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Synthesis and characterization of La₂Ti₂O₇ employed for photocatalytic degradation of reactive red 22 dyestuff in aqueous solution

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1. Introduction

Photocatalytic processes have lately attracted numerous researches in the area of wastewater treatment, especially for treating wastewater containing traces of toxic organic substances. A range of photocatalysts were fabricated and studied extensively in decomposing different organic contaminants. However, the rapid recombination of photogenerated electron-hole pairs critically limits the effectiveness of photocatalytic processes. Recently, several new perovskite structured photocatalysts with highly donor-doped layered structures have been found to be competent on photocatalytic applications, including water-splitting [1–3], Cr(VI) reduction [4], NO oxidation [5] and decomposition of organic compounds [6,7]. Perovskites contains a cubic structure with three different ions, as form of ABO₃ [8]. A series of perovskite structured photocatalysts, such as LaNiO₃ [7], Bi₄Ti₃O₁₂ $[9,\!10], Bi_2Zn_{2/3-x}Cu_xTa_{4/3}O_7$ [11], $BiVO_4$ [12] and $La_2Ti_2O_7$ [6], have been investigated over their photocatalytic properties and applications. The separation of electrons and holes in the perovskites is easier than that in other semiconductor materials because of their narrower depletion layers.

 $La_2Ti_2O_7$ is a layer-structured perovskite that the photogenerated electrons possess enough energy to promote hydrogen production [13,14]. Hwang et al. [15] synthesized various perovskite structured catalysts, including $La_2Ti_2O_7$, $La_4CaTi_5O_{17}$ and

ABSTRACT

Perovskite structured La₂Ti₂O₇ catalyst prepared by polymerized complex method was characterized and examined the photocatalytic activity by decomposing an azo dyestuff, Reactive Red 22, in aqueous solutions under UV irradiation. La₂Ti₂O₇ powders prepared by polymerized complex method exhibit higher surface areas, better homogeneity and are more sensitive to solution than those prepared by solid-state method. The first derivatives of UV-vis DRS patterns confirmed the complete crystallization of La₂Ti₂O₇ sintered at temperatures higher than 900 °C. The effects of sintering temperature of catalyst and solution pH of photocatalytic reaction were studied. The photocatalytic decomposition of Reactive Red 22 per unit surface area was found to be higher for experiments using La₂Ti₂O₇ than using TiO₂. However, the electron-hole recombination was found to be more obvious for La₂Ti₂O₇ than for TiO₂ because the network of metal cations constructed within La₂Ti₂O₇ enhances the mobility of photogenerated electrons and holes.

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 $Sr_2Nb_2O_7$, for photocatalytic water-splitting under UV irradiation, the quantum yields (12–23%) of these catalysts were reported to be much higher than that (<1%) of TiO₂. Abe et al. [2] reported that the high photocatalytic water-splitting activity of these perovskite structured catalysts could be attributed to their octahedral structure to enhance the mobility of photogenerated electrons and holes.

Perovskites are usually synthesized by the solid state reaction (SSR) method in which the precursor oxides are mixed by dry- or wet-grinding and then sintered at temperatures higher than 1000 °C, for a long period [16]. However, perovskites generated by this method usually possess less surface area and low crystalline purity that result in inferior photocatalytic activities. Perovskites are also synthesized by the polymerized complex (PC) method, which is carried out by the formation of a polymerization network by condensing ethylene glycol, citric acid and soluble metal precursors [17,18]. PC method is frequently used in synthesizing homogeneous metal-oxide fine powders with higher surface areas and more uniform morphology, due to the well-mixing of metal ions in molecular level and low preparing temperature [2].

In this study, the perovskites La₂Ti₂O₇ prepared by PC method and sintered at various temperatures was characterized by a sequence of analyses, including TG–DTA, XRD, BET, UV–vis DRS and Zeta potential. Photocatalytic decomposition of a frequently studied dyestuff, Reactive Red 22 (RR22, molecular structure presented in Fig. 1), in aqueous solutions using prepared La₂Ti₂O₇ was studied under various operating conditions and compared with those using commercial P25 TiO₂ and La₂Ti₂O₇ prepared by SSR method.

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Fig. 1. Molecular structure of Reactive Red 22.

2. Experimental

Titanium isoproxide (TTIP, Ti(OCH(CH₃)₂)₄, Acros), ethylene glycol (EG, $C_2H_6O_2$, Acros), citric acid (CA, $C_6H_8O_7$, Acros) and lanthanum nitrate hydrate $(La(NO_3)_3 \cdot 6H_2O, Acros)$ were used as starting materials without further purification. Citric acid was used as the metal chelating agent and ethylene glycol as the polyol [16]. After dissolving 0.1 mol of TTIP in 4 mol of EG, 1 mol of CA was added to the solution to convert TTIP to stabilize the Ti-citric acid complexes. 0.105 mol of $L_a(NO_2)_2$, GH_2O was then added to the solution and the mixture was stirred for 1 h at 50 °C until it became transparent. Upon continuous heating at 130 °C for several hours, the solution became highly viscous with a color change to deep brown and, finally, gelled into a transparent-brown glassy resin. Charring the glassy resin at 350 °C for 2 h in a furnace resulted in black powder, which was then grounded into finer powder referred to as the "powder precursor". Thermogravimetry-differential thermal analysis (TG-DTA, PerkinElmer, Diamond TG/DTA) was employed to analyze the pyrolysis of the powder precursor. The black powder was subsequently heated in a crucible at 500-1100 °C for 2 h, followed by cooling to room temperature to form white La2Ti2O7 powder. The powder was later characterized by a sequence of analyses, X-ray diffraction (XRD, Regaku, RTP 300RC, Cu Ka radiation of λ = 1.5405 Å), Brunauer-Emmett-Teller approach (BET, Quantachrome, Autosorb-1), UV-vis diffuse reflectance spectroscopy (UV-vis DRS, Jasco, ISV-469), zeta meter (Malvern, S2000) and photoluminescence spectra (PL, Jasco, FP-6500LE)

 $La_2Ti_2O_7$ powder was afterward suspended in aqueous solution containing RR22 in a stirred Pyrex reactor (9 cm inter diameter, 25 cm height, 1.65 l volume). All experiments were conducted at 24 ± 1 °C, and the air flow rate entering the photoreactor was kept at 75 ml/min in order to maintain the maximum dissolved oxygen in aqueous solution. The solution pH was kept at desired levels by the additions of sodium hydroxide and/or nitric acid solutions using an automatic titrator. The suspension was put in a dark surrounding for 30 min to achieve adsorption equilibrium before it was irradiated by a pre-warmed 10 W, 254 nm low-pressure mercury lamp with light intensity of 8.35 mW/cm^2 . Aliquots of the reaction solution were sampled at intermittent periods of reaction time, and then centrifuged to remove La₂Ti₂O₇ particles. Concentration of RR22 in aqueous solutions was measured by the UV-vis spectrometer (Jasco, V-550) at 509 nm.

3. Results and discussion

The TG–DTA result of the La₂Ti₂O₇ precursor for a heating rate of 10 °C/min is shown in Fig. 2. The TG curve depicted a significant weight loss at the temperature range from 300 to 500 °C, and a minor weight loss at around 790 °C. The first weight loss is corresponded to the major exothermic peak at 463.5 °C ascribing to the decomposition of most organic compounds contained in the powder precursor. Milanova et al. [16] also prepared La₂Ti₂O₇ by PC method, and reported that there was a continuous weight loss below 500 °C. The minor weight loss related to the second exothermic peak at around 792 °C is attributed to the decomposition of residual organics. Kakihana et al. [19] reported that the TG analysis of perovskite Y₂Ti₂O₇ showed two obvious weight loss at 550 and 800 °C ascribed to the decomposition of most organics and burnout of residual organics, respectively.

Fig. 3 shows the XRD patterns of $La_2Ti_2O_7$ powders prepared by PC method and sintered at various temperatures for 2 h in the 2θ range of 10–90°. When the samples were sintered at temperatures below 600 °C, the XRD patterns indicated the presence of amorphous solids. The crystallization of $La_2Ti_2O_7$ was observed for samples sintered at temperatures higher than 700 °C. Comparing with JCPDS database (no. 81-1066) of $La_2Ti_2O_7$, the XRD reflections of samples sintered at temperatures above 900 °C exhibited a single phase of $La_2Ti_2O_7$ with a monoclinic structure. From the XRD results, the average crystal size of the $La_2Ti_2O_7$ powders determined from the diffraction peak employing the Scherrer formula. The average crystal size of $La_2Ti_2O_7$ samples was increased from



Fig. 2. TG-DTA curves of La2Ti2O7 precursor with a heating rate of 10°C/min.

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