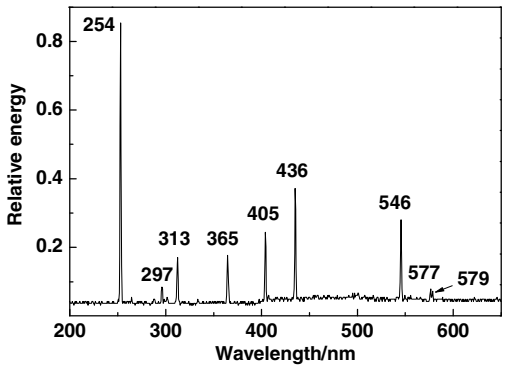

Fig.3（S）The emission spectra of EDL

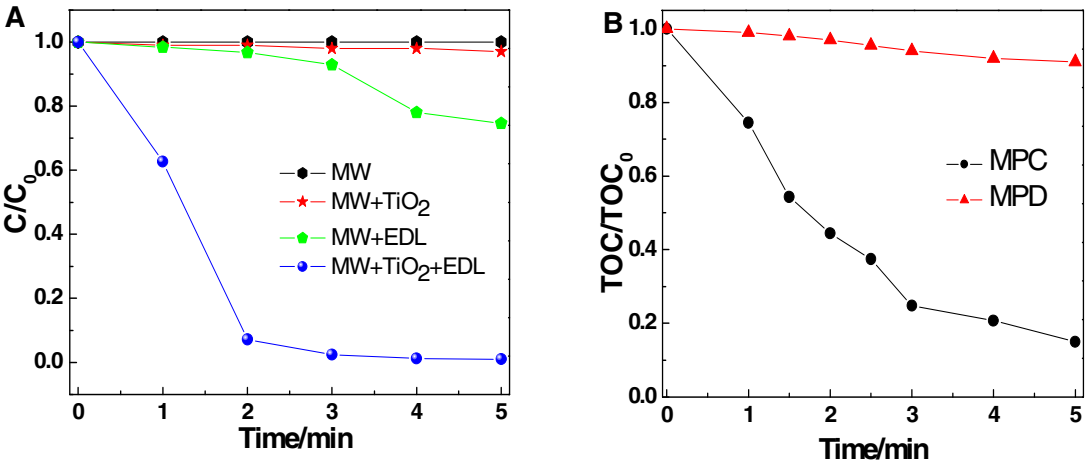

Fig.4（S） The concentration variation of MG (A) and the removal of TOC (B) under different conditions: MW, TiO_2, MW+EDL (MPD), MW+ TiO_2+ EDL (MPC) processes

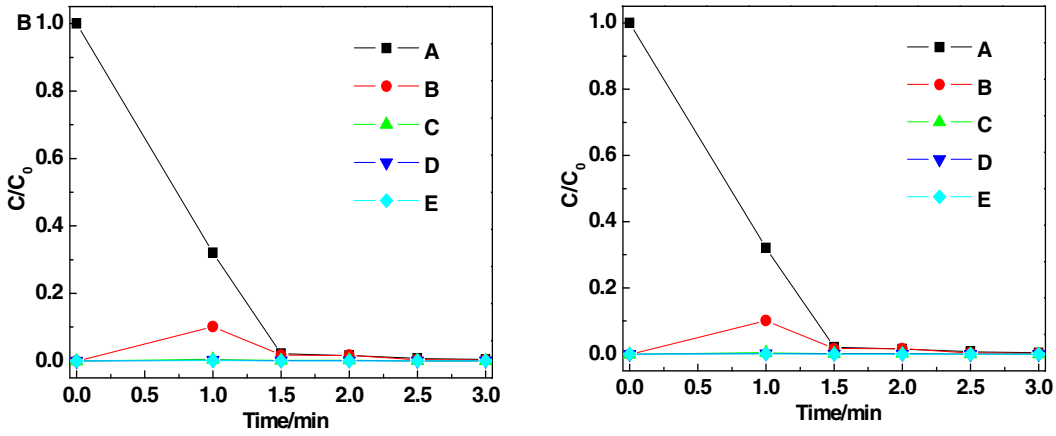

Fig. 5 (S) Variation of main degradation products

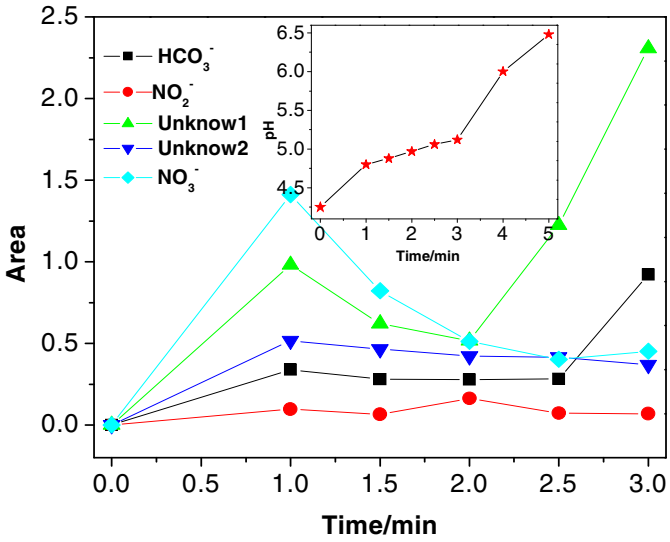

Fig. 6(S) The variation of inorganic ions during the reaction

$$TiO_2 + hv \rightarrow e_{cb}^- + h_{vb}^+$$
$$e_{cb}^- + h_{vb}^+ \rightarrow heat$$
$$h_{vb}^+ + OH_{ads}^- \rightarrow \cdot OH_{ads}$$
$$h_{vb}^+ + H_2O \rightarrow H^+ + \cdot OH_{free}$$
$$e_{cb}^- + O_{2ads} \rightarrow O_2^{-\cdot}$$
$$e_{cb}^- + O_2 + H^+ \rightarrow H_2O_2$$
$$H_2O_2 + O_2^{-\cdot} \rightarrow O_2 + OH^- + \cdot OH_{ads}$$
$$H_2O_2 + e_{cb}^- \rightarrow OH^- + \cdot OH_{ads}$$
$$\cdot OH / O_2 + Dye \rightarrow \text{deg}radation$$
$$h_{vb}^+ / e_{cb}^- + Dye \rightarrow \text{deg}radation$$

Scheme 1 (S) The mechanism of photocatalytic reactions