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Preparation and photocatalytic activity of SnO_2

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ABSTRACT

SnO_2 is prepared by the hydrolysis and the automatic oxidation of $SnCl_2$ in water, it shows the photocatalytic activity for the degradation of methyl orange in water under the UV light illumination. In the above process, methyl orange concentration decreases quickly, the total organic carbon (TOC) decreases slowly; inorganic ions (SO_4^{2-}, NO_3^-, NH_4^+) can be formed; the pH value in the system decreases gradually; a small quantity of $HO^{\cdot}$ can be generated. In order to estimate the roles of active species during the above process, isopropanol, ammonium oxalate, and 1,4-benzoquinone, as the scavengers for $HO^{\cdot}$, h^+, $O_2^{\cdot-}$ are introduced into the systems respectively. Isopropanol and $(NH_4)_2C_2O_4$ are effective scavengers for active species $HO^{\cdot}$ and h^+ respectively; but 1,4-benzoquinone is not a satisfactory scavenger to capture $O_2^{\cdot-}$ at least in this work. At last, SnO_2 is characterized by N_2 sorption, DRS, XRD, SEM and TEM.

1. Introduction

SnO_2 has gained more and more attention due to its gas sensing property. SnO_2 gas sensors are in high demand for many applications including environmental monitoring, prevention of leakage and incomplete combustion, they can be used to detect the toxic gases (e.g. CO, SO_2, NO_x) and flammable gases (e.g. C_2H_2, H_2) [1].

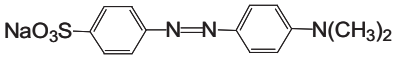
But, on the other hand, SnO_2 can also be used as a photocatalyst to degradate organic pollutants in the heterogeneous system. Heterogeneous photocatalysis is one of effective methods to treat wasterwater with large amounts of azo dyes, active $HO^{\cdot}$ can be generated during this process [2,3]. In the labs, SnO_2 can be prepared by the following methods: (1) $K_2S_2O_8$ oxidizes $SnCl_2$ in water under UV light [4]; (2) Hydrolysis of $SnCl_4$ in NaOH solution [5]; (3) Sonochemical and hydrothermal synthesis from $SnCl_2$ [6]; (4) Cysteine reacts with $SnCl_4$ in water to get SnS_2, SnS_2 is calcinated to get SnO_2 [7]; (5) $SnSO_4$ is dissolved in H_2SO_4 solution, then placed under UV lamp [8], and so on.

In this work, at first, we prepare SnO_2 by the simple method—hydrolysis and automatic oxidation of $SnCl_2$, then we study its photocatalytic activity on the degradation of methyl orange (MO) in water under the UV light illumination (decrease of MO concentration and TOC). At the same time, we measure the inorganic ions and pH change in the system. In order to estimate the roles of active species ($HO^{\cdot}$, h^+, $O_2^{\cdot-}$) during the above processes, isopropanol, ammonium oxalate, and 1,4-benzoquinone as the scavengers are introduced into the systems respectively. At last, we characterize SnO_2 by some techniques.

2. Experimental

2.1. Chemicals and materials

$SnCl_2 \cdot 2H_2O$, NaOH, methyl orange (MO, $C_{14}H_{14}N_3NaO_3S$, MW = 327.33 g/mol, its molecular structural formula seeing (a) below), terephthalic acid ($HOOCC_6H_4COOH$, TA), isopropanol ($CH_3CHOHCH_3$, IPA), ammonium oxalate ($(NH_4)_2C_2O_4$, AO), and 1,4-benzoquinone (BQ) are analytical reagents and used without further purification; the 30 W UV lamp (253.7 nm; Kongjun Houqin, Beijing, China); distilled water is used throughout this work; 0.22 μm filter membrane (micro PES, made in Membrana company, Germany).



(a)

2.2. SnO_2 preparation

A given amount of $SnCl_2 \cdot 2H_2O$ is dissolved in enough distilled water, we can get the precipitate, the precipitate is purified with enough distilled water for some times, and then drying in air naturally.

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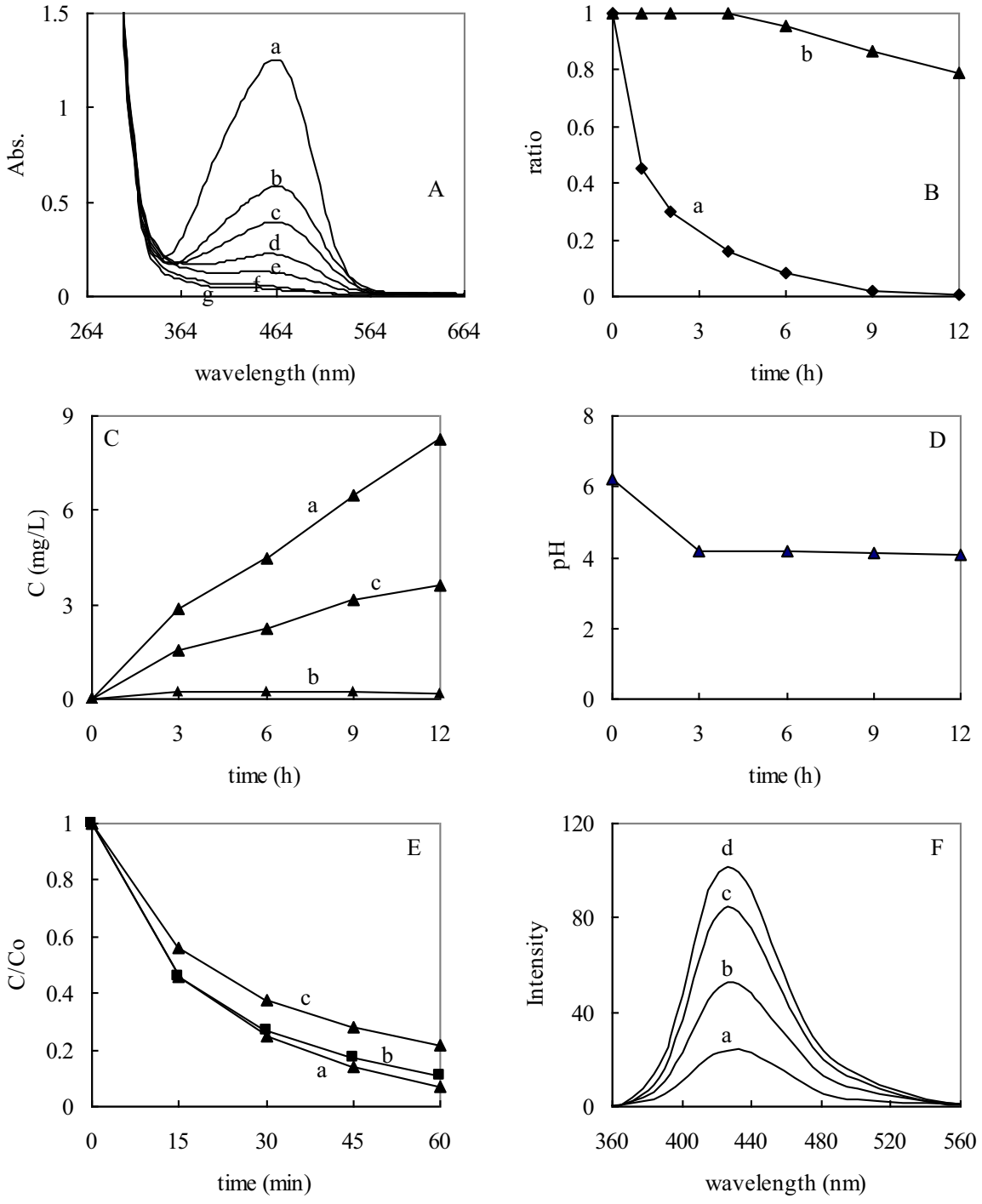

Fig.1. (A) UV-vis spectra change of MO in the system of (100 mg SnO_2+100 mL of 0.10 mM MO) as a function of the illumination time. (a) t=0 h, (b–g) illumination at t=1, 2, 4, 6, 9, 12 h, respectively. (B) Photocatalytic degradation kinetics of MO in the system of (100 mg SnO_2+100 mL of 0.10 mM MO). (a) C/C_o, (b) TOC/TOC_o. (C) The relation between the concentrations of inorganic ions generated in the system of (100 mg SnO_2+100 mL of 0.10 mM MO) and the illumination time. (a) SO_4^{2-}, (b) NO_3^-, (c) NH_4^+. (D) pH change in the filtrates from the system of (100 mg SnO_2+100 mL of 0.10 mM MO) with the illumination time. (E) Photocatalytic degradation of methyl orange (MO) in the different systems with the various scavengers. (a) 100 mg SnO_2+100 mL of 0.04 mM MO; (b) 100 mg SnO_2+100 mL of (0.04 mM MO+0.40 mM IPA); (c) 100 mg SnO_2 +100 mL of (0.04 mM MO+0.40 mM AO). (F) Fluorescent spectra of the filtrates from the system of (100 mg SnO_2+100 mL of 5×10^{-4} M TA) under the UV light illumination. (a) t=0.5 h, (b) t=1 h, (c) t=2 h, (d) t=3 h.

2.3. Methyl orange adsorption test

100 mg SnO_2 and 100 mL of 0.10 mM methyl orange solution are put into a beaker (the total volume is 150 mL) together, the mixture (suspension) is stirred in the dark. At the different time, samples are taken and filtered by the filter membrane, then methyl orange concentrations are measured with the UV–vis spectrophotometer (Varian Cary 50 series) at the absorption peak (λ=464 nm).

2.4. Methyl orange photodegradation process

(1) 100 mg SnO_2 and 100 mL of 0.10 mM MO solution are put into a beaker (the total volume is 150 mL) together, the mixture (suspension) is then put under the 30 W UV lamp vertically, the distance between the UV lamp and the surface of the suspension in the beaker is 4.2 cm. The suspension is stirred in