2019 International Conference on Biology, Chemistry and Medical Engineering (ICBCME 2019)

Preparation of La-doped TiO_2 Photocatalyst by Microwave Hydrothermal Method and Its Photocatalytic Activity

Cheng Chen[a], Yunli Yi[b], and Xianjun Bi[c, *]

Institute of Chemistry and Chemical Engineering Yunnan Normal University Kunming, China

[a]star470013181@126.com, [b]1249681947@qq.com, [c]bixj159@qq.com

*The Corresponding author

Keywords: Microwave hydrothermal method; TiO_2 photocatalys; La doping; Photocatalytic activit; Catalyst characterization

Abstract: The La-doped TiO_2 photocatalyst TiO2-La was prepared by microwave hydrothermal method, and the photocatalytic degradation of methyl orange in simulated wastewater was carried out under ultraviolet light. The results of the experiment show that the optimal preparation conditions of TiO_2-La catalyst are La doping amount $n(La^{3+}):n(Ti^{4+})=0.12\%$, microwave power 650W, reaction temperature 150℃, reaction time 2.5h, the temperature of high temperature muffle furnace calcination 600℃ and the time of calcination 3 h. The structure and characterization of TiO_2-La catalysts were carried out by X-ray diffraction (XRD), Energy dispersive spectrometer (EDS), X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared spectroscopy (FTIR). The results show that the degradation rate of methyl orange could reach 97.4% under the illumination of home-made UV lamp (300W).

1. Introduction

TiO_2 has been studied by a large number of researchers because of its high activity, stable chemical properties and no secondary pollution during photocatalytic degradation of organic pollutants[1]. TiO_2 has a large forbidden band width (Eg=3.2 eV) and can only be stimulated by ultraviolet light, however, most of the sunlight is composed of visible light and only 3-5% of ultraviolet light, resulting in low utilization of sunlight. Time-resolved spectroscopy studies show that the recombination rate of most photo-induced e-/h+ (electron-hole pairs) (about 90%) is very fast, which is one of the reasons why most semiconductor-based photocatalytic reactions are inefficient[2,3].Therefore, extending the response light region of TiO_2 to the visible light region (wavelength 400-800 nm) and reducing the photo-e-/h+ pair recombination rate have become the focus of research on TiO_2 photocatalysis.

Rare earth elements have a special electronic layer structure, which makes the spectral characteristics different from the general element. The rare earth element has 4f electrons, which is easy to produce multi-electron configuration, and its oxide has many crystal forms, strong adsorption selectivity, good electronic conductivity and thermal stability. Due to the large radius of rare earth ions, rare earth ions cannot enter the lattice of TiO_2, but photo-induced e^-/h^+ trapping wells can be formed on the surface of TiO_2 crystals, which can prolong the recombination time of photo-induced e-/h+ pairs and improve photocatalytic activity. However, the excess rare earth ions will precipitate on the surface of the TiO_2 crystal grains in the form of oxides, resulting in a decrease in the photocatalytic activity of TiO_2. Therefore, the optimal concentration of the doped ions exists [4,5]. In this paper, the rare earth metal ion La^{3+} doped TiO_2 photocatalyst TiO_2-La was prepared by microwave hydrothermal method. The methyl orange solution was used to simulate the contaminated water. The optimum conditions for the preparation of La-doped TiO_2 photocatalyst under microwave hydrothermal conditions were investigated.

DOI: 10.25236/icbcme.2019.033

2. Experiment Part

2.1. Main Reagent.

Tetra-n-butyl titanate (AR, Sinopharm Chemical Reagent Co., Ltd.); Lanthanum nitrate hexahydrate $La(NO_3)_3·6H_2O$ (AR, Aladdin reagent); Anhydrous ethanol (AR, Tianjin Sailboat Chemical Reagent Technology Co., Ltd. Company); Concentrated nitric acid (CP, Shanghai Chemical Reagent General Plant); Methyl orange (AR; Sinopharm Chemical Reagent Co., Ltd.); Ultrapure water (homemade).

2.2. Preparation of Catalyst and Photocatalytic Activity Test.

Take a quantitative amount of 4.40 mL of tetra-n-butyl titanate and 17.50 mL of absolute ethanol, and stir magnetically for 10 minutes to obtain solution A. The quantitative lanthanum nitrate is dissolved in dilute nitric acid (pH=2~3) of 18.00 mL and added drop wise to the solution A to form a solution B. The B solution was placed in a microwave water-heat parallel synthesizer (instrument parameters: microwave power 650 W, reaction temperature 150 ℃, reaction time 2.5 h) to obtain a TiO_2 sol for a certain period of time, filtered, dried, milled and the TiO_2-La photocatalyst was obtained by calcination at 600 ℃ in a muffle furnace for 3 h, and the TiO_2 was bottled and placed in a desiccators for use. The photocatalytic activity test method of the catalyst is described in the literature [6, 7].

2.3. Structural Testing and Characterization of the Catalyst.

The structure and characterization of TiO_2-La photocatalysts were carried out by X-ray diffraction (XRD), Energy dispersive spectrometer (EDS), X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared spectroscopy (FTIR).

3. Results and Discussion

3.1. Effect of La^{3+} Doping Amount on the Activity of TiO_2-La Photocatalyst.

Under the conditions of fixed microwave power 650 W, reaction temperature 150 ℃, reaction time 2.5 h, calcination temperature 600 ℃ and calcination time 3 h, the amount of La^{3+} ion doping was changed to investigate the photocatalytic activity of the prepared TiO_2-La catalyst. The results obtained are shown in Figure 1. It can be seen from Figure. 1 that the photocatalytic activity of TiO_2-La increases gradually with the increase of strontium doping amount, and then decreases gradually. When the lanthanum doping amount is 0.12%, the degradation of methyl orange for the catalyst reaches a maximum value 97.4%, excessive or too little rare earth doping will reduce the photocatalytic activity of TiO_2. When the lanthanum is doped at a high concentration, the rare earth element lanthanum is deposited on the surface of the TiO_2 catalyst in the form of oxide La_2O_3 which leads to insufficient absorption of ultraviolet light for TiO_2, and reduces the photocatalytic activity of TiO_2[8]. Therefore, a suitable lanthanum doping concentration is advantageous for increasing the photocatalytic activity of TiO_2. Figure 2 is an XRD spectrum of different La doping amounts of TiO_2. It is clear from the Figure.2 that La doping effectively inhibits the growth of rutile, and a large amount of rutile is not favorable for photocatalytic activity because the rutile has a small specific surface area. The large amount of rutile has poor adsorption capacity for O_2, and photo-induced e^-/h^+ pairs are easy to recombine, so the photocatalytic activity is greatly affected [9].

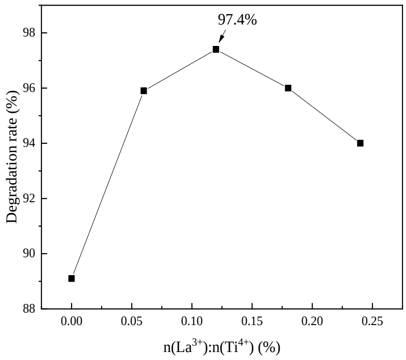

Figure. 1 Effect of La doping amount on photocatalytic activity of TiO2-La

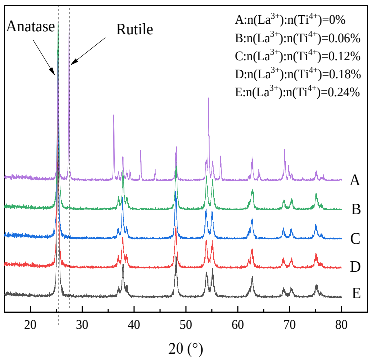

Figure. 2 XRD spectrum of different La3+ doping amount TiO2

3.2. Effect of Calcination Temperature on Photocatalytic Activity of TiO_2-La.

Under the conditions of fixed antimony doping amount of 0.12%, microwave power 650W, reaction temperature 150 ℃, reaction time 2.5 h and calcination time 3 h, the calcination temperature was changed to investigate the effect of calcination temperature on the photocatalytic activity of the prepared TiO_2-La catalyst. The results are shown in Figure 3. Figure 4. is an XRD spectrum of calcined TiO_2-La at different temperatures. In combination with Figure 3, the calcination temperature is too low, and there is more amorphous TiO_2. When the calcination temperature is too high, the anatase TiO_2 begins to transform into rutile TiO_2, two extreme conditions both are not conducive to the improvement of photocatalytic activity. It can also be seen from Figure 3 that when the calcination temperature is 600 ℃, the obtained TiO_2-La catalyst has a high photocatalytic activity, thereby obtaining an optimum calcination temperature of 600 ℃.

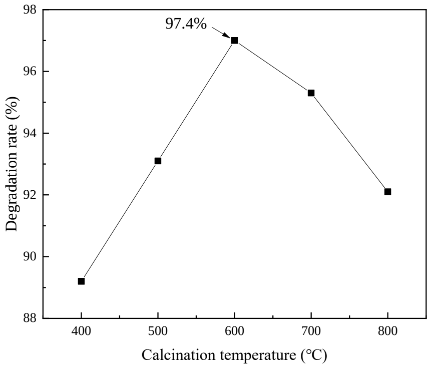

Figure 3. Effect of calcination temperature on photocatalytic activity of TiO2-La

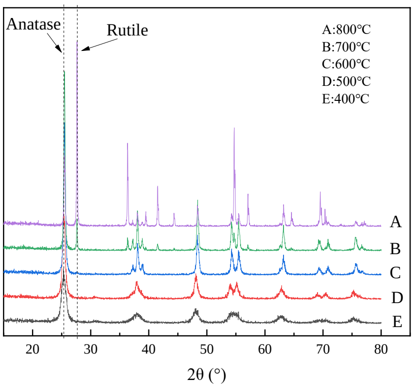

Figure 4. XRD spectrum of calcined TiO2-La at different temperatures

3.3. Energy Dispersive Spectrometer (EDS).

The energy spectrum analysis of TiO_2-La was performed by selecting a specific region, and the results are shown in Figure 5. It can be seen from Figure 5 that the main elements in the catalyst sample are Ti and O, and characteristic peaks of the C and La elements also appear. This indicates that the TiO_2-La sample does contain La element, and the doped TiO_2 catalyst is loaded with La element.

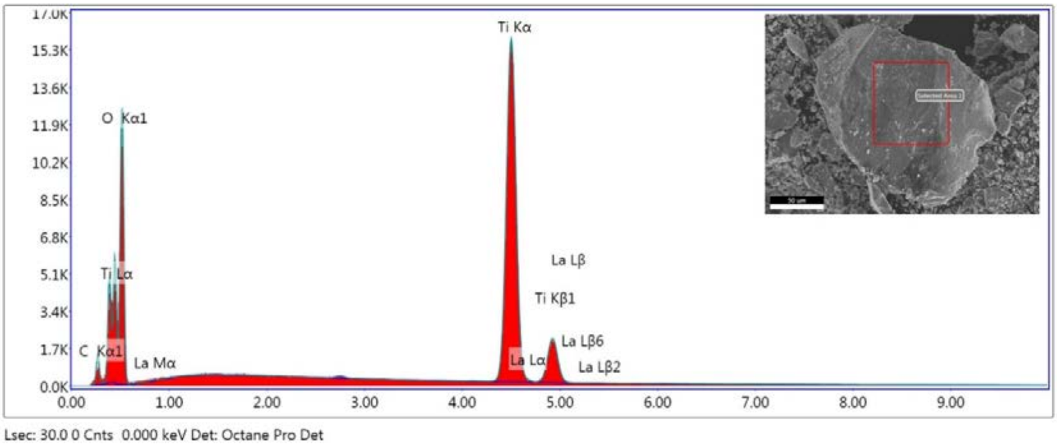

Figure. 5 Energy Dispersive Spectrometer (EDS) of TiO2-La Specific area

3.4. X-ray Photoelectron Spectroscopy (XPS).

The results of XPS analysis of pure TiO_2 (Undoped under the same conditions) and doped TiO_2-La catalysts (Figure 6) show that the pure TiO_2 catalyst contains Ti, O and C elements, while the doped TiO_2-La catalyst contains Ti, O, La and C element, which is consistent with the elemental analysis results of EDS. Figure 6-A is a Ti 2p spectrum. The electron binding energies of Ti in pure TiO_2 and TiO_2-La are 458.69 eV and 458.48 eV, respectively. Figure 6-B is the O1s spectrum. The strongest peak appears at 530.01 eV. It is oxygen in the TiO_2 lattice. In addition, the peaks at 531.35eV and 532.37eV may be related to the surface substance group of TiO_2 (Ti-OH-Ti, TiOx, -CO, -OH) and for TiO_2-La catalyst. The O1s peak in La_2O_3 appeared at 528.58 eV, which is consistent with the La doping result. Figure 6-C is the C1s spectrum, which appears at 284.84, 286.18 and 288.68 eV, mainly in the form of C-C, -C-OH and -CO. In general, XPS can detect C from the atmosphere. In addition, C may also be derived from the precursor of TiO_2 (tetra-n-butyl titanate). Figure 6-D is a La3d spectrum, although the doping amount of La is extremely low(Theoretical doping is 0.12%), but La is still detected in the TiO_2-La catalyst and exists in the form of La_2O_3 on the surface of TiO_2, which is beneficial to form an electron trapping well on the surface of TiO_2, effectively suppressing electron-hole recombination, thereby increasing the photocatalytic activity of the catalyst [10,11].

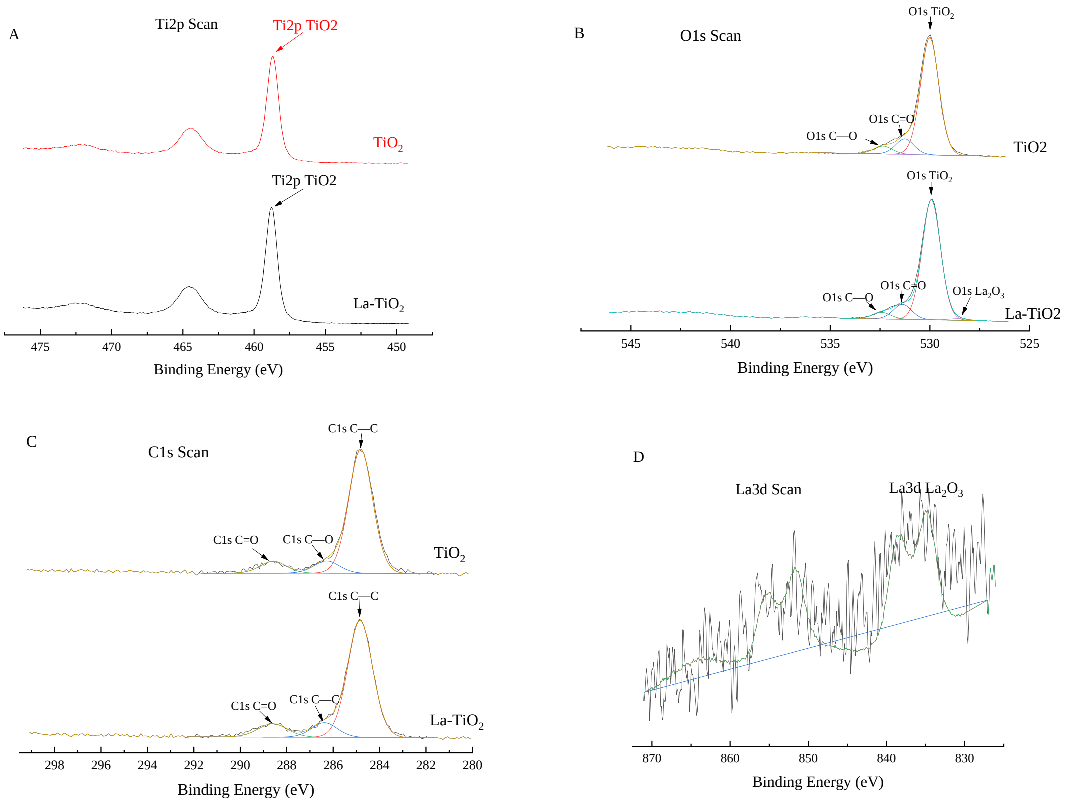

Figure. 6 XPS spectrum of pure TiO2 andTiO2-La (A: Ti2p Scan B: O1s Scan C: C1s Scan D: La3d Scan)

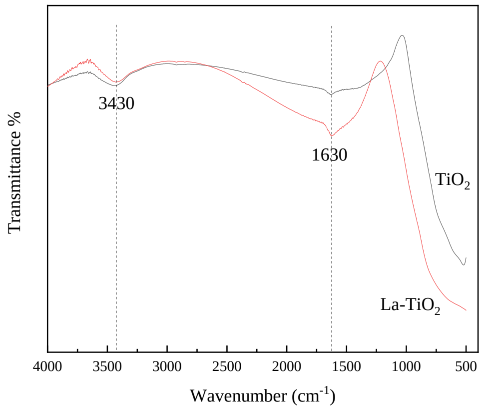

Figure. 7 FTIR spectrum of pure TiO_2 andTiO_2-La

3.5. Fourier Transform Infrared Spectroscopy (FTIR).

The pure TiO_2 (undoped under the same conditions) and TiO_2-La were separately analyzed by FTIR, and the results obtained are shown in Figure 7. It can be seen from Figure 7 that the broad peak appearing at a wave number of 3430 cm^{-1} can be attributed to the tensile vibrational peak of the hydroxyl group bonded to the surface of TiO_2, and these surface hydroxyl substances can affect the photocatalytic activity of TiO_2[11]. The peak appearing at a wave number of about 1630 cm^{-1} is considered to be the OH bending vibration in the water molecules adsorbed on the surface of TiO_2[12]. The possible source of water can be attributed to the adsorption of water molecules in the air by TiO_2, while the water peaks in TiO_2-La. The strength is significantly greater than that of pure TiO_2. The possible reason is that the doped TiO_2-La has a larger specific surface area than pure TiO_2, which is more conducive to absorbing water molecules.

4. Conclusion

The optimal conditions for the preparation of La-doped TiO_2 photocatalyst by microwave hydrothermal method are La doping amount n(La^{3+}):n(Ti^{4+})=0.12%, microwave power 650 W, reaction temperature 150 ℃, reaction time 2.5h, the temperature of high temperature muffle furnace calcination 600 ℃ and the time of calcination 3 h. The degradation rate of methyl orange could reach 97.4% when the TiO_2-La catalyst prepared at the optimal conditions used for degrading the methyl orange solution for 30 minutes in the self-made UV lamp irradiation.

The results of XRD, EDS, XPS and FTIR show that the lanthanum element is doped into TiO_2 and supported on the surface of TiO_2 in the form of oxide, and the doping of lanthanum causes more active hydroxy species on the catalyst surface which is advantageous for increasing the photocatalytic activity of the catalyst.

References

[1] Y.Z. Gou, D.P. He, Y.W. Liao, P. Jiang and L. Wang. Catalytic performance of Au-doped TiO_2 prepared by hydrothermal homogeneous precipitation and calcination at high temperature[J]. Applied Chemical Industry, 2011, 40(9):1559-1562

[2] Thomas J, Radhika S, Yoon M. Nd^{3+}-doped TiO_2 nanoparticles incorporated with heteropoly phosphotungstic acid: a Novel Solar Photocatalyst for degradation of 4-Chlorophenol in water[J]. Journal of Molecular Catalysis A Chemical, 2016, 411(23):146-156.

[3] Schneider J, Matsuoka M, Takeuchi M, et al. Understanding TiO_2, Photocatalysis: Mechanisms and Materials [J]. Chemical Reviews, 2014, 114(19):9919-9986.

[4] Y.F. Zhu, W.Q. Yao and R.L. Zong. Photocatalysis: Application on Environmental Purifiction and Green Energy[M]. Chemical Industry Press, 2015

[5] M.W. Li, M. Zhang and X.J. Bi, Preparation of Ce-doped TiO_2 photocatalyst and its microwave enhanced photocatalytic activity[J]. Industtial Catalysis, 2015, 23(12):986-990.

[6] X. Wang, C. Chen and X. Bi. Preparation of Cu Doped TiO_2 Photo-catalyst by Microwave Hydrothermal Method and Study on Its Photo-catalytic Activity[C] Advances in Intelligent Systems Research.2017, 156, 841-845

[7] X. Wang, C. Chen and X. Bi. Preparation of Rare Earth Yb Doped TiO_2 Photo-catalyst by Microwave Hydrothermal Method and Its Photo-catalytic Activity[C] Advances in Intelligent Systems Research.2017, 156, 858-862

[8] Y. Li. Study on Photocatalytic Degradation of Methyl Orange by La^{3+}-doped TiO_2[J]. Journal of Filtration & Separation, 2014, 24(2):14-16.

[9] G.D. Sheng, J.X. Li, S.W. Wang and X.K. Wang, Modification to Promote Visible-Light Catalytic Activity of TiO_2[J]. Progeress in Chemistry, 2009, 21(12): 2492-2504.

[10] Patrycja Parnicka , Paweł Mazierski , Tomasz Grzyb , Zhishun Wei , Ewa Kowalska , Bunsho Ohtani ,Wojciech Lisowski , Tomasz Klimczuk , Joanna Nadolna. Preparation and photocatalytic activity of Nd-modified TiO_2, photocatalysts: Insight into the excitation mechanism under visible light[J]. Journal of Catalysis, 2017, 353:211-222.

[11] X.Q. Yan, C. Xue, B.L. Yang and G.D. Yang. Novel three-dimensionally ordered macroporous Fe^{3+}-doped TiO_2 photocatalysts for H2 production and degradation applications[J]. Applied Surface Science, 2017, 394:248-257.

[12] X.Y. Wang. Catalyst characterizationEast[M]. China University of Science and Technology Press, 2008.