

Photocatalytic decoloration of RBR X-3B on aggregated 0.1%Al-TiO₂ spheres: the role of calcination

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Aluminum doped TiO₂ in an aggregated sphere form was synthesized by sol-gel method. Graphical spheres were used as template to prepare the aggregated 0.1%Al-TiO₂ spheres. Anatase TiO₂ in the preferred orientation of (101) plane is the sole phase in all the samples. Increasing calcination temperature leads to enlarging cell volume and growing crystallite size. BET surface area of the 0.1%Al-TiO₂ reduces from 37.0 m²/g at 400 °C to 3.4 m²/g at 600 °C. The 0.1%Al-TiO₂ calcined at 500 °C has the maximum photocatalytic activity. 43.6% of the total number of RBR X-3B molecules is decomposed after 30 min of illumination. The apparent reaction rate constant is 0.031 min⁻¹ of the 0.1%Al-TiO₂ sample. Decoloration efficiency is reduced from 100% to 80% after five photocatalytic cycles.

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1. Introduction

Organic pollutants in aquatic system and atmosphere can be decomposed through photocatalytic oxidation. After decades of studying, this technique has been widely applied to deal with many serious environmental problems [1-3]. Photocatalytic oxidation of organic substances requires both photocatalytic material and light source. Although researchers developed many kinds of materials for this purpose, the most utilized photocatalyst is still TiO₂ matrix material [4-6]. However, modification is always necessary to promote decomposition efficiency on TiO₂ [7,8]. Metal ion doping into TiO₂ matrix is proven to be a successful method to enhance the activity [9,10]. The role of metal ion in TiO₂ can be related to promoting quantum efficiency, reducing band gap energy or extending lifetime of photogenerated charge carriers. Besides the most applied transition metals and rare earth metals, aluminum can be applied as dopant to improve porosity and activity of TiO₂ [11,12].

Photocatalyst in wastewater treating device is usually in powder or supported forms [13]. Powder form normally has better purification efficiency than supported form. However, fine powders are hard to be separated from water after treatment. Particles with low density and suitable particle size are the optimal choice. Researchers developed low density macroporous materials to resolve this problem [14-16]. This kind of material can easily suspend in wastewater under stirring. Meanwhile, the large particles can quickly settle down after ceasing stirring to discharge the water.

In the present work, aluminum doped TiO₂ in an aggregated sphere form was synthesized by sol-gel method. Firstly, the authors prepared graphical spheres through a hydrothermal route. The graphical spheres were used as template to synthesize the aggregated 0.1%Al-TiO₂

spheres. The materials were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and N₂ adsorption-desorption analyzes. RBR X-3B is an azo dye that has to be removed before discharging [17,18]. Photocatalytic degradation of RBR X-3B dye was conducted to show the effect of calcination temperature on activity of the 0.1%Al-TiO₂ aggregated spheres.

2. Experimental

Sol-gel preparation of 0.1% Al-TiO₂

Firstly, graphical spheres were prepared from glucose by hydrothermal method [19]. The reaction was performed at 180 °C for 12 h. The graphical spheres were filtrated, washed and dried before use. Secondly, the Al-doped TiO₂ was prepared by a sol-gel method. The precursor was composed of tetrabutyl titanate, aluminum isopropoxide and anhydrous ethanol. The precursor and graphical spheres were ultrasonically treated for 60 min. After 24 h aging at room temperature, the mixture was filtrated and cleaned with distilled water and ethanol. The solid was calcined for 2 h to obtain the 0.1%Al-TiO₂ aggregated spheres.

Characterization methods

X-ray diffraction patterns of the materials were measured on D8 Advance X-ray diffractometer coupled with monochromatized Cu K α ($\lambda=0.15416$ nm) radiation. The surface morphology was observed on QUANTA 250 scanning electron microscope at an accelerating voltage of 30 kV. A thin layer of gold was coated on the samples to avoid charging. Specific surface area and pore characters

of the materials were measured on F-sorb 3400 analyzer through N₂ adsorption-desorption.

Decoloration of RBR X-3B

The molecular formula of RBR X-3B is C₁₉H₁₀Cl₂N₆Na₂O₇S₂. Photocatalytic activity of the materials was evaluated in a device that was made of quartz reactor and UV light source. The light source can irradiate photons at 253.7 nm with intensity of 1200 μW/cm². 30 min stirring of 50 mL 40 mg/L RBR X-3B solution and 10 mg 0.1%Al-TiO₂ in the dark ensured adsorption-desorption equilibrium. Subsequently, photocatalytic oxidation of the dye started right after turning on the light. The photocatalyst and solution were separated through filtration, and then RBR X-3B solution concentration was measured on 721E spectrophotometer.

3. Results and discussion

Fig. 1 shows XRD patterns of 0.1%Al-TiO₂ aggregated spheres prepared at different calcination temperatures. Calcination is essential to crystallization of the samples. Anatase TiO₂ in the preferred orientation of (101) plane is the sole phase in all the samples. The diffraction intensity increases with rising calcination temperature. There is no diffraction pattern of any aluminum-containing substances in the figure.

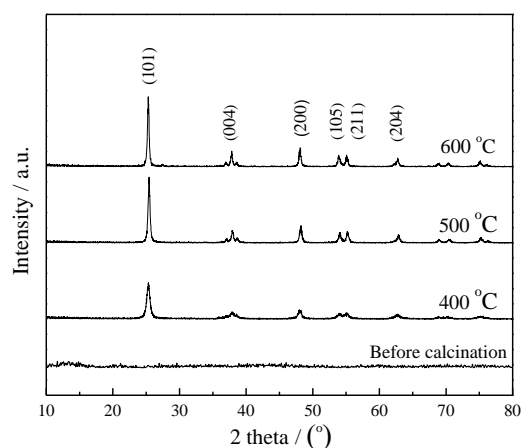


Fig. 1. XRD patterns of 0.1%Al-TiO₂ aggregated spheres prepared at different calcination temperatures

The (101) plane of anatase TiO₂ is used to calculate crystallite size by Scherrer formula [20,21]. Crystallite sizes of the 0.1%Al-TiO₂ samples calcined at 400, 500 and 600 °C are 11.3, 13.7 and 30.3 nm, respectively. Table 1 presents the lattice parameters of anatase TiO₂ cell as a factor of calcination temperature. The TiO₂ cell expands at all of the three lattice directions. Cell volume of anatase TiO₂ expands from 0.13314 nm³ at 400 °C to 0.13494 nm³ at 600 °C. Increasing calcination temperature leads to

enlarging cell volume and growing crystallite size.

Fig. 2 shows SEM images of 0.1%Al-TiO₂ samples prepared at different calcination temperatures. The as-prepared sample is composed of aggregated spheres in the size as large as 500 nanometers. The graphical spheres are coated with a layer of polymerized Ti-O-Ti gel during sol-gel process. The spheres tend to aggregate to form large particles due to dehydration of Ti-OH groups. Calcination not only results in anatase TiO₂ formation, but also leads to removal of the graphical spheres. As can be seen from the figure, the 0.1%Al-TiO₂ can hardly maintain spherical shape after calcination. The spheres tend to aggregate into large particles. While the graphical spheres are burnt out during calcination, the strengthened crystallization force reduces diameter of the resulting external 0.1%Al-TiO₂ shell. Moreover, some of the 0.1%Al-TiO₂ shells collapse into small parts.

Table 1. Lattice parameters of 0.1%Al-TiO₂ aggregated spheres

Calcination temperature/ °C	a(=b) / nm	c / nm	V / nm ³
400	0.37546	0.94447	0.13314
500	0.37613	0.94693	0.13396
600	0.37824	0.94825	0.13494

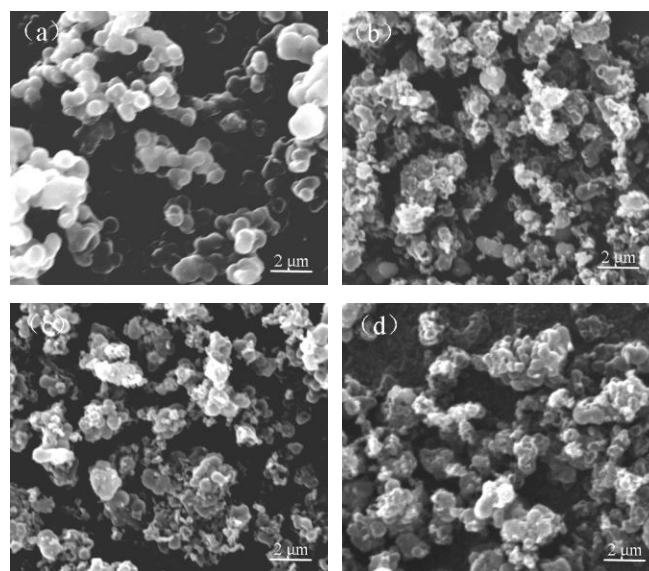


Fig. 2. SEM images of 0.1%Al-TiO₂ samples prepared at different calcination temperatures. (a) Before calcination, (b) 400 °C, (c) 500 °C, (d) 600 °C

Fig. 3 presents N₂ desorption isotherms of 0.1%Al-TiO₂ samples calcinated at different temperatures. N₂ adsorption amount reduces at higher temperature in the whole relative pressure range. The samples calcined at low temperature seem to adsorb more N₂ molecule. The

amount of adsorbed N_2 smoothly increases with rising relative pressure for all the samples. Monolayer N_2 molecules tend to be adsorbed on the surface of 0.1% Al-TiO₂ at low N_2 pressure. The sharp increase of the adsorbed N_2 amount is due to capillary condensation of N_2 molecules at high relative pressure, i.e. more than 0.9.

BET surface area and porous properties of 0.1% Al-TiO₂ aggregated spheres are affected by calcination temperature, as indicated in Table 2. The specific surface area was calculated using the multipoint BET method. Pore size distribution was calculated using the Barrett, Joyner, and Halenda (BJH) method. BET surface area of the 0.1% Al-TiO₂ reduces from 37.0 m²/g at 400 °C to 3.4 m²/g at 600 °C. Anatase TiO₂ is the only substance in the samples in the calcination temperature range. The decline in surface area can be attributed to crystal growth and particles aggregation at high temperature.

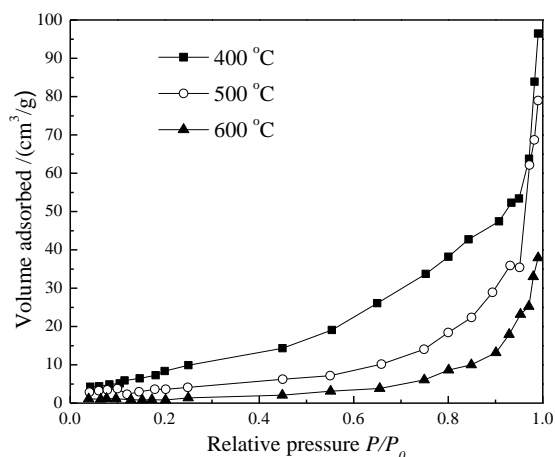


Fig. 3. N_2 desorption isotherms of 0.1% Al-TiO₂ samples at different calcination temperatures

At the same time, average pore size and total pore volume of 0.1% Al-TiO₂ constantly increase with rising calcination temperature. Micropore and mesopore in the material emerge into large macropores at high temperature. Macropores become the major porous structure in the sample calcined over 600 °C. On the other hand, the graphical template spheres are burnt out during calcination, leaving macropores in the produced 0.1% Al-TiO₂ spheres. The process is favored at high temperature.

Table 2. BET surface area and porous properties of 0.1% Al-TiO₂ aggregated spheres

Calcination temperature / °C	BET surface area / m ² /g	Average pore size / nm	Pore volume / cm ³ /g
400	37.0	18.7	0.0613
500	12.9	40.4	0.1038
600	3.4	71.9	0.1312

3.1. Decoloration of RBR X-3B

Photocatalytic activity of the 0.1% Al-TiO₂ aggregated spheres was measured using RBR X-3B dye as the organic pollutant, as shown in Fig. 4. Adsorption percent of the initial dye was measured after adsorption-desorption equilibrium. As can be seen from the figure, adsorption percent of the dye on the materials is quite small. Adsorption of RBR X-3B molecules on the 0.1% Al-TiO₂ is not only related to the surface area of the material, but also related to affinity between adsorbate and adsorbent. Decoloration of the dye is mostly contributed by photocatalytic oxidation process.

Photocatalytic degradation efficiency depends on calcination temperature. A sharp linear increase of degradation efficiency occurs from 300 °C to 500 °C. Crystallization at suitable temperature is essential to the formation of anatase TiO₂. The 0.1% Al-TiO₂ calcined at 500 °C has the maximum photocatalytic activity. 43.6% of the total number of RBR X-3B molecules is decomposed after 30 min of illumination. With increasing calcination temperature, crystal growing, particles aggregation, reducing surface area, and even phase transformation from anatase TiO₂ to rutile TiO₂ can put detrimental effect to the overall photocatalytic activity of the 0.1% Al-TiO₂.

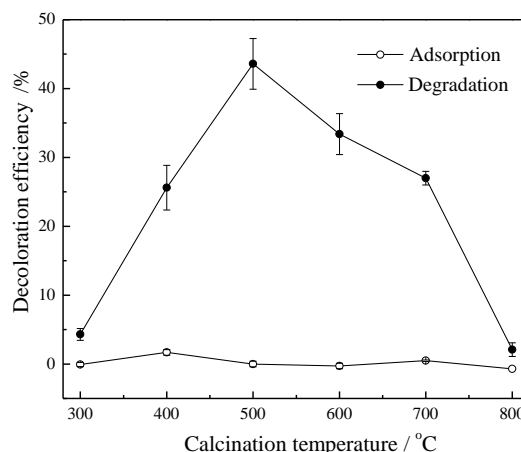


Fig. 4. Adsorption and photocatalytic degradation of RBR X-3B on 0.1% Al-TiO₂ aggregated spheres. The irradiation time was 30 min

The 0.1% Al-TiO₂ calcined at 500 °C was used for kinetic studying of photocatalytic degradation reaction. The RBR X-3B solution can be fully decolorized after 75 min of irradiation. Fig. 5(a) shows UV-Vis absorption spectrum of RBR X-3B solution during illumination in the presence of 0.1% Al-TiO₂. The azo dye, RBR X-3B, has a chromophoric group absorbing in the wavelength between 450 nm and 570 nm in the spectrum. The maximum absorption intensity of the chromophoric azo group is at 539 nm. The benzene ring and triazine group in RBR X-3B molecule have strong absorptions in the ultraviolet region.

All the absorption peaks shrink with extending irradiation time. The absorptions of azo group in the

visible region disappear after 75 min, while weak absorptions in the ultraviolet region can still be found in the spectrum. It is known that the triazine group is hard to be fully degraded through photocatalytic oxidation. Fig. 5(b) illustrates the kinetic plot of photocatalytic degradation of RBR X-3B using 0.1%Al-TiO₂. Photocatalytic oxidation of RBR X-3B follows the law of first order reaction, $\ln(C_0/C)=k_{app} \times t$. The apparent reaction rate constant is 0.031 min⁻¹ of the 0.1%Al-TiO₂.

The reusability of 0.1%Al-TiO₂ aggregated spheres for photocatalytic degradation of RBR X-3B is shown in Fig. 6. The photocatalyst is filtrated after each decoloration process. The obtained powders are washed with distilled water and dried in the furnace at 80 °C for 5 h before the next cycle. Each decoloration cycle contains adsorption of RBR X-3B and photocatalytic oxidation for 75 min on the material. The reused photocatalyst may lose slight part of activity in the next cycle, because very fine particles are removed from the material during filtration. Majority of the activity is maintained after five cycles, and decoloration efficiency is reduced from 100% to 80% after five cycles.

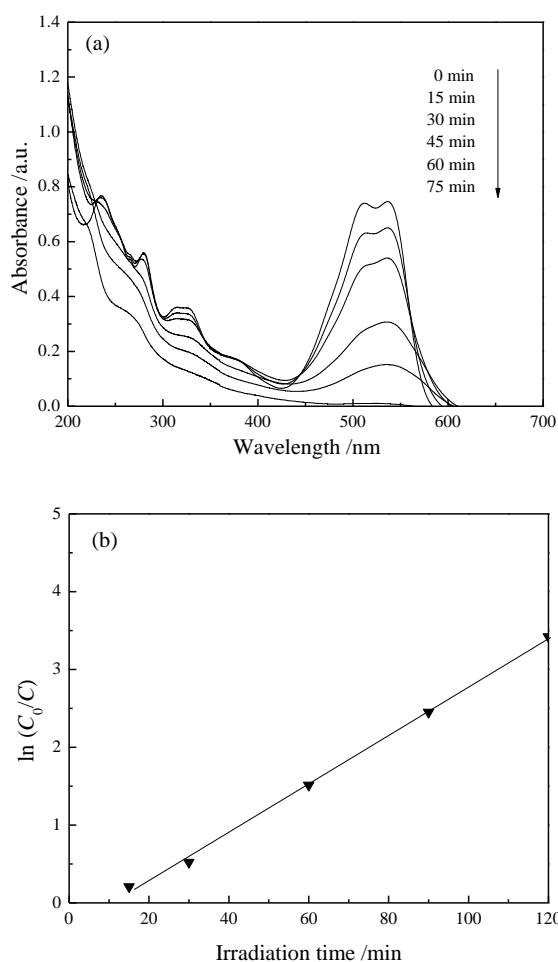


Fig. 5. (a) UV-Vis absorption spectrum of RBR X-3B solution during illumination in the presence of 0.1%Al-TiO₂, (b) Kinetic plot of photocatalytic degradation of RBR X-3B on 0.1%Al-TiO₂. The sample was prepared at 500 °C

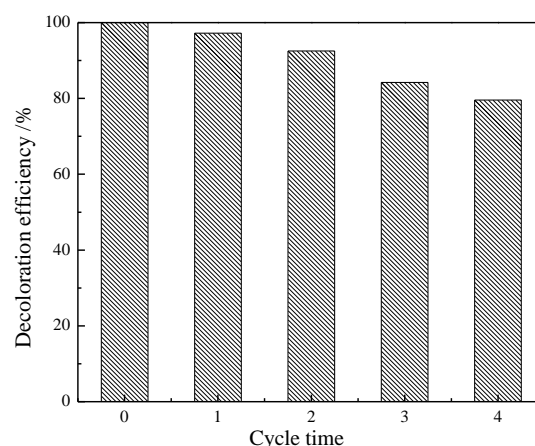


Fig. 6. Reusability of 0.1%Al-TiO₂ aggregated spheres for RBR X-3B decoloration. The sample was prepared at 500 °C.

4. Conclusions

0.1%Al-TiO₂ aggregated spheres were synthesized by sol-gel method using graphical spheres as template. Crystallite sizes of the 0.1%Al-TiO₂ samples calcined at 400, 500 and 600 °C are 11.3, 13.7 and 30.3 nm, respectively. The decline in surface area can be attributed to crystal growth and particles aggregation at high temperature. Average pore size and total pore volume of 0.1%Al-TiO₂ constantly increase with rising calcination temperature. The apparent reaction rate constant is 0.031 min⁻¹ on the 0.1%Al-TiO₂ sample calcined at 500 °C, which is the maximum activity. Decoloration efficiency is reduced from 100% to 80% after five treating cycles on that sample.

Acknowledgments

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