In recent years, many catalytic techniques have been used to treat environmental pollution. Among them, heterogeneous photocatalysis is a promising technology for the detoxification of wastewater. Particularly, titanium dioxide (TiO$_2$) as photocatalyst has received much attention for the possible application of photocatalytic degradation of organic dyes [1–5]. It is well known that the TiO$_2$ powder generally presents in three crystal phases: anatase, rutile and brookite. In general, anatase phase TiO$_2$ powder is used as photocatalyst to treat various wastewaters due to its high photocatalytic activity [6]. However, anatase phase TiO$_2$ powder can only absorb the light below the wavelength of 387.5 nm because its energy band gap is 3.2 eV. In order to extend the absorption region of anatase phase TiO$_2$ powder to visible light and enhance its photocatalytic activity under visible light irradiation, some modification methods have been introduced, such as depositing of noble metal [7, 8], coupling with narrow energy band gap semiconductors [9, 10] and doping of transition metal ion [11, 12]. Among them, because of simpleness, cheapness and facileness, the iron doping is considered to be a promising improved technique [13–15]. In principle, the iron doping can not only extend the absorption range of anatase phase TiO$_2$ powder to visible light, but also restrain the recombination of photogenerated electron–hole pairs and the phase transformation can enhance the absorption of visible light. Furthermore, other influence factors such as azo fuchsine concentration, solution acidity, Fe$^{3+}$ ion content and irradiation time were also studied. Thus, this method is applicable for the treatment of wastewater.

**Abstract** — In this work, the Fe-doped mixed crystal TiO$_2$ photocatalyst which can utilize visible light was prepared by sol–gel and heat-treated methods. During heat-treatment, the phase transformation of Fe-doped TiO$_2$ powder occurs and the process is characterized by XRD and TG-DTA technologies. Otherwise, the sizes and shapes of Fe-doped and undoped TiO$_2$ powders were also compared using TEM images. The azo fuchsine in aqueous solutions, as a model compound, was treated under visible light irradiation using Fe-doped mixed crystal TiO$_2$ powders as photocatalyst. The results showed that, under visible light irradiation, the (0.25%) Fe-doped mixed crystal TiO$_2$ powder heat-treated at 600°C for 3.0 h behaved very high photocatalytic activities for degradation of azo fuchsine. The remarkable improvement of the photocatalytic activity of TiO$_2$ powder was elucidated through the cooperative effects of iron doping and phase transformation. The iron doping can restrain the recombination of photogenerated electron–hole pairs and the phase transformation can enhance the absorption of visible light. Furthermore, other influence factors such as azo fuchsine concentration, solution acidity, Fe$^{3+}$ ion content and irradiation time were also studied. Thus, this method is applicable for the treatment of wastewater.

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In the present work, the Fe-doped mixed crystal TiO$_2$ powder was prepared by sol–gel and heat-treated methods. And the cooperative effects of iron doping and phase transformation on the photocatalytic activity of TiO$_2$ powder under visible light irradiation were studied.
investigated. Azo fuchsine (as shown in Scheme 1) was used as a model compound because it is a typical azo dyestuff. In addition, some influence factors, such as Fe$^{3+}$ ion content, heat-treated temperature, addition amount of TiO$_2$ catalyst, initial concentration and pH value of azo fuchsine solution, on the photocatalytic degradation were also studied. It was found that, for some given conditions, the Fe-doped mixed crystal TiO$_2$ powder behaved high photocatalytic activity during degradation of azo fuchsine under visible light irradiation. The iron doping and phase transformation display an obvious cooperative effect on improving the photocatalytic activity of anatase phase TiO$_2$ powder. So, this method is an emerging treatment technology for the detoxification of wastewater because it can efficiently utilize visible light.

**EXPERIMENTAL**

**Preparation of Fe-doped mixed crystal TiO$_2$ powder.** A series of Fe-doped mixed crystal TiO$_2$ powders were prepared according to the following procedure. 40 mL tetrabutyl titanate (Ti(OBu)$_4$, SP, Shanghai Chemistry Reagent Corporation, China) was dissolved into 160 mL ethanol alcohol (solution A). Solution B consisted of distilled water and iron nitrate (Fe(NO$_3$)$_3$·9H$_2$O, AR, Tianjin Tianhe Chemistry Reagent Corporation, China) in the required stoichiometry (the atomic ratios of Fe to Ti = 0.00, 0.25, 0.50 and 0.75%, respectively). Then the solution B was added to solution A drop-wise under vigorous stirring. At the same time, a small quantity of hydrochloric acid (HCl, AR, 38%, Beijing Chemistry Reagent Corporation, China) solution was added to the mixed solution for adjusting pH value to prevent the rapid formation of TiO$_2$ precipitates. The resultant mixture was stirred at room temperature for about 4.0 h for hydrolysis until the transparent sol was obtained. The sol was then aged for 4.0 days till the formation of gel, and then the gel was dried in oven at 110°C and became gel powder after grinding. After that, the gel powder was heat-treated at different temperature for 3.0 h in muffle furnace. Correspondingly, the undoped mixed crystal TiO$_2$ powder was also prepared in this way without the addition of iron nitrate.

**Characterization of Fe-doped mixed crystal TiO$_2$ powder.** The X-ray powder diffraction (XRD) patterns were determined by X-ray powder diffraction measurements (Bruker Axs, D8 Advance, Bruker Company, Germany) using Ni-filtered CuK$_\alpha$ radiation in the range of 20 from 10° to 70° for confirming the phase transformation of Fe-doped TiO$_2$ powder. The transmission electron microscopy (TEM) images were obtained by a transmission electron microscopy spectrometer (Philips EM-400T, Philips Corporation, Netherlands) to observe the sizes and shapes of samples. The crystallization behaviors of the xerogel powder were monitored with a thermogravimetric-differential thermal analysis (TG-DTA) instrument (Mettler Toledo TGA/SDTA 851°, Mettler Toledo Company, USA). It was performed in the presence of Ar atmosphere (200 mL/min) from room temperature to 800°C at a heating rate of 10°C/min.

**Measurements of photocatalytic activities of Fe-doped mixed crystal TiO$_2$ powder.** The experiments of the degradation of azo fuchsine in aqueous solution were performed for evaluating the photocatalytic activities of Fe-doped mixed crystal TiO$_2$ powders. The experimental conditions such as 10.0 mg/L azo fuchsine, 1.5 g/L Fe-doped mixed crystal TiO$_2$ powder, 50 mL total volume and 5.0 h visible light irradiation were kept throughout the course of the investigation, except for special illumination. The detailed processes are as follows. The Fe-doped mixed crystal TiO$_2$ powder was first mixed with azo fuchsine solution well by vigorous stirring and then placed in the dark for 30 min. After the equilibrium of adsorption and desorption, the suspension was irradiated by four triphosphor lamps (FL40T8EXD/36, Toshiba Company, Japan). Correlated color temperature 4000 K and illumination intensity 10000 lux). The triphosphor blend is a combination of three narrow-band rare phosphors that reproduce three primary colors of the spectra, each with a very narrow bandwidth, so there is no ultraviolet region involved. The suspensions at definite intervals were sampled to monitor the changes of concentration. Sampled suspensions were centrifuged at 4000 rpm for 30 min to remove the TiO$_2$ powder and then analyzed with spectrophotometry. UV-vis spectrophotometer (Cary-50, Varian Corporation, USA) and ion chromatography (ICS-90, Dionex Corporation, USA) were used to observe the degradation of azo fuchsine and the formation of mineralized anions during the photocatalytic degradation.

**RESULTS AND DISCUSSION**

**XRD and TEM of Fe-doped mixed crystal TiO$_2$ powder.** Figure 1 shows the changes of the XRD patterns of (0.25%) Fe-doped and undoped mixed crystal TiO$_2$ powders with various heat-treated temperatures from 400°C to 700°C. The average crystallite sizes for the Fe-doped and undoped TiO$_2$ sample is about 25.28 nm and 73.56 nm, respectively, as calculated by applying the Scherrer equation to the full-width at half-maximum of the (101) crystal phase of anatase TiO$_2$. For both Fe-doped and undoped mixed crystal TiO$_2$ powders, it was found that the diffraction peak at 27.5° (20), which is a characteristic peak of rutile phase TiO$_2$, began to appear when the heat-treated temperature reached 500°C. It indicated that the rutile phase TiO$_2$ has already been formed on the surface of anatase phase TiO$_2$ particles. Afterwards, it became higher and higher with the increase of heat-treated temperature. Finally, all diffraction peaks of anatase phase TiO$_2$ disappeared almost at 700°C, while all characteristic diffraction peaks of rutile phase TiO$_2$ appeared synchronously, which revealed that all unsta-