An efficient CaTiO3 nano sonocatalyst toward the dye degradation under ultrasonic irradiation

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In this work, the sonocatalytic property of CaTiO3 nanoparticles synthesized via a polyacrylamide gel route was investigated by degrading rhodamine B (Rhb), methyl orange (MO) and methylene blue (MB) under ultrasonic irradiation. It is revealed that CaTiO3 particles exhibit an excellent sonocatalytic activity toward the dye degradation. The influence of various experimental parameters [reaction solution temperature, catalyst dosage, initial dye concentration, pH value, and inorganic anions (including NO3, SO42, H2PO4, and HCO3)] on the sonocatalytic efficiency was systematically investigated. Hydroxyl (·OH) radicals were detected by fluorometry using terephthalic acid as a probe molecule and are found to be produced over the ultrasonic-irradiated CaTiO3 particles. The addition of ethanol, which acts as a ·OH scavenger, leads to a quenching of ·OH radicals and a simultaneous decrease in the dye degradation. This suggests that ·OH radicals are the dominant active species in the present sonocatalytic reaction. In addition, the recycling sonocatalytic experiment reveals that CaTiO3 particles exhibit a good stability in their sonocatalytic activity and crystal structure.

Key-words : CaTiO3 nanoparticles, Sonocatalytic activity, Influencing factors, ·OH radicals

1. Introduction

With the rapid development of global industrialization, the industrial wastewater containing various organic pollutants (such as organic dyes) has become an impending environmental problem that confronts mankind today. Various technologies have been developed to eliminate organic pollutants in the wastewater. Among them, semiconductor-based photocatalysis has attracted considerable attention since it allows the use of sunlight (a clean and renewable energy source) for the destruction of dye pollutants. However, the penetrating ability of light is generally limited in dye wastewater because the dye wastewater is usually non-transparent and highly-concentrated. This indicates that the semiconductor photocatalysis is not suitable for the treatment of non-transparent and highly-concentrated dye wastewater. Semiconductor-based sonocatalysis is an alternative technology to degrade organic pollutants in wastewater and shows advantages over photocatalytic technology because the ultrasonic wave has a strong penetrating ability in any water medium. The sonocatalytic mechanism can be understood based on the acoustic cavitation in liquid induced by ultrasonic irradiation. The sono-excited electrons and holes migrate to the catalyst particle surface and participate in a series of redox reactions to produce a number of active species like hydroxyl (·OH) radicals. Moreover, the catalyst particles can act as additional nuclei for the formation of cavitation bubbles, thus leading to an increase in the sonocatalysis reaction.

Perovskite-type oxides have been known as an important class of multifunctional materials. CaTiO3 is one of the interesting perovskite-type oxides, possessing promising luminescent, dielectric, thermomechanical, and catalytic properties. In particular, CaTiO3 has been shown to exhibit a pronounced photocatalytic activity toward the degradation of organic pollutants. Moreover, the CB and VB edges of CaTiO3 straddle the redox potentials of H+/H2 and O2/H2O, thus making it have the ability to photocatalytically split water into H2 and O2. In this work, we demonstrate that CaTiO3 can be used as an excellent sonocatalyst for the dye degradation. The influences of various experimental factors on the sonocatalysis efficiency were systematically investigated. The sonocatalytic mechanism involved was investigated and discussed.

2. Experimental

CaTiO3 nanoparticles used in the present sonocatalytic experiments were prepared by a polyacrylamide gel route as described in the literature. 0.0075 mol of Ca(NO3)2·4H2O and 0.0075 mol of Ti(OC4H9)4 were dissolved in 20 mL of dilute nitric acid solution were successively added 0.0225 mol of tartaric acid, 20 g aqueous ammonia. The resultant solution was heated at 70°C on a hot plate to initiate the polymerization reaction. The formed gel was dried at 120°C for 24 h in a thermostat drier.

DOI http://dx.doi.org/10.2109/jcersj2.16142
xerogel was ground into powder and submitted to calcination at 600°C for 6 h, finally yielding CaTiO3 nanoparticles.

The UV–visible diffuse reflectance spectrum of the sample was measured using a UV–visible spectrophotometer equipped with an integrating sphere. The particle morphology of the sample was investigated by a field-emission scanning electron microscope (SEM). The Brunauer–Emmett–Teller (BET) specific surface area of the sample was measured by the N2 adsorption–desorption technique on an ASAP2020M system.

The sonocatalytic activity of CaTiO3 nanoparticles was evaluated by degrading rhodamine B (RhB), methyl orange (MO) and methylene blue (MB) in aqueous solution under ultrasonic irradiation. In a typical experimental process, 0.02 g of the catalyst was added into 20 mL of 5 mg L⁻¹ RhB solution loaded in a glass beaker (the catalyst concentration was 1 g L⁻¹) with inner diameter of 32 mm and height of 75 mm. The reaction solution was placed in an ultrasonic bath (Jinan Bake Ultrasonic Tech Co. Ltd.) and irradiated by ultrasound at a frequency of 40 kHz. After magnetically stirred for 20 min in the dark, the mixed solution was ultrasonically irradiated at a frequency of 40 kHz. The reaction solution temperature was fixed at 40°C. A small amount of the reacted solution was pipetted out and centrifuged for 10 min at 4000 rpm to remove the catalyst. The upper clear solution in the centrifuge tube was then used for the PL measurements at a fluorescence spectrophotometer with the excitation wavelength of 315 nm. Ethanol was added by 10% of volume ratio to the reaction solution to investigate its effect on the •OH yield.

3. Results and discussion

Figure 2 shows the UV–visible diffuse reflectance spectrum of the as-prepared CaTiO3 particles along with the corresponding first derivative of the diffuse reflectance (R) with respect to wavelength (i.e., dR/dλ). It is seen that the particles have an absorption edge at ~342.5 nm, from which their bandgap energy (Eg) is obtained to ~3.62 eV. The insert in Fig. 2 shows an SEM image of CaTiO3 particles, revealing that the particles are regularly shaped like spheres and have an average size of ~36 nm. The BET specific surface area of CaTiO3 particles is obtained to be 42.7 m² g⁻¹.

Figure 3 shows the sonocatalytic degradation of the dyes (RhB, MO and MB) over CaTiO3 particles as a function of ultrasonic time (t) at different temperatures, where the initial dye concentration is C₁ = 5 mg L⁻¹, the catalyst loading is Ccatalyst = 2 g L⁻¹, and the pH value of the reaction solution is pH = 6.4 (normal pH). The corresponding blank experiment result is also shown in Fig. 3, revealing a good stability of the dyes under ultrasonic irradiation without catalyst, and their degradation is almost negligible after 60 min of ultrasonic irradiation. In the absence of ultrasonic irradiation, CaTiO3 particles show a weak adsorption toward the dyes, where the adsorption percentage after 20 min of adsorption is about 6–8, 2–4 and 2–3% for RhB, MO and MB, respectively. On irradiation with ultrasound in the presence of CaTiO3 particles, the degradation of the dyes increases substantially with increasing irradiation time, implying that...
CaTiO₃ particles exhibit an excellent sonocatalytic activity. The sonocatalytic degradation of the dyes has a high dependence on the temperature of the reaction solution. With increasing the solution temperature, the dye degradation increases initially and then exhibits a slight decreasing trend, where the optimum temperature is observed at 40°C. After sonocatalysis for 60 min, the degradation percentage of RhB, MO and MB at the optimum temperature is ³85, ³77 and ³52%, respectively. Generally, most chemical reactions closely depend on temperature, and their reaction rates become quicker with the increase of temperature. However, rising temperatures can easily cause the degassing of the solution, thereby reducing the number of gas nuclei available for the formation of cavitation bubbles. This indicates that an appropriate temperature is beneficial to enhance the sonocatalysis efficiency. In addition, one can see that the sonocatalysis efficiency has a dependence on the type of dye, and under the present experimental conditions, the degradation rate of the three dyes is in the following order: RhB > MO > MB. Numerous factors are expected to collectively contribute to the differences between the degradation rates of the dyes, such as the dye adsorption properties on the catalyst particles and the molecular structure of the dye.

The influences of other experimental factors on the sonocatalysis efficiency were further investigated by degrading RhB. Figure 4(a) shows the effect of CaTiO₃ concentration on the sonocatalytic degradation of RhB, where \( C_{\text{RhB}} = 5 \text{ mg·L}^{-1}, T = 40^\circ\text{C}, \) and \( \text{pH} = 6.4 \) (normal pH). At low catalyst concentrations, the number of available surface active sites is getting small, generally resulting in a low degradation efficiency of the dye. With raising the catalyst concentration, the sonocatalysis efficiency is seen to increase initially due to an expected increase in the surface area and the number of active sites. However, when the catalyst is added in excess, it will bring the active sites reduce due to the aggregation between catalyst particles. Furthermore, excessive dosage of catalyst can possibly reduce the transmission of ultrasound waves and flash lights near the catalyst surface. These collectively lead to a decrease in the sonocatalysis efficiency at high catalyst loading. In the present experiments, the optimum loading of CaTiO₃ particles is obtained to be 2 g·L⁻¹.

Figure 4(b) shows the effect of initial RhB concentration on its sonocatalytic degradation, where \( C_{\text{catalyst}} = 2 \text{ g·L}^{-1}, T = 40^\circ\text{C}, \) and \( \text{pH} = 6.4 \) (normal pH). It is seen that the degradation rate of RhB exhibits a decreasing trend with increase in the initial concentration of RhB. This phenomenon can be ascribed to the increase in the number of dye molecules on the surface of the catalyst with increasing the dye concentration. The increased dye adsorption is expected to reduce the adsorption of \( \text{H}_2\text{O}/\text{OH}^- \) onto the catalyst surface, and as a result, \( \text{H}_2\text{O}/\text{OH}^- \) is decreasingly available for the reaction with holes to generate \( \cdot\text{OH} \) radicals that are verified to be the main active species in the present sonocatalysis. Furthermore, the dye molecules at high concentrations could shield catalyst particles from receiving the sonoluminescence.

Figure 4(c) shows the effect of solution pH value on the sonocatalytic degradation of RhB, where \( C_{\text{RhB}} = 5 \text{ mg·L}^{-1}, C_{\text{catalyst}} = 2 \text{ g·L}^{-1}, \) and \( T = 40^\circ\text{C}. \) It is seen that the degradation of RhB exhibits a decreasing trend with increasing the pH value. One of the possible reasons for the decreasing degradation of

![Fig. 3. Sonocatalytic degradation of (a) RhB, (b) MO and (c) MB over CaTiO₃ particles as a function of ultrasonic time (t) at different temperatures, along with the corresponding blank experiment result.](image-url)
RhB is ascribed to the decrease in the dye adsorption onto the catalyst (as seen from Fig. 6). It is noted that with increasing the pH value, the surface charge of CaTiO₃ particles undergoes a change from positive to negative (where the isoelectric point for CaTiO₃ is at \( \text{pH} \approx 8.132 \)), and this surface charge change results in a decrease in the dye adsorption. In fact, however, the effect of pH on the dye degradation is rather more complicated because the pH value can affect not only the properties of the catalyst and the dye, but also the generation of active species. For example, different pH values can lead to different forms of dyes in aqueous solution, i.e., molecular form or ionic form. All those factors could affect positively or negatively the degradation efficiency of the dye.

The industrial dye wastewater usually contains various inorganic anions like \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{H}_2\text{PO}_4^- \) and \( \text{HCO}_3^- \). Investigation of the influence of those inorganic anions on the sonocatalytic degradation of dyes has a vital significance to promote the industrial application of sonocatalysts in dye wastewater treatment. Figure 5 shows the effect of \( \text{NO}_3^- \) (1 mM), \( \text{SO}_4^{2-} \) (1 mM), \( \text{H}_2\text{PO}_4^- \) (1 mM) and \( \text{HCO}_3^- \) (1 mM) on the degradation percentage of RhB after ultrasonic-irradiation for 60 min and the adsorption percentage of RhB after 20 min of adsorption (\( C_{\text{RhB}} = 5 \text{ mg L}^{-1} \), \( C_{\text{catalyst}} = 2 \text{ g L}^{-1} \), \( T = 40^\circ\text{C} \), \( \text{pH} = 6.4 \)). It is seen that the sonocatalytic degradation of RhB is inhibited to some extent when adding the anions. This can be attributed to the following reasons: (i) \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{H}_2\text{PO}_4^- \) and \( \text{HCO}_3^- \) can react with \( \cdot \text{OH} \) radicals and/or holes to produce \( \cdot \text{NO}_3, \cdot \text{SO}_4, \cdot \text{H}_2\text{PO}_4 \) and \( \cdot \text{HCO}_3 \), respectively,\(^{34,35}\) and the four species are less reactive than \( \cdot \text{OH} \); (ii) The introduction of the anions results in a slight decrease in the RhB adsorption due to the competitive adsorption of the anions against RhB onto the catalyst.

In most cases, \( \cdot \text{OH} \) radicals are regarded to be the primary active species responsible for the dye degradation. It is known that ethanol can be used as the scavenger of \( \cdot \text{OH} \) radicals.\(^{26}\) By investigating the effect of ethanol on the sonocatalysis efficiency of CaTiO₃ particles toward the dye degradation, we can clarify the role of \( \cdot \text{OH} \) radicals in the present sonocatalysis. Figure 6(a)
shows the effect of ethanol (10% of volume ratio) on the degradation of RhB after 60 min of ultrasonic irradiation and the adsorption of RhB after 20 min of adsorption ($C_{RhB} = 5 \text{ mg L}^{-1}$, $C_{catalyst} = 2 \text{ g L}^{-1}$, $T = 40^\circ\text{C}$, pH = 6.4). It is found that when adding ethanol to the reaction solution, the sonocatalytic degradation of RhB undergoes a significant decrease from $\sim$85% under normal condition to $\sim$10%. This result implies that ethanol exhibits a substantial suppression on the dye degradation, and hence $\cdot$OH radicals are suggested to play an important role in the sonocatalysis. The addition of ethanol leads to a slight decrease in the RhB adsorption, which is possibly due to the competitive adsorption of ethanol against RhB onto the catalyst.

Figure 6(b) shows the PL spectra of the TPA solution after reaction for 60 min over the ultrasonic-irradiated CaTiO$_3$ particles without ethanol and with adding 10% volume fraction of ethanol, along with the blank experiment results.

- OH radicals caused by ethanol. As the introduction of ethanol simultaneously results in a drastic decrease in the sonocatalytic degradation of the dye, $\cdot$OH radicals are therefore suggested to be the dominant active species causing the dye degradation.

The stability of CaTiO$_3$ particles was examined by the recycling sonocatalytic experiment. After the first cycle of sonocatalysis was completed, the catalyst was collected by centrifugation, washed with water, and dried. The recovered catalyst was introduced to the fresh RhB solution for the next cycle of the sonocatalytic experiment under the same conditions. This process was repeated four times. Figure 7(a) shows the degradation of RhB after ultrasonic irradiation for 60 min over CaTiO$_3$ particles during the five sonocatalytic cycles ($C_{RhB} = 5 \text{ mg L}^{-1}$, $C_{catalyst} = 2 \text{ g L}^{-1}$, $T = 40^\circ\text{C}$, pH = 6.4). It reveals that the degradation percentage of RhB maintains 81 to 85% for five consecutive recycles. The tiny or negligible lose of the sonocatalysis efficiency indicates an excellent sonocatalytic reusability of CaTiO$_3$ particles.

Figure 7(b) shows the XRD patterns of CaTiO$_3$ particles before and after five cycles of sonocatalysis, along with the standard XRD line pattern for CaTiO$_3$ orthorhombic structure (PDF card No. 42-0423).
during the sonocatalysis experiments, which exhibit a good structural stability.

4. Conclusions

The sonocatalytic experiments reveal that CaTiO₃ nanoparticles synthesized via a polyacrylamide gel route exhibit a good sonocatalytic activity toward the dye degradation under ultrasonic irradiation. The sonocatalysis efficiency is shown to have a close dependence on the reaction solution temperature, catalyst dosage, initial dye concentration, and pH value. The addition of inorganic anions NO₃⁻, SO₄²⁻, H₂PO₄⁻ and HCO₃⁻ leads to a moderate decrease in the sonocatalytic degradation of the dye. When adding a •OH scavenger—ethanol to the reaction solution, the dye degradation is significantly inhibited. •OH radicals are found to be produced over the ultrasonic-irradiated CaTiO₃ particles, and caused to be quenched by adding ethanol. Based on the experimental results, •OH radicals are suggested to be the primary active species in the sonocatalysis. In addition, CaTiO₃ particles are shown to exhibit a good stability in their sonocatalytic activity and crystal structure according to the recycling sonocatalytic experiment.

Acknowledgments This work was supported by the National Natural Science Foundation of China (Grant No. 51262018), the Fundamental Research Funds for Universities of Gansu Province (Grant No. 056003) and the Hongli Outstanding Talents Foundation of Lanzhou University of Technology (Grant No. J201205).

References