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O-17 Preparation and characterization of TiO_2 and M^{n+}/TiO_2 and their utilization in microwave assisted photocatalytic reactions

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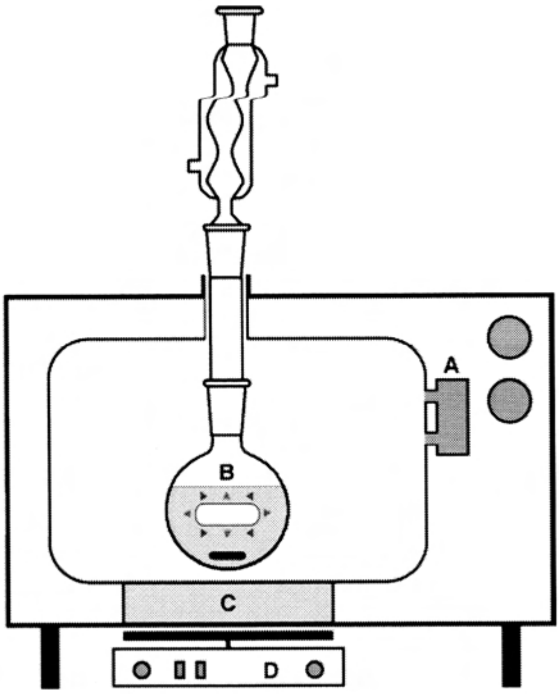
Microwaves are well known for their heating effects on polar substances and are widely used domestically and industrially. Recently, microwaves have been used to assist photochemical and photocatalytic reactions for degradation of organic pollutants. As source of light was used an electrodeless discharge lamp (EDL) which generates ultraviolet (UV) radiation after placed into microwave field. The EDL consists of a glass tube filled with an excitable substance (Hg) and sealed under a lower pressure (20 Torr) of argon. The preparation of EDL was described elsewhere [1]. Comparative studies showed that EDL provides a high yield of product in shorter reaction time [2].

Titanium dioxide was prepared using a sol-gel method. A titanium butoxide was dissolved in acetylacetone and used as a molecular precursor of TiO_2. The resulting reaction originated a solution into which the solvent ethyl alcohol was added gradually. Then the water used for hydrolysis was added dropwise under mechanical stirring. For doped TiO_2 photocatalysts, the synthesis process was the same described above, but in acetylacetone was dissolved an appropriate amount of metal acetylacetonate. The integration of dopants into the sol during gelation process offers the ions to have direct interaction with TiO_2. Therefore, dopants could be incorporated into the lattice of TiO_2. Doping with transition metal ions M^{n+} (M=V, Cr, Mn, Fe, Co, Ni, Zr, Ag) allows prolonging the light absorption to the visible region. The thin films were prepared by dip-coating of pretreated supports (EDLs) into TiO_2 gel. The films were then dried at room temperature and finalized by thermally treatment at 773 K for 2 hours (2 °C/min). The crystal phase of titanium dioxide was analyzed by XRD and Raman spectroscopy. The observed structure phases revealed anatase as the predominant crystalline phase. The crystallite size of the sample was estimated under 10 nm. The absorption edge of TiO_2 was detected by UV-Vis absorption spectroscopy at a wavelength of about 364 nm. From AFM images we can recognize homogeneous film of TiO_2 with approximately uniform crystallite size. The X-ray photoelectron spectroscopy was employed to examine surface stoichiometries of the prepared layers.

The photocatalytic activity was evaluated by degradation of mono-chloroacetic acid (MCAA) in a microwave field using batch reactor [3]. Experimental set-up is consisted of round-bottom flask equipped with Dimroth condenser. In each experiment, the reactor was filled with an aqueous solution of MCAA (0.1 mol l^{-1}). Then the titania coated EDL was placed into the reaction mixture and microwave field induced UV radiation. Samples were analyzed by chloride ion-selective electrode. Several factors influencing the degradation of MCAA, such as light intensity of EDL, initial pH value, H_2O_2 dosage, presence of ions, gas bubbling, initial pollutant concentration and the presence of dopants have been studied in detail.

Mono-chloroacetic acid was totally decomposed to HCl, CO_2 and water over irradiated titanium dioxide thin film in microwave field. This study revealed that the reaction efficiency depends on the intensity of light and initial pH value of the solution. Moreover, the degradation of MCAA was enhanced in an alkaline solution and in the presence of H_2O_2, and significantly enhanced by increasing the intensity of light. Furthermore, this work also disclosed that efficiency of UV irradiation is not influenced by air bubbling. Mono-chloroacetic acid also yielded no observed organic intermediates under these thermal reaction conditions.

In this work we submit another possibility how to carry out the photocatalytic reactions. This special arrangement of photocatalyst and source of light provides complete utilization of TiO_2. We suppose shorter reaction time and higher efficiency of microwave assisted photocatalytic reactions.



Experimental set-up for microwave assisted photocatalytic reactions (batch reactor): (A) magnetron, (B) reaction mixture with titania coated EDL, (C) aluminum plate, (D) magnetic stirrer

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