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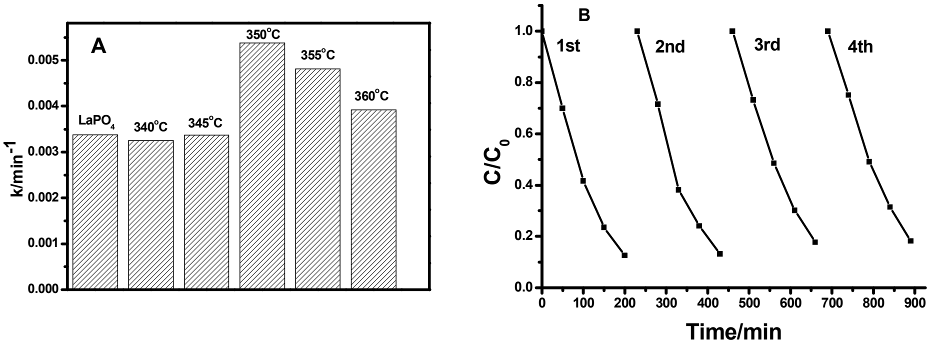
Graphic abstract



The photocatalytic activity reached the maximum at 350°C by vacuum heat treatment and almost 1.6 times higher than that of untreated $LaPO_4$. The v-$LaPO_4$ photocatalyst has good stability.

Photocatalytic Activity Enhancement of $LaPO_4$ via Surface Oxygen Vacancy

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Abstract

Monoclinic $LaPO_4$ photocatalyst with surface oxygen vacancies (v-$LaPO_4$) was prepared by hydrothermal and vacuum heat treatment method. The photocatalytic activity reached the maximum at 350°C by vacuum heat treatment for 3h and the photocatalytic activity and photocurrent of v-$LaPO_4$ are almost 1.6 and 2.3 times higher than that of pure $LaPO_4$, respectively. The improvement of photocatlytic activity is attributed to the high separation efficiency of photogeneration electron-hole pairs. The main oxidative species are hydroxyl radicals. The photocatalytic activity of v-$LaPO_4$ for the degradation of MB does not decrease after four cycles, indicating that the v-$LaPO_4$ photocatalyst has good stability.

Keywords: vacuum heating; $LaPO_4$; surface oxygen vacancies; photocatalysis

1. Introduction

The rare earth phosphate has magnetism, sensitive nature, and electric conductivity due to its good chemical, thermal stability and unique structure characteristics[1-5]. Therefore, it has a wide application in optical materials, magneto-optical materials, dielectric materials and chemical sensors. Generally, Lanthanum phosphate is doped

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with other rare earth materials[6], such as, the synthesis of rare earth $LaPO_4$: Ce, Tb crystal is a green-emitting photoluminescent material which is widely used in the production of phosphor[7]. It can also be used for the modification of molecular sieve, which has a unique role in catalytic chemistry. As is known to all, the preparation of nanomaterials has a significant influence for its morphology and performance. Syntheses of small particles, uniform morphology nano-powders are the premise of high performance materials. Currently, the main preparation method of $LaPO_4$ could be high temperature solid phase, precipitation, hydrothermal[8-13]. The solid phase method cause high temperature, and the product obtained by precipitation has poor crystallinity. The nanomaterials crystal prepared by hydrothermal method has good crystallinity and small particle size, which will help to improve the performance of materials. For years, a lot of research work on the photoluminescence of $LaPO_4$ mainly[14-16], the photocatalytic activity is rarely reported. Therefore, to develop the new application of rare earth phosphate has great significance. In this work, we have considered the high fluorescence quantum efficiency of $LaPO_4$, and mainly study on the photocatalytic activity of $LaPO_4$ with the surface treatment, that is an efficient way to improve its photocatalytic, as well as its stability. .

In summary, monoclinic $LaPO_4$ photocatalyst with surface oxygen vacancies was prepared by hydrothermal and vacuum heat treatment method. The photocatalytic performances of v-$LaPO_4$ are obviously improved than that of pure $LaPO_4$. The possible photocatalytic degradation mechanism is also proposed. The stability of v-$LaPO_4$ was investigated. So this study could be an efficient way to improve the photocatalytic activity of materials and decrease the fluorescence intensity, which is helpful to extend the application of $LaPO_4$

2. Experimental

2.1 Materials resource and photocatalyst preparation

Sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) and sodium sulfate (Na_2SO_4) are purchased from Sinopharm Chemical Reagent Co., Ltd. Lanthanum nitrate ($La(NO_3)_3 \bullet 6H_2O$), benzoquinone, tert-Butanol are purchased from Beijing Chemical Works. EDTA-2Na and methylene blue are obtained from Tianjin Chemical Reagent Co., Ltd. All chemicals are of analytical grade and used without further purification. Deionized water is used throughout the whole experiment.

3mmol $La(NO_3)_3 \bullet 6H_2O$ was added to 15mL deionized water under magnetic stirring, and then 15mL 0.2M $NaH_2PO_4 \bullet 2H_2O$ aqueous solution was dropped slowly to the above solution. After stirring for 1h, the solution was transferred into a teflon-lined stainless steel autoclave and maintained at 180^oC for 12h and then cooled to room temperature. Then the product was washed with deionized water and dried at 80^oC for 12h. After that, the synthesized $LaPO_4$ powders were proceed with vacuum heat treatment, and the heating time were (1h, 2h, 3h, 4h, 5h) and temperature were (340^oC, 345^oC, 350^oC, 355^oC, 360^oC), respectively. The vacuum pressure in the heating treatment was about 10-20mTorr. Finally, the samples were cooled naturally to room temperature.

2.2 Characterization

A high-resolution transmission electron microscope (HR-TEM) (Hitachi, JEM2010F) operated at an accelerating voltage of 200kV. The morphology and size of the obtained samples were characterized by scanning electron microscope (Hitachi, SU8010, 10.0kV) The in situ electron paramagnetic resonance (ESR) measurement was carried out using an Endor spectrometer (JEOL, ES-ED3X) at room temperature. The g factor was obtained by taking the signal of manganese. The ESR spectrometer was coupled to a computer for data acquisition and instrument control. The room temperature photoluminescence (PL) spectra of samples were investigated utilizing the PerkinElmer LS55 spectrophotometer equipped with xenon (Xe) lamp with an excitation wavelength of 251nm. X-ray photoelectron spectroscopy (XPS) were measured by Quantera (ULVAC-PHI, Japan). The photocurrent was measured on an electrochemical system (CHI-660B, ChenHua, Shanghai, China). UV light was obtained from an 11 W germicidal lamp (Institute for Electric Light Sources, Beijing). A standard three-electrode cell with a working electrode, a platinum wire as counter electrode and a standard calomel electrode (SCE) as reference electrode were used in photoelectric studies. 0.1M Na_2SO_4 was used as the electrolyte solution. Potentials were given with reference to the SCE. The photoelectric responses of the photocatalysts as light on and off were measured at 0.0 V. Ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS) was performed in Hitachi U-3010, $BaSO_4$ was used as reference.

2.3 Photocatalytic evaluation

The photocatalytic activities of the as-prepared samples were evaluated by the decomposition of methylene blue (MB) in solution under UV light. UV light source was obtained by a 20W UV germicidal lamp (λ =254 nm). 25mg photocatalyst was added into prepared 50mL 1×10^{-5}M MB aqueous solution. Before the light irradiation, the suspensions were firstly magnetically stirred for 30 min in dark to reach the absorption-desorption equilibrium. At given time intervals, 3mL aliquots were sampled and centrifuged to remove the photocatalyst particles. Synchronously, the filtrates of MB solutions at different conditions were analyzed by recording variations of the maximum absorption peak in the UV-vis spectra using a Hitachi U-3010 UV-vis spectrophotometer.

3. Results and discussion

3.1 Photocatalytic activity enhancement via surface oxygen vacancy

The photocatalytic activities of $LaPO_4$ and $LaPO_4$ after vacuum heating treating with different temperature and time for the degradation of MB were investigated. The degradation process is fitted to pseudo-first-order kinetics, and the values of the rate constant k are shown in Fig. 1A, B, respectively. The UV photocatalytic activities of vacuum-treated $LaPO_4$ samples are gradually improved with the increase of vacuum heating temperature and time. The photocatalytic activity of v-$LaPO_4$ has been confirmed to reach the maximum at the temperature of 350^{o}C, time is for 3h. The apparent rate constant k is 0.00538 min^{-1} and it is about 1.6 times higher than that of untreated $LaPO_4$. However, the degradation rate decreases with the increase of treating temperature and time, that still higher than that of $LaPO_4$. The differences of photocatalytic activities were caused by the concentration of oxygen vacancies among these samples, showing that the proper vacuum heating temperature and time have an effect on the photocatalytic activities. Besides, the UV photocurrent responses of $LaPO_4$ and v-$LaPO_4$ are shown in Fig. 1C. The photocurrent of v-$LaPO_4$ is about 2.3 times higher than that of $LaPO_4$. The improvement of UV photocurrent verifies the increase of the charge separation efficiency greatly. This result is consistent with the improvement of the photocatalytic activity for $LaPO_4$ samples.

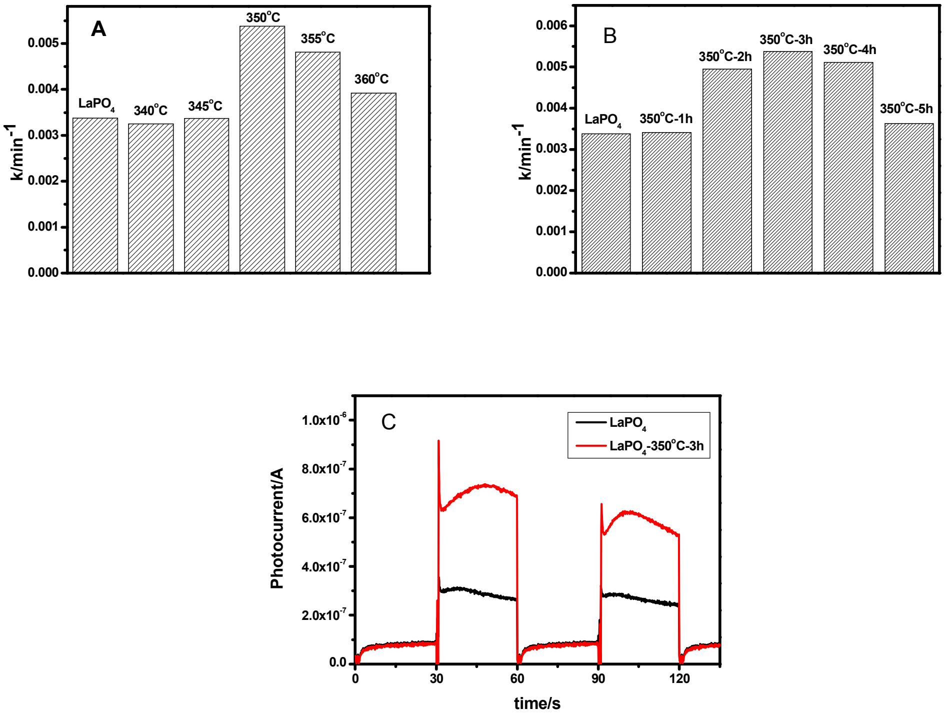


Figure 1. UV photocatalytic activity of $LaPO_4$ and v-$LaPO_4$ with (A) various temperature for 3h and (B) various time at 350°C for the degradation of MB, respectively; (C) photocurrent of $LaPO_4$ and v-$LaPO_4$ (treated at 350°C for 3h) under UV light (λ=254nm).

3.2 Structure of $LaPO_4$ and v-$LaPO_4$ photocatalysts

In order to observe the structural changes of samples before and after vacuum-treated, SEM, XRD and UV diffuse reflectance spectra were investigated, shown in Figure 2 and Figure 3A, B. It can be found that the samples maintain stable monoclinic phase structure, no matter with vacuum-treated or not. These are nanorods both $LaPO_4$ and v-$LaPO_4$ (Figure 2). It can be seen from the SEM images that the morphology and diameter of v-$LaPO_4$ almost the same, and the diameter of nanorods is about 20nm. So this method would not affect the morphology of $LaPO_4$ by vacuum heat treatment. As shown in Figure 3B, the absorption band edge has a slight red shift after vacuum-treated, and the light absorption improves from 200nm to 800nm slightly, that may be due to the introduction of surface oxygen vacancies.

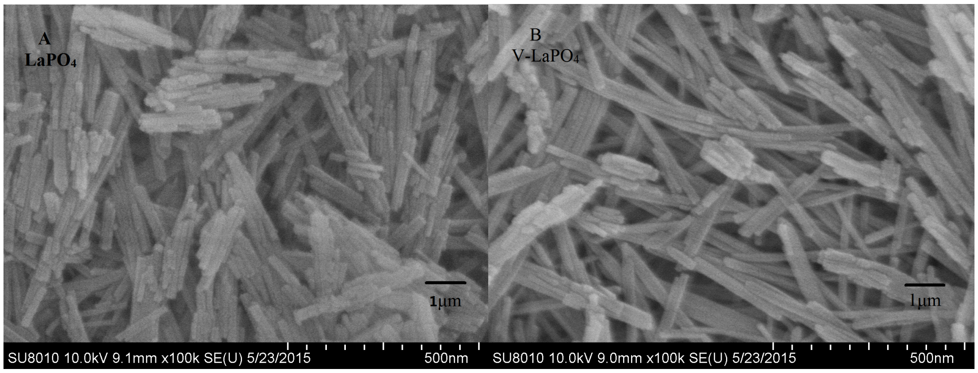
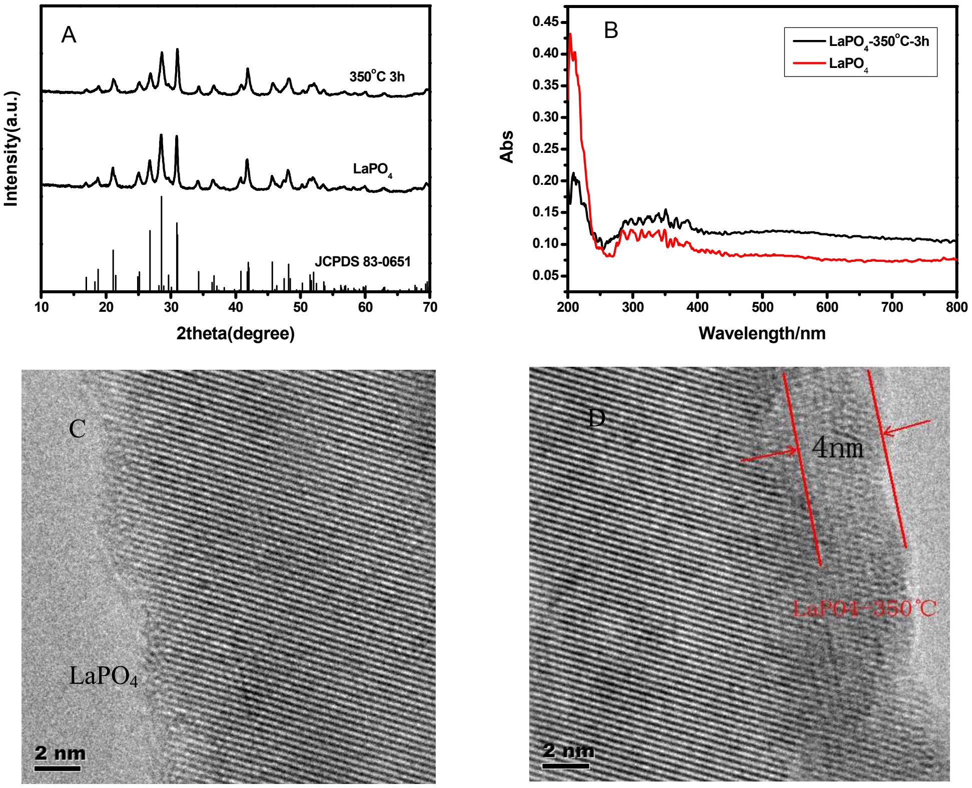


Figure 2. SEM images of $LaPO_4$ (A) and v-$LaPO_4$ (B)

To verify the generated surface oxygen vacancies, HR-TEM, ESR and XPS of the samples were investigated as shown in Figure 3C, D and Table 1, respectively. Both $LaPO_4$ and v-$LaPO_4$ that could observe the clear lattice fringes inside from the Figure

3C, D. But the edge of vacuum-treated particles become disordered (Figure 3D) indicates that surface structure was damaged and there is a vacancy layer about 4nm wide. It confirms that the vacuum treatment affects the condition of surface structure. Besides, ESR is a direct and sensitive technique to detect various behaviors of vacancy[17]. Figure 3E shows the ESR signal of $LaPO_4$ and v-$LaPO_4$. The ESR signal of v-$LaPO_4$ appears at g~2.03484 and g~1.99152, which can be attributed to the presence of surface oxygen vacancies[18-20]. Furthermore, the surface atomic concentration (molar ratio, at%) of La and O were investigated by XPS, as shown in Table 1. The result indicates that the surface atomic concentration (La:O) of v-$LaPO_4$ increase to 20.1% which higher than 18.9% of $LaPO_4$. The XPS result further confirms the formation of surface oxygen vacancies of v-$LaPO_4$.



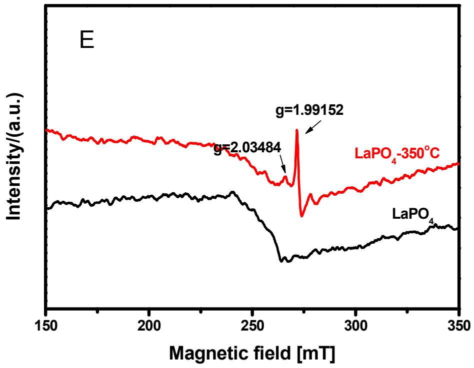


Figure 3. (A) XRD of $LaPO_4$ and v-$LaPO_4$; (B) UV-DRS of $LaPO_4$ and v-$LaPO_4$; (C) $LaPO_4$ and (D) v-$LaPO_4$ HR-TEM; (E) ESR signal of $LaPO_4$ and v-$LaPO_4$, respectively.

Table 1. Surface atomic concentration of La and O (molar ratio, at%)

	O1s	La3d5	La:O
$LaPO_4$	56.38	10.63	18.9%
v- $LaPO_4$	55.96	10.73	20.1%

In addition, the ability of light absorption has a certain increase of v-$LaPO_4$ (Figure 3B), and the photocatalytic activity of $LaPO_4$ and v-$LaPO_4$ were investigated under 365nm UV light for the degradation of MB, as shown in Figure 4A. According to the UV diffuse reflection spectrum (Figure 3B), $LaPO_4$ can only absorb the ultraviolet light no more than 275nm. In other words, the pure $LaPO_4$ itself can not be excited by UV light at 365nm, and almost no photocatalytic activity under UV light at 365nm

(Figure 4A). However, the v-$LaPO_4$ shows obvious enhancement of photocatalytic activity under UV light at 365nm. After UV irradiation for 200min, the degradation rate for MB is about 24%, and the apparent rate constant k is $0.0013min^{-1}$. Figure 4B compares the photocatalytic activities of $LaPO_4$ and v-$LaPO_4$ for the degradation of MB at different wavelength. It can be found that, $LaPO_4$ has higher photocatalytic activity for the degradation of MB at 254nm, while it almost has none of photocatalytic activity at 365nm. Thus, it illustrates that the improvement of light response of v-$LaPO_4$ is due to the surface oxygen vacancies. Besides, the valence band width was broadened with the presence of surface oxygen vacancies, which result in the narrow band gap[21,22], and is consistent with the red shift of absorption band edge from UV diffuse reflectance (Figure 3B).

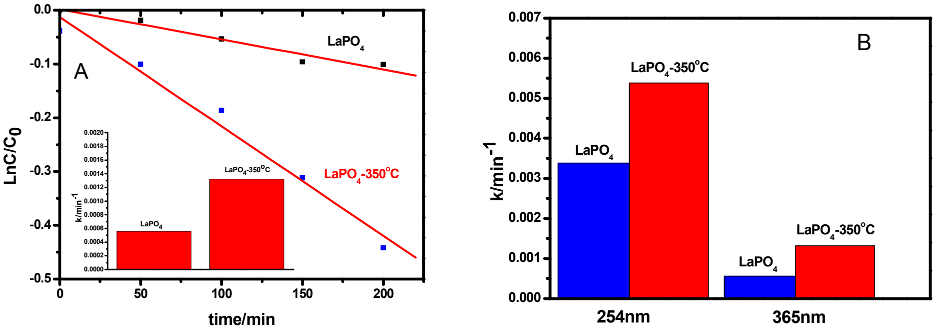


Figure 4. (A) UV photocatalytic activity of $LaPO_4$ and v-$LaPO_4$ for the degradation of MB at 365nm; (B) comparison of photocatalytic activities of $LaPO_4$ and v-$LaPO_4$ for the degradation of MB at different wavelength (λ=254nm and 365nm).

3.3 Mechanism of enhancement of UV activity and stability of v-$LaPO_4$

The photocatalytic mechanism was investigated by detecting the main oxidative species. The main oxidative species could be detected through trapping experiments of radicals, $\bullet O_2^-$ and holes by t-BuOH, quinone and EDTA-2Na, respectively[23-25]. Figure 5 shows the results of detecting oxidative species in the photodegradation of $LaPO_4$ and v-$LaPO_4$ under UV light. The addition of t-BuOH causes an obvious change in the photodegradation of MB both $LaPO_4$ and v-$LaPO_4$. On the contrary, the addition of quinone and EDTA-2Na only cause little change in the photodegradation of MB. It is considered that the main oxidative species of the photodegradation are hydroxyl radicals of $LaPO_4$ as same as that of v-$LaPO_4$.

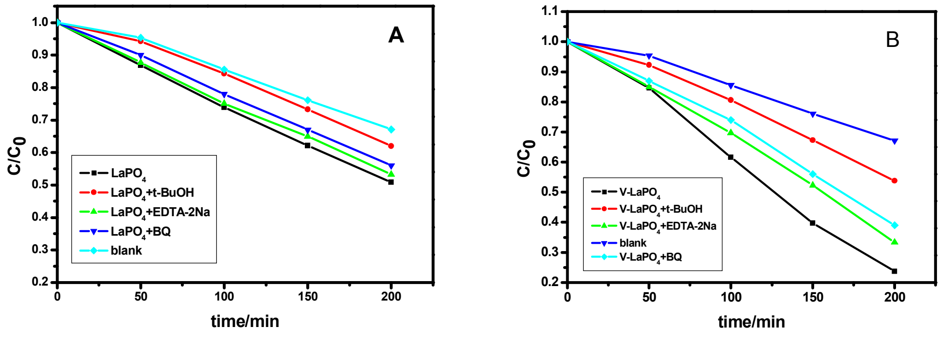


Figure 5. photogenerated carriers trapping for the degradation of MB of (A) $LaPO_4$ and (B) v-$LaPO_4$ under UV light, respectively.

In addition, further to study the mechanism of increasing photocatalytic activity of v-$LaPO_4$, the adsorption capacity of MB under darkroom conditions, PL spectra and electrochemical impedance spectroscopy of $LaPO_4$ and v- $LaPO_4$ (350°C for 3h) were measured, shown in Fig. 6. It can be seen from Fig. 6A that the adsorption capacity of $LaPO_4$ for MB solution almost unchanged no matter with vacuum treatment or not, therefore the adsorption capacity is not the main factor of enhanced photocatalytic activity. Figure 6B compares the PL spectra of $LaPO_4$ and v-$LaPO_4$ (350°C for 3h), in which the fluorescence intensity was significantly decreased nearly 40% after vacuum treatment. Therefore, the separation efficiency of electron-hole is improved. The EIS spectra were measured in the dark and under UV irradiation (254nm) of $LaPO_4$ and v-$LaPO_4$ (350°C for 3h), respectively (Fig. 6C). We all know that the smaller electrochemical impedance curve radius, the smaller charge-transfer resistance of the electrode is. In Figure 6C, the EIS curve radius of v- $LaPO_4$ (350°C for 3h) are less than that of $LaPO_4$ both in the dark and under UV light. So the higher photocatalytic activity of v-$LaPO_4$ was due to the improvement of electron-hole separation efficiency.

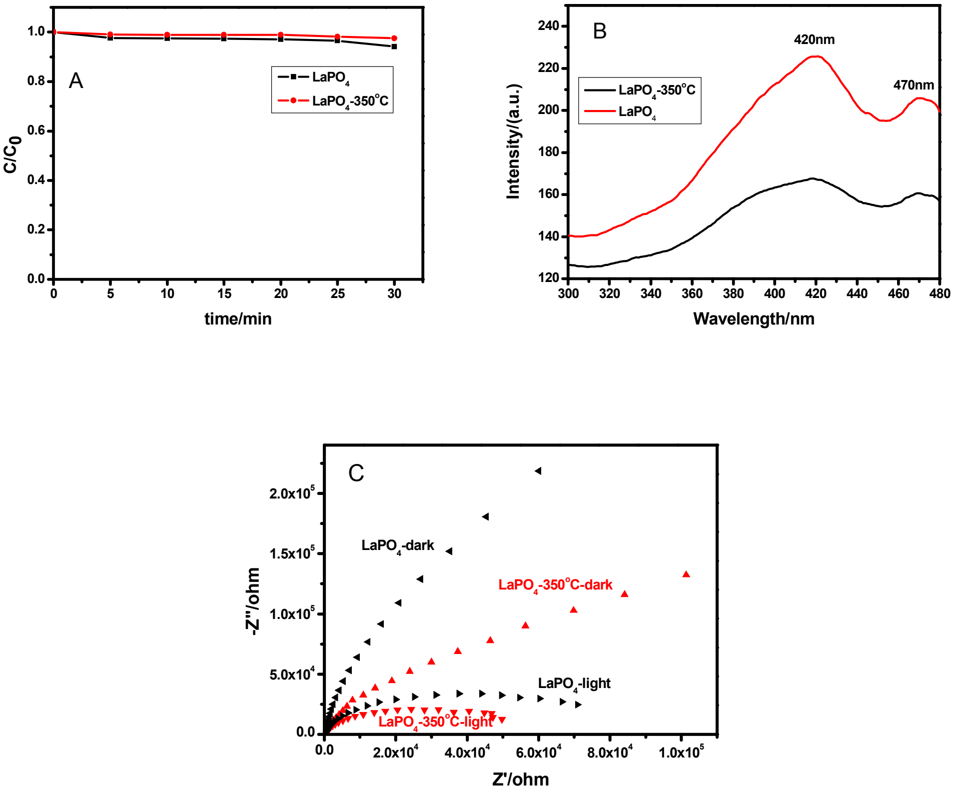


Figure 6. (A) adsorption capacity of MB under dark condition of $LaPO_4$ and v-$LaPO_4$

(350^{o}C for 3h); (B) PL spectra of $LaPO_4$ and v-$LaPO_4$ (350^{o}C for 3h) and (C) electrochemical impedance spectroscopy of $LaPO_4$ and v-$LaPO_4$ (350^{o}C for 3h) in the dark and under UV light.

Finally, the stability of v-$LaPO_4$ for the degradation of MB was measured, and the result was shown in Figure 7. The photocatalytic activity of v-$LaPO_4$ for the degradation of MB does not decrease after four cycles, indicating that the v-$LaPO_4$ photocatalyst has good stability.

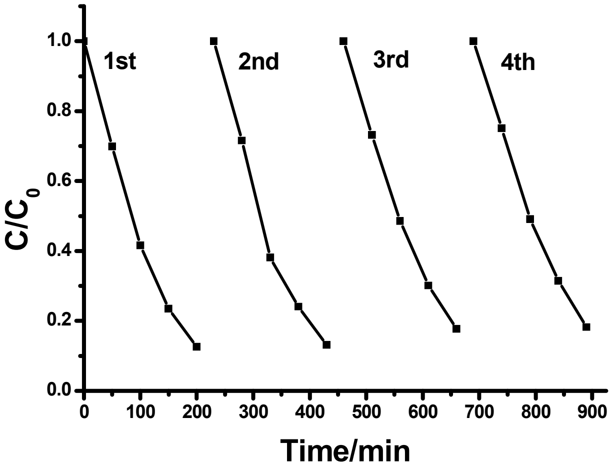


Figure 7. stability of v-$LaPO_4$ for the degradation of MB after four cycles

4. Conclusions

Monoclinic $LaPO_4$ photocatalysts with surface oxygen vacancies was prepared by hydrothermal and vacuum heat treatment method. The UV photocatalytic performance of $LaPO_4$ was greatly enhanced and the light absorption has improved after vacuum heat treatment. The main oxidative species are considered to be hydroxyl radicals. The decreased fluorescence intensity and improvement of electron-hole separation efficiency are considered to be the factors of enhanced photocatalytic activity. The v-$LaPO_4$ has good stability after four cycles for the degradation of MB. And this work extends the application of $LaPO_4$ which might provide a theoretical guidance.

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