

PREPARATION OF POROUS AND RECYCLABLE PVA-TiO₂HYBRID HYDROGEL

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ABSTRACT

Nano TiO₂, one of the most effective photocatalysts, has extensive use in fields such as air purification, sewage treatment, water spitting, reduction of CO₂, and solar cells. Nowadays, the most promising method to recycle nano TiO₂ during the photocatalysis is to immobilize TiO₂ onto matrix, such as polyvinyl alcohol (PVA). However, due to the slow water permeability of PVA after cross-linking, the pollutants could not contact with nano TiO₂ photocatalyst in time. To overcome this problem, we dispersed calcium carbonate particles into a PVA-TiO₂ mixture and then filmed the glass. PVA-TiO₂-CaCO₃ films were obtained by drying. Through thermal treatment, we obtained the cross-linked PVA-TiO₂-CaCO₃ films. Finally, the calcium carbonate in the film was dissolved by hydrochloric acid, and the porous PVA-TiO₂ composite photocatalyst was obtained. The results show the addition of CaCO₃ has no obvious effect on PVA cross-linking and that a large number of cavities have been generated on the surface and inside of porous PVA-TiO₂ hybrid hydrogel film. The size of the holes is about 5-15 μm, which is consistent with that of CaCO₃. The photocatalytic rate constant of porous PVA-TiO₂ hybrid hydrogel film is 2.49 times higher than that of nonporous PVA-TiO₂ hybrid hydrogel film.

KEYWORDS

Hybrid Hydrogel, Photocatalysis, TiO₂, PVA

1. INTRODUCTION

Titanium dioxide, TiO₂, one of the white pigments, is widely used in paints, plastics, and cosmetics. Different from silicon dioxide, calcium carbonate, clay, and other materials, TiO₂ has its unique photocatalytic function. The photocatalytic principle of TiO₂ is shown in Fig.1 [1]. When TiO₂ is exposed to sunlight, especially ultraviolet rays, its valence electrons moved to the conduction band, resulting in free electron-hole pair. The free electron-hole pair has strong oxidation-reduction capability and can react with oxygen and water in the air to produce reactive oxygen and hydroxyl radicals. When benzene, toluene, formaldehyde, bacteria, viruses and other pollutants adsorb on the surface of TiO₂, they are going to combine with free electrons or holes, have an oxidation reduction reaction, and be decomposed into carbon dioxide, water, etc. Therefore, TiO₂ is one of the photocatalysts with huge potentials and has been widely applied to air purification, sewage treatment, water spitting, reduction of CO₂ and solar cells [2-5]

With the continuous decrease of TiO₂ particle size, the specific surface area of TiO₂ increases continuously, and its photocatalytic activity also increases accordingly [6]. Therefore, all TiO₂ used for photocatalysis is nano TiO₂. However, it is difficult to separate and recycle nanometer TiO₂ in the process of application. If not recycled, the loss of nano TiO₂ particles to the environment will be threatening to the ecosystem and human health. To separate P25 from the water, researchers usually have to use centrifuge (10000r/min, 5min) or filter (0.22 μm ultrafiltration membrane, 3MPa). The

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process is complicated and expensive. In order to overcome this application bottleneck of nano TiO_2 , the most effective method is to load nano TiO_2 particles in large-size solid carriers to prepare nano TiO_2 photocatalyst. The carriers can be categorised into inorganic carriers and organic carriers. The former mainly includes glass beads, ceramics, clay and aluminium foil [7], while the latter mainly includes polyethylene terephthalate, polypropylene, cellulose and activated carbon [8]. Shang et al. [9] coated the TiO_2 sol on the surface of stainless steel wire mesh and obtained the high specific surface area and high catalytic activity loaded TiO_2 by calcining. The results showed that the loaded TiO_2 had good photocatalytic effect on formaldehyde. Shiva et al. [10] used alkali and surfactant to treat polyester fabrics to make the polyester fiber surface have some holes and hydrophilic groups, then immersed the fabric into the dispersion liquid of nanometer TiO_2 , took it out after ultrasonic treatment, and carried out high temperature treatment. The results demonstrated that the fabric has good catalytic effect on methylene blue.

Polyvinyl alcohol (PVA) is a kind of water-soluble polymer material that contains a lots of hydroxyl groups. Due to its excellent film-forming, water-soluble, mechanical properties and biodegradability, it has been widely applied in the fiber, film, emulsifying agent, binder, and other fields. Pure PVA film has no obvious absorption of UV and visible light and is very suitable for support nanometer TiO_2 photocatalyst [11]. However, due to the slow water permeability of PVA after cross-linking, the pollutants could not contact with nano TiO_2 photocatalyst in time. Therefore, the rate of photocatalysis of nanometer TiO_2 photocatalyst will decrease when loaded into the PVA film. To solve this problem, Song et al. [12] coated the PVA/ TiO_2 composite photocatalyst on the glass plate and tried to prepare thinner composite film. Zhang et al. [13]

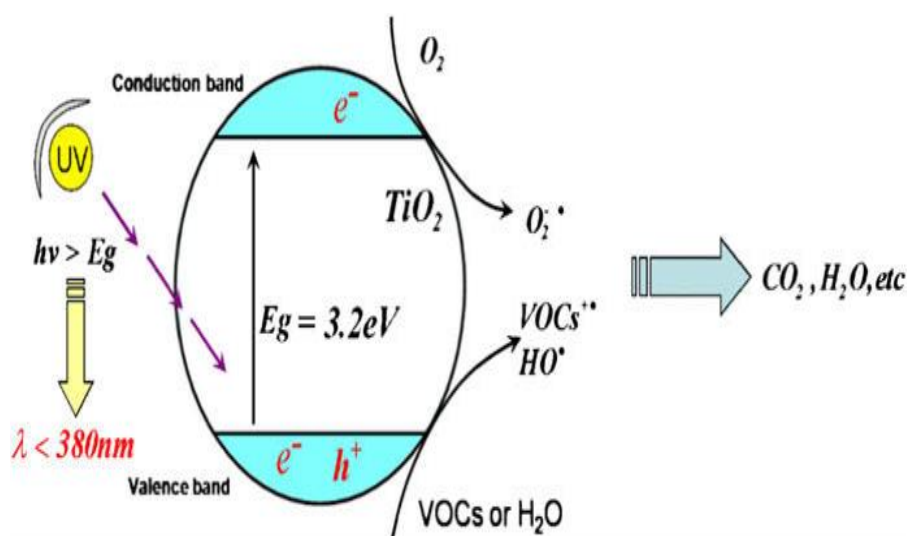


Fig. 1. A schematic diagram of the catalytic degradation of pollutants by TiO_2 under UV radiation

coated the PVA/ TiO_2 composite photocatalyst on the honeycomb ceramics in an attempt to prepare a more active photocatalyst. Nguyen et al. [14] prepared a porous PVA/ TiO_2 composite photocatalyst by freeze-drying and improved the photocatalytic activity of the catalyst. Lee et al. [15] prepared nano PVA/ TiO_2 composite fiber membranes by electrostatic spinning, and found that the photocatalytic activity of the composite catalyst was inversely proportional to the diameter of the fiber. However, there are still many challenges in developing a cheap and environmentally friendly method for the preparation of efficient and recyclable TiO_2 composite photocatalyst.

As far as we know, no one has prepared a porous PVA- TiO_2 composite photocatalyst by etching calcium carbonate from hydrochloric acid. Here, we dispersed calcium carbonate particles into a PVA- TiO_2 mixture and then filmed the glass. PVA- TiO_2 - CaCO_3 films were obtained by drying.

Through thermal treatment, we obtained the cross-linked PVA-TiO₂-CaCO₃ films. Finally, the calcium carbonate in the film was dissolved by hydrochloric acid, and the porous PVA-TiO₂ composite photocatalyst was obtained. The morphology, structure, and photocatalytic performance of the composite catalyst were also characterised.

2. EXPERIMENT

2.1 MATERIALS

PVA (average degree of polymerisation 1750±50): Beijing Yili chemical co. LTD. Calcium carbonate (AR): Sinopharm chemical reagent co. LTD. Hydrochloric acid (AR): Beijing Chemical Plant. P25 (about 20% rutile and 80% anatase with an average particle size of 21nm): Germany Evonik Company. Methyl Orange (model pollutant): Zhejiang Yongjia Chemical co.

2.2 PROCEDURE

Preparation of PVA Solution: add 15g PVA to a 250ml beaker, and then add 185ml of deionised water. Agitate mechanically (300r/min). After swelling up for an hour, raise the temperature to 95°C. Dissolve for three hours and get a transparent and homogeneous PVA solution with a solubility of 7.5%.

Add 300mg TiO₂ to a 150ml beaker, add 15ml deionised water, disperse by ultrasonic for 2min, then add 40g PVA solution (7.5% solubility), and stir for 15 min to get PVA-TiO₂ solution. Add 1.5g CaCO₃ and 5ml deionised water to a 10ml centrifuge tube. After ultrasonic dispersion for 2min, the solution was added to PVA-TiO₂ solution, and the PVA-TiO₂-CaCO₃ solution was obtained after keeping stirring for half an hour. Pour the dispersing liquid onto the glass plate and use the film laying machine to lay a 1mm thick film. The thickness of the film after natural drying was about 45µm. Cover the dried film with two pieces of A4 paper to prevent curling and place inside a 140°C oven. Take it out after cross linking for 2 hours in the vacuum state, and get the cross linked PVA-TiO₂-CaCO₃ film. Cut a certain amount of cross linked film and put in 300ml 1% HCl solution. Lots of bubbles were produced on the surface. After soaking for half an hour, clean the film with deionised water for 6 times and get a porous PVA-TiO₂ hydrogel film.

2.3 EXPERIMENTAL INSTRUMENTS

Scanning Electron Microscope (SEM, SU8020) was used to observe the morphology of the sample, and the acceleration voltage was 15KV.

The sample's Fourier Transform Infrared Spectroscopy (FTIR) analysis used Thermal Fisher company's Nicolet Avatar 6700 reflection accessory of FTIR Nicolet Smart Orbit Accessory (Thermo Fisher Scientific). The wave number range was 4000-650cm⁻¹. The resolution was 4cm⁻¹ and scanned 32 times.

UV-Vis Diffuse reflection spectrum (UV-Vis DRS) was measured by Shimadzu Company's UV-2600 ultraviolet spectrophotometer, equipped with integral ball attachments. The test resolution was set to 1nm, using Barium Sulfate for baseline correction, and the scanning range was 200-800nm.

The Thermo-gravimetric analysis under air(TGA-air) used Perkin-Elmer TGA-7 series thermal analysis system. The temperature range was 100°C to 700°C. The heating rate was 20°C/min, and the air velocity was 20ml/min.

2.4 PHOTOCATALYTIC DEGRADATION

Methyl Orange (MO) was selected as the target pollutant to evaluate the photocatalytic performance of the new UV light catalyst. The initial concentration of methyl orange was 15mg/L. The UV light catalytic experiment was carried out in the photochemical reactor produced by Beijing Zhongjiao Jinyuan Company. The light source was a 500W xenon lamp, and the ultraviolet light of $365\pm 15\text{nm}$ was obtained by the addition of the filter. Before illumination, measured a sample containing 20mg TiO_2 nanoparticles and put into a beaker containing 40ml methyl orange solution. Avoid light and absorb for 2 hours to achieve the adsorption-desorption equilibrium. After illumination, the absorbance of 5ml filtrate was measured at regular intervals of every half an hour. The photocatalytic mechanism of Methyl Orange by TiO_2 is shown in the figure below[16]. The absorbance of MO solution at the maximum absorption wavelength of 465 nm was measured by the ultraviolet visible absorption spectrometer (Lovibond, ET99731). Measurement was repeated three times. The mean value was calculated. C_t/C_0 ($=A_t/A_0$) was used to describe the degradation degree of MO, and the C_t/C_0 -t curve was drawn.

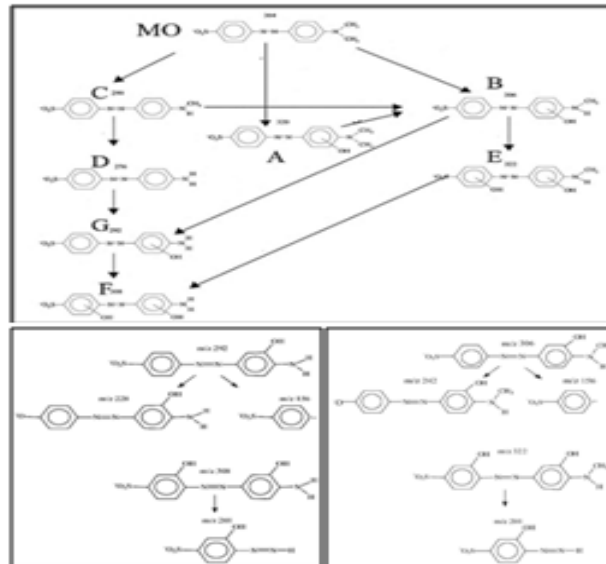


Fig.2. Possible degradation pathway for MO during photocatalysis

3. RESULTS AND DISCUSSIONS

3.1 PICTURES

Fig.3. is the pictures of pure PVA, PVA- TiO_2 , and PVA- TiO_2 - CaCO_3 films. Picture A shows that the pure PVA film is transparent, so it is very suitable for TiO_2 loading. After adding TiO_2 , the film turns out to be white with a slightly reflective surface. PVA- TiO_2 - CaCO_3 film is also white, but the surface reflect light significantly diminishes, showing that its diffuse reflection is serious, and its surface is rough comparing to that of PVA- TiO_2 .

3.2 FTIR GRAPH ANALYSIS OF CaCO_3 , PVA, PVA- TiO_2 , AND PVA- TiO_2 - CaCO_3 FILMS

Fig. 4. is the FTIR curves of CaCO_3 , PVA, PVA- TiO_2 , and PVA- TiO_2 - CaCO_3 thin films. In Fig.4., the infrared spectrum of CaCO_3 mainly has two absorption peaks, 1377cm^{-1} and 864cm^{-1} ,

respectively, corresponding to the symmetric stretching vibration of C-O and the deformation vibration peak of external CO surface. Pure PVA in 3276cm^{-1} , 2920cm^{-1} , 1655cm^{-1} , 1427cm^{-1} , and 1080cm^{-1} has obvious absorption peaks. Those absorption peaks correspond to the OH stretching vibration, CH_2 stretching vibration, OH bending vibration, CH_2 bending vibration and C-O stretching vibration, respectively. The infrared absorption peak of PVA- TiO_2 after cross-linking is consistent with that of pure PVA, indicating that the addition of TiO_2 has no obvious effect on the cross linking of PVA. It is worth noting that PVA- TiO_2 - CaCO_3 film has a wide absorption peak in the 1400cm^{-1} , and the absorption peak becomes sharp in 874cm^{-1} , which is mainly caused by the addition of CaCO_3 . After comparing the infrared spectroscopy of PVA- TiO_2 - CaCO_3 and PVA, it can be shown that the addition of CaCO_3 has no effect on PVA cross-linking. This report does not include the analysis on the intensity change of different data because under FTIR's reflection mode, the intensity of peaks is related to the sample pressure. Additionally, combining the result of TGA curves, the initial degradation temperature of PVA is higher than 250°C , indicating that the thermal treatment at 140°C by P25 and CaCO_3 has no effect on PVA.



Fig. 3. Pictures of pure PVA, PVA- TiO_2 , and PVA- TiO_2 - CaCO_3 films

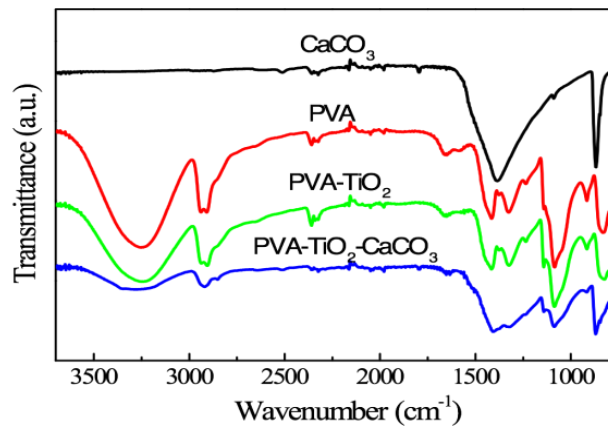


Fig. 4. FTIR graph of CaCO_3 , PVA, PVA- TiO_2 , and PVA- TiO_2 - CaCO_3 films

3.3 TGACURVE ANALYSIS OF PURE PVA, PVA- TiO_2 , AND PVA- TiO_2 - CaCO_3 FILMS

Fig. 5. is the TGA curves of pure PVA, PVA- TiO_2 , and PVA- TiO_2 - CaCO_3 films. The figure shows that the pure PVA film has good heat resistance, with only about 0.7% of weight loss before 250°C , which is due to PVA intermolecular cross linking dehydration. PVA thermal degradation is mainly consisted of three stages. The first phase is between 250 - 350°C . The process is mainly the hydroxyl removal and the chain break of part of the PVA molecular chain. The second phase is 350 - 450°C .

The process is mainly the oxidation degradation of PVA molecular chain and carbide of the molecular chain. The third phase is 450-570°C. The process is the oxidation and degradation of PVA carbide products. After adding TiO₂, the initial pyrolysis temperature of PVA was slightly advanced, which may be caused by the thermal catalysis of TiO₂. PVA-TiO₂-CaCO₃ film's initial thermal decomposition temperature also moves in advance compared to that of pure PVA, but based on the curve of the process of degradation, TiO₂ and CaCO₃ only slightly reduced the heat resistance of PVA, but have not effect on the degradation of PVA. In addition, pure PVA's thermal weight loss above 600°C is 100%, proving that it can decompose completely, so the residual weights of PVA-TiO₂ and PVA-TiO₂-CaCO₃ films under 600°C are the contents of inorganic matters, about 10% and 40% respectively, demonstrating that PVA-TiO₂ film contains 10% of TiO₂ and PVA-TiO₂-CaCO₃ film contains 10% TiO₂ and 30% CaCO₃.

3.4 SEM ANALYSIS OF PURE TiO₂

Fig. 6. is the SEM photos of pure TiO₂. The figure shows that the pure TiO₂ has some agglomerates, with size of around 5-15µm. Based on the high power photos, the aggregates are composed of nano TiO₂ particles with even smaller size. The primary size of TiO₂ particles is less than 50nm and is uniform, proving that nanoscale TiO₂ is used.

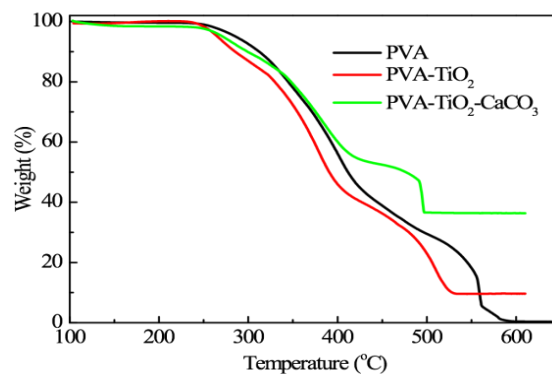


Fig. 5. TGA curves of pure PVA, PVA-TiO₂, and PVA-TiO₂-CaCO₃ films (air, 20°C/min)

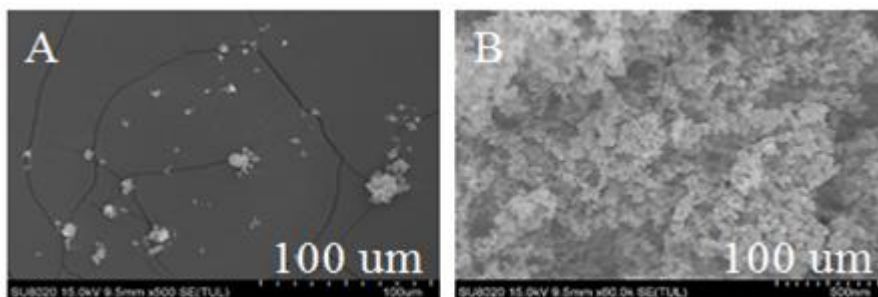


Fig. 6. SEM photos of pure TiO₂

3.5 SEM ANALYSIS OF CaCO₃, PVA-TiO₂, AND PVA-TiO₂-CaCO₃ FILMS

Fig. 7. shows the SEM photos of CaCO₃, PVA-TiO₂, and PVA-TiO₂-CaCO₃ films. As can be seen from Picture A, CaCO₃ particles are mainly micron particles with uneven size. Most of them are 5-15µm irregular particles, and a large number of CaCO₃ particles with a size of 1-5µm also exist in the system. Based on Picture B, the surface of PVA-TiO₂ film surface is smooth without holes,

which is not conducive to the entry and exit of pollutant solution. In addition, a large number of white areas can be seen on the surface of PVA-TiO₂ film, which may be the aggregates of TiO₂. The size of these white areas is about 10µm, indicating that TiO₂ has agglomeration in PVA. As shown in Picture C, after etching, PVA-TiO₂-CaCO₃ film surface appears to have a large number of cavity. The size of the holes is about 5-20µm, which is consistent with that of CaCO₃, showing that CaCO₃ in the film is dissolved and a porous PVA film is successfully obtained. Moreover, it can be seen from Picture D that the thickness of PVA-TiO₂-CaCO₃ film is about 45µm. There are also a large number of holes in in the inner part of PVA-TiO₂-CaCO₃ film, proving that the method of etching CaCO₃ can successfully prepare porous PVA hydrogels. Till this point, the SEM pictures prove that there are large number of cavities, which sizes are the same as those of CaCO₃, as shown in Picture A and C. We plan to carry out AFM test and water permeability test in the next step.

3.6 ANALYSIS OF THE CHANGE OF METHYL ORANGE CONCENTRATION

Methyl Orange is used as model pollutant to characterise the catalytic activity of nonporous and porous PVA-TiO₂ hybrid hydrogels under UV lights. Prior to the experiment, pure methyl orange solution was placed under UV light for two hours, and its concentration remains unchanged. As shown in Fig. 7, the concentration of methyl orange continues to decrease under the light, indicating that both nonporous and porous PVA-TiO₂ hybrid hydrogels can catalyse the degradation of methyl orange. Nonporous PVA-TiO₂ hybrid film degrades about 54% of methyl orange under UV light for 2 hours, while porous PVA-TiO₂-CaCO₃ film degrades about 86% of methyl orange, showing that the porosity of the film allows pollutants to contact with the film at a faster rate and increases the contact of TiO₂ and pollutants, and then improves the photocatalytic performance of the film.

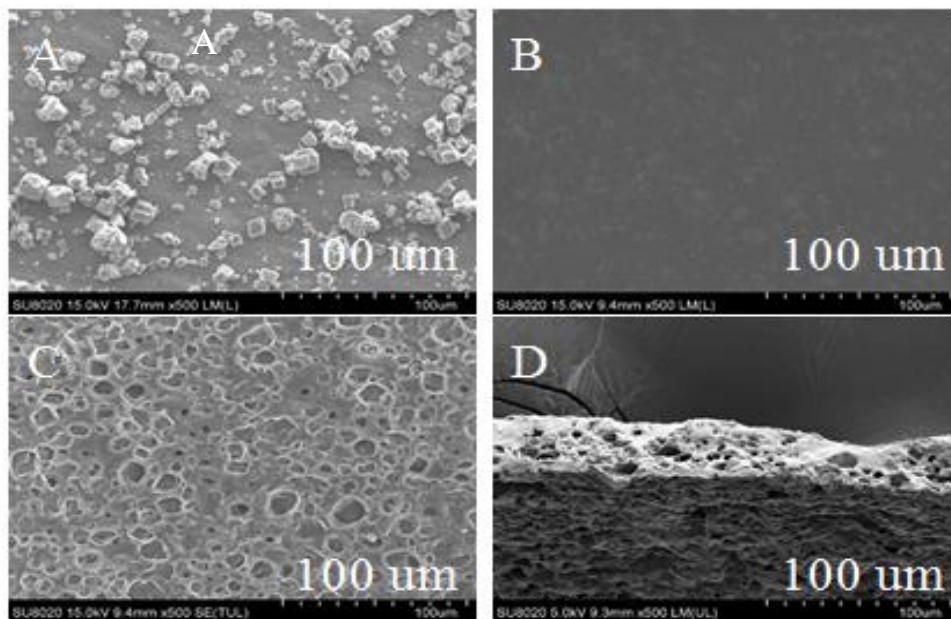


Fig. 7. SEM photos of CaCO₃, PVA-TiO₂, and PVA-TiO₂-CaCO₃ films

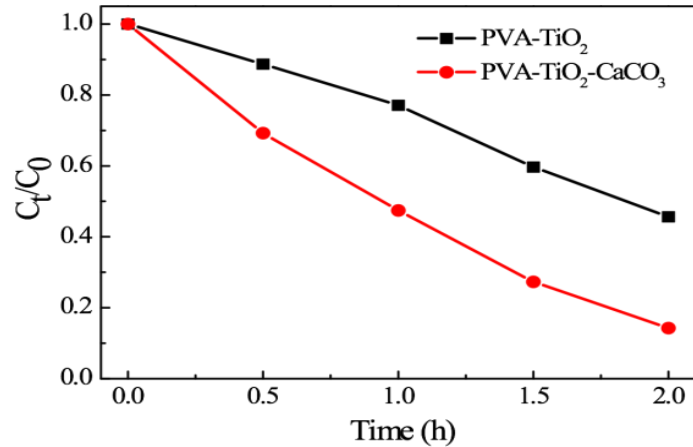


Fig. 8. The change curves of Methyl orange concentration catalysed by UV light

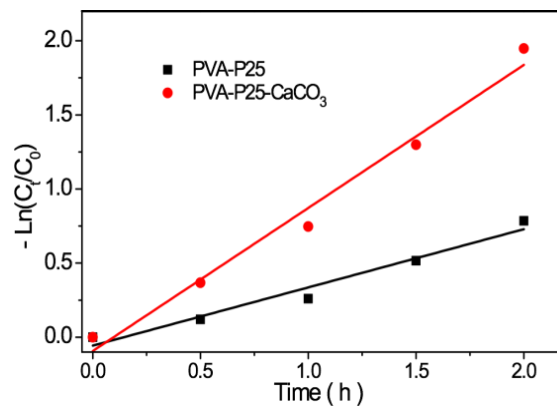


Fig. 9. Photocatalytic degradation of methyl orange reaction rate fitting curve

The rate of degradation process of methyl orange catalysed by PVA-TiO₂-CaCO₃ film decreases slightly as the the concentration of methyl orange decreases, indicating that the photocatalytic reaction accords with first-order reaction. In Fig. 8, to draw ultraviolet illumination time t based on $\ln(C_t/C_0)$ and perform linear fitting, the slope of the linear fitting is the photocatalytic reaction rate constant. PVA-TiO₂ and PVA-TiO₂-CaCO₃ film photocatalytic rate constants are 0.39h^{-1} and 0.97h^{-1} , respectively. The higher the rate constant, the higher the photocatalytic efficiency, indicating that the photocatalytic rate of porous PVA-TiO₂-CaCO₃ film is 2.49 times than that of nonporous PVA-TiO₂ film.

3.7 ANALYSIS OF THE RECYCLABILITY OF POROUS PVA-TiO₂-CaCO₃ FILM

In Fig. 10, it shows that the degradation curve of methyl orange photo-catalysed by porous PVA-TiO₂-CaCO₃ film fits the first-order kinetics, so the photocatalytic effect of PVA-TiO₂-CaCO₃ film is pretty stable. However, figure 10 also demonstrates that the hybrid film's photocatalytic activity slightly decreases after testing for five times. It was probably because the degradation products of methyl orange stay in the hybrid film or get absorbed on the surface of TiO₂. Moreover, under UV light irradiation, TiO₂ could probably catalyse the matrix of PVA, leading to the slight decrease of TiO₂'s photocatalytic activity. In conclusion, after repeating the cycle of photocatalysis for 5 times, the hybrid film still has photocatalytic activity, with only slight decrease. In later experiment, we will try to prepare more stable film.

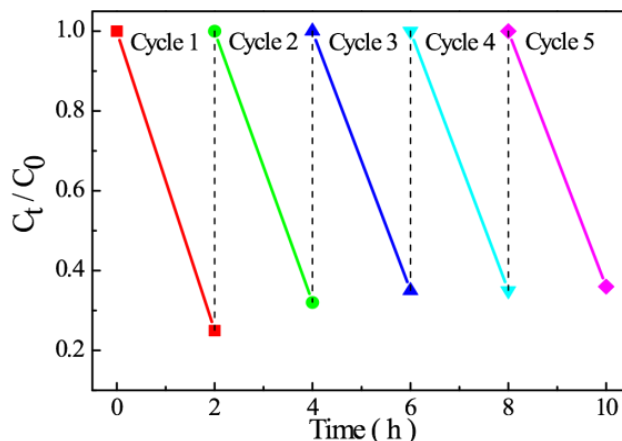


Fig. 10. Cycle photocatalytic performance test of PVA-TiO₂-CaCO₃ under UV light irradiation

4. CONCLUSION

Porous PVA-TiO₂ hybrid hydrogel film was successfully prepared by etching CaCO₃ with hydrochloric acid. This method is safe, green, simple, and easy to be prepared in large quantities.

TGA shows that the addition of CaCO₃ volume is about 30%. FTIR shows the addition of CaCO₃ has no obvious effect on PVA cross-linking. SEM shows that a large number of holes has been generated on the surface and inside of porous PVA-TiO₂ hybrid hydrogel film. The size of the holes is about 5-15 μ m, which is consistent with that of CaCO₃.

Porous PVA-TiO₂ hybrid hydrogel film has significantly high photocatalytic efficiency than that of nonporous hybrid hydrogel film. The photocatalytic rate constant of porous PVA-TiO₂ hybrid hydrogel film is 2.49 times higher than that of nonporous PVA-TiO₂ hybrid hydrogel film since the porosity increases the contact area and rate of TiO₂ and pollutants. The film is recyclable and its photocatalytic rate does not decrease when repeating the experiment.

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