Photocatalytic Activity Investigation of $\alpha$-Zirconium Phosphate Nanoparticles Compositing with C$_3$N$_4$ under Ultraviolet Light

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ABSTRACT: In order to further develop efficient ultraviolet light-driven photocatalysts for environmental application, $\alpha$-zirconium phosphate ($\alpha$-ZrP) and carbon nitride (C$_3$N$_4$) were synthesized, respectively. Then, C$_3$N$_4$−ZrP compositing nanomaterials were prepared by compositing $\alpha$-ZrP nanocrystals and C$_3$N$_4$ with different mass ratios. C$_3$N$_4$−ZrP compositing nanomaterials were characterized by X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The results illustrated that $\alpha$-ZrP and C$_3$N$_4$ were successfully composited, and the polarization of the compositing nanomaterials was reduced compared with raw materials. The photocatalytic performances of C$_3$N$_4$−ZrP compositing nanomaterials with different mass ratios were studied by photodegradation of RhB under ultraviolet irradiation. All of the degradation rates of the C$_3$N$_4$−ZrP compositing nanomaterials system were achieved more than 90% after 18 min. When the mass ratio of C$_3$N$_4$−ZrP compositing nanomaterials is 2:1, the degradation efficiency achieved 99.95%, which is more efficient than other tested mass ratios. The result indicated the possibility of utilizing C$_3$N$_4$−ZrP compositing nanomaterials for environmental pollutants degradation.

1. INTRODUCTION

Graphitic carbon nitride (g-C$_3$N$_4$) is a new nonmetal organic semiconductor.$^{1-4}$ In 2009, Wang et al.$^3$ found that by using g-C$_3$N$_4$ as a catalyst under visible light, hydrogen can be produced from water. g-C$_3$N$_4$, with table physical properties and a narrow band gap, can absorb the blue-violet light, with a wavelength less than 475 nm, from sunlight. It can more effectively absorb the visible light from sunlight and enhance the utilization of sunlight. Graphitic carbon nitride has two basic structure units, triazine ring (C$_3$N$_3$) and heptazine ring (C$_6$N$_7$), and among the two, g-C$_3$N$_4$ with a basic structure of a heptazine ring has a more stable structure. The infinite extension of the basic structure unit forms g-C$_3$N$_4$ with a reticular structure. The adjacent layers are combined by van der Waals forces, and the interlayer distance is 0.325 nm.$^4$

The band gap of g-C$_3$N$_4$ is 2.7 eV, which has good visible light response. Thus, the photocatalytic performance of graphitic carbon nitride has attracted a lot of researcher’s attentions.$^{1,5,6}$ Some researchers composited g-C$_3$N$_4$ with broad band gap semiconductors, hoping to get catalysts with better photocatalytic performance than pure semiconductors. Yu et al.$^7$ synthesized g-C$_3$N$_4$−TiO$_2$ photocatalysis by simple calcination methods and applied it for the degradation of formaldehyde in the air. They found that the performance of this synthesized Z system catalyst largely depends on the amount of g-C$_3$N$_4$, and the reaction apparent rate constant of the g-C$_3$N$_4$−TiO$_2$ with an optimum mass ratio is 2.1 times that of the pristine P25 TiO$_2$'s. Wang research group$^8$ utilized a simple soft chemical method and achieved direct interfacial assembly of g-C$_3$N$_4$ nanosheets with TiO$_2$ nanoparticles. Compared with other metal compounds/carbon nitride nanocomposites, their synthesized TiO$_2$/CN nanocomposites can more quickly photocatalytically degrade rhodamine B (RdB) dye and has good performance of photocatalytically generating hydrogen. They proposed that after the compositing of TiO$_2$ with g-C$_3$N$_4$, synergistic effects were generated, and the effects can more effectively separate the photo-generated electrons−holes, subsequently enhancing the photocatalytic activity of nanocomposites.$^9$

In our previous work,$^{10}$ we have analyzed the photocatalytic performance of $\alpha$-ZrP with different morphologies and selected $\alpha$-ZrP nanoparticles with optimum photocatalytic performance. However, due to a broad band gap, $\alpha$-ZrP did not
demonstrate satisfactory photocatalytic performance. In this paper, to further enhance the photocatalytic performance of the α-ZrP nanocrystal and achieve better photodegradation effects than a pure α-ZrP nanocrystal, we employed the selected α-ZrP nanocrystal and composited it with g-C3N4 nanosheets. We also discussed the photocatalytic performance of C3N4−ZrP compositing nanomaterials with different mass ratios and selected out the optimum mass ratio.

2. EXPERIMENTAL SECTION

2.1. Materials. Zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) and phosphoric acid (H₃PO₄, 85 wt %) were supplied by Kelong Ltd., Chengdu, China. g-C3N₄ was synthesized in the laboratory. All reagents were used as received.

2.2. Preparation of α-Zirconium Phosphate Catalysts. ZrOCl₂·8H₂O powder (4.83 g) was placed in a polypropylene container, and then a certain amount of 85 wt % H₃PO₄ was added (the H₃PO₄/Zr molar ratio is 3). After stirring with a glass rod, the container was capped and placed in an oven at 80 °C for 12 h. The product was washed with deionized water three times to remove the excess acid and was collected by centrifugation. The final products were dried overnight and then ground into powders with a mortar and pestle.¹¹

2.3. Preparation of C3N4−ZrP Compositing Nanomaterials. g-C3N₄ was prepared by a typical method.¹² Urea powder (10 g) was prepared as a precursor and then heated to a temperature of 575 °C in a muffle furnace. The resultant yellow powder was collected for use without further treatment. Then, 300 mg of g-C3N₄ powder was dispersed in 30 mL of concentrated phosphoric acid under stirring for 12 h at ambient temperature. The product was diluted with 100 mL of deionized water and treated by ultrasonication for 2 h. Then, the mixture was centrifuged and washed with deionized water to get rid of the excess acid. Thereafter, the precipitate was diluted with 30 mL of deionized water and processed with ultrasonication for 2 h. Then, the C3N₄ colloids were obtained by centrifugation, and the mass concentration of the obtained C3N₄ colloids is approximately 18–20 mg/L.

A certain mass ratio of α-ZrP nanoparticles and C3N₄ colloid was dispersed in deionized water and ultrasonicated for 3 h. Thereafter, the mixture was stirred at 80 °C for 3 h, and then the product was dried in a vacuum oven at 65 °C for 12 h. The C3N₄−ZrP compositing nanomaterials were collected by grinding. Various mass ratios were applied, and the compositing nanomaterials were named after the mass ratio.⁶

2.4. Characterization. X-ray powder diffraction (XRD) patterns were collected by a PANalytical X’pert PRO MPD diffractometer that uses a Cu Kα radiation source. The tube pressure and current operated at 40 kV and 40 mA, respectively. The diffraction angle 2θ ranges from 5 to 40°.

Scanning electron microscopy (SEM) images were obtained with an FEI Quanta 450 instrument and ZEISS EVO MA15 at 20 kV. The samples were coated with a thin layer of Au prior to the measurement.

X-ray photoelectron spectra (XPS) were obtained on a KRATOS XSAM800 ESCA (electron spectrometer for chemical analysis), using MgKa X-ray (hv = 1486.6 eV) as the excitation source.

The photoluminescence (PL) spectra of the samples were provided using a PerkinElmer (LS 55) fluorescence spectrophotometer with an excitation wavelength of 360 nm.

2.5. Photocatalytic Activity. The photocatalytic experiments were carried out by dispersing 0.1 g of C3N₄−ZrP compositing nanomaterials in 100 mL of RhB solution (5 × 10⁻⁵ mol/L). The suspensions were stirred by magnetic stirring in a dark environment for 30 min prior to irradiation to achieve adsorption–desorption equilibrium. Thereafter, the system was irradiated by a mercury lamp (300 W, BL-GHX-V, Shanghai Bilon Instrument Manufacturing Co., Ltd., Shanghai, China, at room temperature). The emission spectra were recorded from 200 to 800 nm, and the light density of the sample position was 14.5 mW cm⁻². The lamp kept the temperature constant by circulating cooling water. For every 5 min interval during the irradiating time, 5 mL of the sample solution was taken and centrifuged to get rid of the catalyst. The photocatalytic efficiency of catalysts can be calculated by the following equation:

\[ D = \left( c_0 - c_t \right) / c_0 \times 100\% \]

where D is the photodegradation ratio of RhB, c₀ (mol/L) is the initial concentration of RhB solution, and cₜ (mol/L) is the concentration of RhB solution at t time.

3. RESULTS AND DISCUSSION

3.1. Characterization of C3N₄−ZrP Compositing Nanomaterials. Figure 1 presents the XRD patterns of pristine α-ZrP and C3N₄ and C3N₄−ZrP compositing nanomaterials with different mass ratios.

![XRD pattern of pristine α-ZrP and C3N₄ and C3N₄−ZrP compositing nanomaterials with different mass ratios.](image)

pristine α-ZrP (JCPDS:33−1482), C3N₄ (JCPDS: 87−1526) and C3N₄−ZrP compositing nanomaterials with different mass ratios. The interlayer distance of α-ZrP nanoparticles can be calculated by the Bragg equation

\[ 2d\sin \theta = n\lambda \]

where d is the interlayer distance, θ is the incident angle, n is the order of diffraction, and λ is the X-ray wavelength of irradiation. It can be seen from Figure 1 that the C3N₄−ZrP compositing nanomaterials still remain the characteristic peak. The strong peak and peak position had hardly changed. The results indicate that the compositing process exert no influence for the crystallinity and interlayer structure of the α-ZrP crystal. They show that the compositing of the α-ZrP crystal with g-C3N₄ nanosheets mostly happened on the surface, and the g-C3N₄ nanosheets did not get into the interlayers of α-ZrP, which also means the crystal structure of α-ZrP nanoparticles is very stable, which were synthesized by a minimal solvent method. It can be clearly seen that with the increase in g-C3N₄ colloid, the characteristic peak of g-C3N₄...
When the mass ratio of g-C3N4 and α-ZrP reached 1:3, there is a weak peak that appeared on 2θ = 27.4°, and this is the characteristic peak of the (002) crystal face of g-C3N4, which represents the stacking of the crystal layer with a π-conjugated aromatic system.13 When g-C3N4 nanosheets were treated with exfoliation, the peak of C3N4−ZrP compositing nanomaterials at 27.4° should disappear or get flat. However, with the increase in g-C3N4 colloids, some exfoliated g-C3N4 layers inclined to re-stack into the bulk structure. Hence, the intensity of the peak becomes stronger while the width becomes narrower, and the shape of the peak becomes sharper. When 2θ is 13.0°, it is the characteristic peak of the (001) crystal face of g-C3N4, which represents the order of the crystal face. It can be seen from the figure that this characteristic peak is not obvious, which indicates that the plane size of g-C3N4 is relatively small.3,14,15

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied to observe the microstructure of C3N4−ZrP compositing nanomaterials. The surface morphology of various mass ratios of C3N4−ZrP compositing nanomaterials is shown in Figure 2.

It can be seen from Figure 2a–f that the Tremella-like g-C3N4 has irregular agaric-like layers with nonuniform size distribution. The size of g-C3N4 varies from 200 nm to a few micrometers, and the layers are buckled and back folded at the edges.11 When the mass ratio is 1:5 (Figure 2b), the materials are mainly aggregated granular substances, which can be attributed to that the adding g-C3N4 is few, so most of the compositing materials are still α-ZrP nanoparticles, and the aggregation would be more serious after compositing. With the increasing of the g-C3N4 proportion, it can be seen from Figure 2b–e that the dispersion of C3N4−ZrP compositing nanoparticles is getting better than the former, also small buckled g-C3N4 nanosheets can be seen in the α-ZrP nanoparticles, which indicates the compositing of g-C3N4 nanosheets and α-ZrP nanoparticles succeeded, and the adding of g-C3N4 nanosheets restricted the re-stacking process of α-ZrP nanoparticles. In the TEM image (Figure 2g) of C3N4-ZrP, the thickness of the outermost part is estimated to be about 0.34 nm, which is close to the thickness of the monolayer of g-C3N4 (ca. 0.325 nm).16 During compositing, the layered g-C3N4 assembled on the surface of α-ZrP to achieve a minimum surface energy, which would facilitate the transfer of photogenerated charge carriers between g-C3N4 and α-ZrP in the photocatalyst performance.

Figure 3 presents the FTIR spectra of α-ZrP, C3N4−ZrP (mass ratio: 4:1), and g-C3N4. For the pure C3N4, several bands in the range of 1100–1700 cm⁻¹ correspond to the typical stretching modes of the CN heterocycles.17 Additionally, other two characteristic peaks appeared at 810 and 889 cm⁻¹, which can be attributed to out-of-plane bending modes of CN heterocycles.18 For the pure α-ZrP nanoparticles, the characteristic peak at 1047 cm⁻¹ is the symmetrical stretching vibration peak of PO4³⁻ groups.19 The band located at 594 cm⁻¹ is assigned to Zr–O bonds.20 All of the characteristic
peaks of g-C$_3$N$_4$ and $\alpha$-ZrP were observed in the C$_3$N$_4$–ZrP compositing nanomaterials. The sharp bands located at 3510 and 3590 of cm$^{-1}$ of pure $\alpha$-ZrP can be ascribed to the asymmetric and symmetric stretching of the intercalated water.$^{21}$ The two bands disappeared in the spectra of C$_3$N$_4$–ZrP and that might be because some C$_3$N$_4$ entered the interlayers of $\alpha$-ZrP nanoparticles and displaced the crystal water during the compositing process.

X-ray photoelectron spectroscopy (XPS) was utilized to further analyze the surface of $\alpha$-ZrP and C$_3$N$_4$–ZrP (mass ratio: 4:1), and the result is shown in Figure 4.

The XPS spectra of g-C$_3$N$_4$ can be found in other literature.$^{22}$ It can be seen from the C 1s spectrum (Figure 4e) that the C$_3$N$_4$–ZrP compositing nanomaterials showed the two C 1s peaks located at 284.3 and 287.8 eV. The former can be assigned to the adventitious hydrocarbon from the XPS instrument and defect-containing sp$^2$-hybridized carbon atoms present in graphitic domains, and the latter one is assigned to C–N–C coordination.$^{12,23}$ In the N 1s spectrum (Figure 4f), the binding energy (BE) of N 1s is 398.3 eV, which represents triazine rings (C–N–C), indicating the successful compositing of C$_3$N$_4$ and ZrP. For O 1s spectra (Figure 4d), the BE of O 1s at 530.7 eV is associated with the oxygen that forms the (PO$_4$)$_3^-$ bonds, while the BE of 531.7 eV represents the –OH groups or the interlayer water molecule of ZrP.$^{24}$ A broad peak in the range of 131–135 eV of the P 2p spectra can be seen from both $\alpha$-ZrP and C$_3$N$_4$–ZrP, which corresponds to the phosphorus from PO$_4$$_3^-$ (Figure 4c).$^{25}$ In the Zr 3d spectrum of $\alpha$-ZrP (Figure 4b), two peaks are observed at 183.3 and 185.7 eV, which represent 3d$_{3/2}$ and 3d$_{5/2}$ energy states of tetravalent Zr(IV) species.$^{26}$ For the C$_3$N$_4$–ZrP 3d spectrum, both energy states are slightly reduced (183.0 and 185.4 eV). The reduced Zr 3d binding energies for the C$_3$N$_4$–ZrP indicate a reduced polarization of the Zr–O bonds in C$_3$N$_4$–ZrP.$^{27}$

Figure 4. XPS spectra of (a) $\alpha$-ZrP and C$_3$N$_4$–ZrP. Survey spectra of (b) Zr 3d, (c) P 2p, (d) O 1s, (e) C 1s, and (f) N 1s.
For the photocatalyst, when it was irradiated by incident light with a certain wavelength and then adsorbed light energy, the electron was promoted from the valence band to the conduction band and left a hole; thereafter, the fluorescence was produced by the combination of surface electrons and holes. The intensity of fluorescence is proportional to the combination rate of surface electrons and holes. Fluorescence spectrum analysis was applied to study the combination situation of the photogenerated electron−hole of the C3N4−ZrP compositing nanomaterials. α-ZrP, g-C3N4, and C3N4−ZrP compositing nanomaterials with different mass ratios were dispersed in pure water, and the fluorescence emission spectra were obtained with an excitation wavelength of 360 nm. The result is shown in Figure 5.

It can be seen from Figure 5 that with an excitation wavelength of 360 nm, C3N4−ZrP compositing nanomaterials with different mass ratios produce an emission peak at 435 nm, and g-C3N4 had the strongest peak, while α-ZrP barely produced an emission peak. With the decrease in the C3N4−ZrP mass ratio, emission peak intensity decreased, which indicates the decrease in the photogenerated electron−hole combination rate. This is because when α-ZrP nanoparticles were compositied with g-C3N4 nanosheets, a heterostructure was formed, and the high recombination rate of photogenerated carriers, which is the intrinsic property of g-C3N4, can be efficiently reduced. However, the recombination rate of photogenerated carriers is just one aspect that affects the ability of the photocatalyst. To further analyze the material, photocatalytic ability tests were conducted with the prepared C3N4−ZrP compositing materials of different mass ratios.

3.2. Photocatalytic Activity. Under the irradiation of ultraviolet light and visible light with RhB at a concentration of $5 \times 10^{-5}$ mol/L, the photocatalytic behavior of α-ZrP, g-C3N4, and the C3N4−ZrP compositing material was tested by procedures previously reported in the literature. The results are shown in Figures 6 and 7.

It can be seen from Figure 6a that α-ZrP demonstrated weak photodegradation efficiency of RhB since it could not be excited by visible light irradiation. After incorporation with g-C3N4, the efficiency was improved slightly. As pristine α-ZrP had poor response within visible light due to its wide band gap energy (3.94 eV), the improvement resulted from g-C3N4 hybridization. In the condition of ultraviolet light, the photodegradation efficiency of C3N4−ZrP compositing material (mass ratio: 1:1) was much higher than α-ZrP and g-C3N4. After irradiation of 10 min, the photodegradation efficiency of α-ZrP and g-C3N4 reached 63.6 and 66.6%, respectively, while the photodegradation efficiency of C3N4−ZrP compositing material (mass ratio: 1:1) reached 98.0%. Figure 7 shows the photocatalytic efficiency for RhB by C3N4−ZrP with different mass ratios. It can be seen from Figure 7 that when the mass ratio was 1:50, the photodegradation efficiency of C3N4−ZrP was the slowest, while the ratios of 1:1 and 2:1 both had higher efficiency. After irradiation for 9 min, the degradation efficiency of C3N4−ZrP with mass ratios 1:1 and 2:1 reached...
The photocatalytic performance of C3N4 was found to be significantly enhanced through the formation of heterostructures with other materials. The conduction band of g-C3N4 was transferred to the conduction band of the heterostructure. The photogenerated electrons from the conduction band of α-ZrP reduced the dissolved O2 into O2− radicals. Further, the O2− radicals can be transformed to reactive OH radicals at the CB of the composite, and more photogenerated holes from the valence band of g-C3N4 directly oxidatively degraded the RhB. However, for the potential of the valence band of g-C3N4 that is more negative than that of OH/OH−, it has a lower oxidative capacity, which means in the process of photodegrading RhB, g-C3N4 played the main role. Appropriate g-C3N4 would benefit the separation photogenerated electron−hole pairs, while excess g-C3N4 would block some of the ultraviolet light arriving at the surface of ZrP nanoparticles and then cause a decrease in the photodegradation rate. Thereby, there would be an optimal mass ratio for the hybrid and in this work, the optimal mass ratio is 2:1 (g-C3N4/ZrP).

4. CONCLUSIONS

In summary, we have successfully composited α-ZrP nanoparticles with g-C3N4 nanosheets and synthesized C3N4−ZrP compositing nanomaterials. The phase structure, morphology, and optical properties of C3N4−ZrP compositing nanomaterials were characterized, and the photocatalysis performances of C3N4−ZrP compositing nanomaterials with different mass ratios were also studied. As the study showed, with the increasing C3N4−ZrP mass ratio, the dispersion of the compositing nanoparticles was getting better than the former, and an effective heterostructure was formed between g-C3N4 and α-ZrP. In the experiment of RhB photodegradation, all of the degradation rates of the C3N4−ZrP compositing nanomaterial system achieved more than 90% after 18 min. However, with the further increase in the C3N4−ZrP mass ratio, the photocatalysis effect first increased and then decreased. Among all of the systems, the C3N4−ZrP compositing nanomaterial system with a mass ratio of 2:1 had the optimum photodegradation performance, which had a degradation of 99.95%.

Table 1. Kinetic Constants of Photodegradation of RhB by α-ZrP, g-C3N4, and C3N4−ZrP with Different Mass Ratios

| catalysts(C3N4−ZrP) | regression equation | k (min−1) | R² |
|----------------------|---------------------|-----------|----|
| g-C3N4               | y = −0.108x + 0.2039 | 0.108     | 0.997 |
| α-ZrP               | y = −0.074x + 0.1524   | 0.074     | 0.985 |
| 1:50                | y = −0.145x + 0.1572   | 0.145     | 0.986 |
| 1:10                | y = −0.234x + 0.2739   | 0.234     | 0.984 |
| 1:3                 | y = −0.277x + 0.0041   | 0.277     | 0.985 |
| 1:1                 | y = −0.326x − 0.2531   | 0.326     | 0.985 |
| 2:1                 | y = −0.427x + 0.1494   | 0.427     | 0.981 |
| 3:1                 | y = −0.324x + 0.1411   | 0.324     | 0.987 |
| 4:1                 | y = −0.258x + 0.2689   | 0.258     | 0.983 |

The kinetic fitting data revealed that all the apparent rate constants of C3N4−ZrP with different mass ratios were greater than the apparent rate constants of pristine α-ZrP and g-C3N4. Among those data, C3N4−ZrP with a mass ratio of 2:1 had the greatest apparent rate constant, which is 0.427 min−1, and it is 5 and 4 times that of α-ZrP and g-C3N4 respectively. The results indicated that compared with pristine α-ZrP and g-C3N4, the photocatalytic performance of C3N4−ZrP compositing nanomaterials have been significantly enhanced. The reason for this might be that after the α-ZrP nanocrystal composited with g-C3N4 nanosheets, the sp2 hybridization between carbon and nitrogen in g-C3N4 built the π-conjugated structure, which is similar to graphene. A strong covalent bond is the cause of the synergy between ZrP and g-C3N4. Under the irradiation of ultraviolet, the photoinduced holes on the valence band of α-ZrP were transferred to the valence band of g-C3N4 through the heterostructure. The photogenerated electrons from the conduction band of g-C3N4 transferred to the conduction band of α-ZrP, which achieved effective separation of photogenerated electron−hole pairs and reduced the recombination rate of electron−hole pairs. Hence, more photogenerated electrons from the conduction band of α-ZrP reduced the dissolved O2 into O2− radicals. Further, the O2− radicals can be transformed to reactive OH radicals at the CB of the composite, and more photogenerated holes from the valence band of g-C3N4 directly oxidatively degraded the RhB. However, for the potential of the valence band of g-C3N4 that is more negative than that of OH/OH−, it has a lower oxidative capacity, which means in the process of photodegrading RhB, g-C3N4 played the main role. Appropriate g-C3N4 would benefit the separation photogenerated electron−hole pairs, while excess g-C3N4 would block some of the ultraviolet light arriving at the surface of ZrP nanoparticles and then cause a decrease in the photodegradation rate. Thereby, there would be an optimal mass ratio for the hybrid and in this work, the optimal mass ratio is 2:1 (g-C3N4/ZrP).

Figure 8. Kinetics of photodegradation of RhB by α-ZrP, g-C3N4, and C3N4−ZrP with different mass ratios.
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Notes
The authors declare no competing financial interest.

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