Preparation of ZnO/SnO\textsubscript{2} Composite Nanometer Photocatalyst and Photocatalytic Treatment of Marine Diesel Pollution

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Preparation of ZnO/SnO₂ Composite Nanometer Photocatalyst and Photocatalytic Treatment of Marine Diesel Pollution

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Abstract. The ZnO/SnO₂ composite nanophotocatalyst studied in this paper was prepared by a chemical precipitation method, which were characterized by XRD and SEM. The results show that the prepared samples were rutile SnO₂ particles and the average grain size is 8.41 nm. In this paper, the factors for the degradation efficiency of marine diesel oil degraded by ZnO/SnO₂ composite nanophotocatalyst are the catalysts’ doping ratio, the initial concentration of oil, the pH value of seawater, the dosage of catalyst and the dosage of hydrogen peroxide. The results show that the ZnO/SnO₂ composite nanophotocatalyst can effectively degrade seawater diesel oil under UV light. When the doping ratio of ZnO and SnO₂ is 0.35, the reaction time is 2.5 hours, the pH value of seawater with oil is 7, The concentration of diesel oil is 0.1 g/L, the dosage of catalyst is 0.3 g/L and the dosage of hydrogen peroxide is 0.1 g/L, the highest degradation rate is 91.54%.

1. Introduction
With the continuous strengthening of national power, China's resource utilization is in transition gradually. More attention is paid to the ocean with treasure, but a lot of offshore oil extraction and oil transport also exacerbated the risk of marine oil pollution. Marine oil pollution is sudden mostly, and the oil pollution would spread with the ocean currents, waves and other spread[1]. Petroleum hydrocarbons consist of tens of thousands of ingredients, and different fractions will be toxic to creatures. The effects of teratogenic death are caused by petroleum hydrocarbon contaminants in the waters on marine life. Petroleum hydrocarbons also affect the higher organisms through the food chain. Because of the seriousness of this pollution, mankind began to seek the treatment methods of marine oil pollution. At present, the methods of governance are mainly divided into physical, biological and chemical management. It is well known that chemical method is a cost saving and fast processing method. The method used in this paper is photocatalytic degradation method in chemical treatment method. Photocatalytic degradation is an environmentally friendly treatment method that does not undermine the background environment and has the advantage of efficient treatment [2-5].

In this paper, self-made ZnO/SnO₂ composite nano-photocatalysts is used for photocatalytic degradation of oil. ZnO is widely used as a nanophotocatalyst and has a remarkable effect[6]. Nano-SnO₂ is usually used to modify other materials, but studies have shown that it also has a good catalytic degradation effect. It is expected to obtain more efficient photocatalyst by using ZnO to modify other materials.
2. Materials and methods

2.1 Materials, apparatus and reagents
The main reagents and equipment are the SnCl₄ • 5H₂O, NH₃ • H₂O/NH₄Cl, ZnCl₂, magnetic stirrer, muffle furnace, UV photocatalytic reaction box, transmission electron microscopy, X-ray diffraction, 752 UV spectrophotometer etc[7].

2.2 Preparation of Composite Photocatalyst
In this experiment, nano composite photocatalyst was prepared by chemical precipitation method with tin tetrachloride pentahydrate and ZnCl₂. The different doping ratios of the catalyst were determined by different molar ratios of tin ion and zinc ion in the catalysts. The specific process of preparation is as follows in Figure 1:

![Figure 1. preparation process of photocatalyst](image)

3. Experimental method
Take 50mL of a certain concentration of oil contaminated seawater and measure the pH value. The addition of a certain amount of SnO₂/ZnO composite photocatalyst was carried out under ultraviolet light, after a certain period of time of irradiation to extract. The amount of residual diesel in seawater was determined by UV-Vis spectrophotometry method, and the photocatalytic degradation efficiency was calculated.

4. Results

4.1 Products of characterization by transmission electron microscopy

4.1.1 Analysis of transmission electron microscopy
From the above two figures for the doping ratio of 0.2,0.25 composite nano-tin dioxide catalysts, it can be clearly seen that the composite nano-tin dioxide particles are irregular balls. Its size is relatively uniform. The larger particles are gathered by many small particles to form the catalyst particle size
between 10-30nm. The resulting particle size is consistent with the Scherrer formula. Please see Figure 2.

![Figure 2. SEM images of composite photocatalyst particles](image)

4.1.2 X-ray diffraction analysis (XRD)

In this paper, by using XRD analysis method for the preparation of compound SnO₂ / ZnO photocatalyst doped ratio 0.25 when the particle size and particle shape is analyzed, as shown in Figure 3.

Doping ratio 0.25, when 2 theta is 26.5569 °, has the obvious peak value, the average crystallite size of nanometer SnO₂ light catalyst Scherrer formula can be used. The lattice constants a, b and c were 8.7148Å, 8.7013Å and 6.2862Å, (211) diffraction peak, by calculation can be concluded that nano light catalyst SnO₂ average crystallite size of 8.41 nm, with the JCPDS card in SnO₂ (01-079-1164) card, determine the preparation of samples for the rutile structure morphology of SnO₂ particles.

4.2 Effect of pH value of seawater on degradation of marine diesel pollutant

10mg of 0.2g/L simulated oil seawater was taken in six 100mL beakers and 50mL of seawater was added. The calcination temperature of nanometer composite photocatalyst was 500 °C, the dosage was 0.2 g/L, the pH values were 6, 7, 8, 9, 10 and 11. 1 mL of 0.3 g/L hydrogen peroxide was added. The absorbance was measured after stirring for 2 hours under ultraviolet light. The effect of different doping ratios on the removal of oil in seawater is calculated by the degradation efficiency, as shown in Figure 4.

It can be seen from Figure 4 that the pH value in the solution is getting higher and higher, and the removal rate of the oil in the solution gradually increases and then decreases. It can be seen that the degradation rate of the composite catalyst to the seawater is best when the pH of the solution is 10, and
the removal rate is the fastest when the pH value between 9 and 10. But when the pH value increases again, the removal rate drops rapidly and the removal effect is poor.

![Figure 4. Effects of different pH on the reaction](image)

![Figure 5. Effects of doping ratios on the reaction](image)

4.3 Effect of doping ratio of photocatalyst on degradation of marine diesel pollutant

10mg of 0.2g/L simulated oil seawater was taken in six 100mL beakers and 50mL of seawater was added. The calcination temperature of nanometer composite photocatalyst was 500 °C, the doping ratio of Zn and Sn was 0.2, 0.25, 0.3, 0.35, 0.4 or 0.45. 1 mL of 0.3 g/L hydrogen peroxide added. The absorbance was measured after stirring for 2 hours under ultraviolet light. The degradation efficiency was calculated to obtain the effect of different doping ratios on the removal of oil from seawater, as shown in Figure 5.

As can be seen from Figure 5, when the doping ratio is 0.25, the treatment efficiency is better than 0.2. But when the doping ratio increases again, the removal rate begins to decrease. The reason for the decrease in the removal rate may be: When the doping ratio is gradually increasing, the separation efficiency of the dopant carriers on the composite catalyst decreases and the recombination rate decreases, reducing the activity of the catalyst and decreasing the removal rate [9]. When the doping ratio is 0.45, it can be seen that the removal rate is increased in a small range. In order to study and verify, the validation test are carried out with doping ratio of 0.5, 0.55 and 0.6. It is seen from the data that the removal rate of oil is relatively constant and tends to be gentle.

4.4 Effect of photocatalytic reaction time on degradation of marine diesel pollutant

10mg of 0.2g/L simulated oil seawater was taken in six 100mL beakers and 50mL of seawater was added. The calcination temperature of nanometer composite photocatalyst was 500 °C, the dosage was 0.2 g/L and doping ratio was 0.25. Reaction time was 0.5, 1, 1.5, 2, 2.5 or 3 h. 1 mL of 0.3 g/L
hydrogen peroxide was added. After extraction, the absorbance was measured and the degradation efficiency was calculated to obtain the effect of different doping ratios on the removal of oil in seawater, as shown in Figure 6.

![Figure 6. Effects of illumination time on the reaction](image)

![Figure 7. Effects of the hydrogen peroxide concentration on reaction](image)

It can be seen from Figure 6 that the amount of photocatalytic oxidation will increase with the increase of ultraviolet light time in the initial stage of the reaction, but the removal rate is high at 0.5h. But when the UV light time is higher than 2 hours, the seawater oil removal rate began to decline slowly, may be due to the mixed oil and catalyst that prevent the catalyst for catalytic reaction.

4.5 Effect of Hydrogen Peroxide Concentration on Degradation of Diesel pollutant

10mg of 0.2g/L simulated oil seawater was taken in six 100mL beakers and 50mL of seawater was added. The calcination temperature of nanometer composite photocatalyst was 500°C, the dosage was 0.2 g/L and doping ratio was 0.25. 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g/L hydrogen peroxide 1 mL was add and stirred for 2 hours under ultraviolet light. The degradation efficiency was calculated to obtain the effect of different concentration of hydrogen peroxide on the removal of oil from seawater, as shown in Figure 7.

It can be seen from Fig. 7 that the removal rate is the highest when the concentration of H₂O₂ is 0.3g/L. The possible reason is that H₂O₂ is the electron acceptor, which competes with the catalyst for electrons, making the tin dioxide surface electron-hole pairs difficult to compound and generating strong oxidizing ions. Thus, the photocatalytic activity was enhanced.

4.6 Effect of Composite Photocatalyst Dosage on Degradation of Marine Diesel pollutant

10mg of 0.2g/L simulated oil seawater was taken in six 100mL beakers and 50mL of seawater was added. The calcination temperature of nanometer composite photocatalyst was 500°C, the dosage was
0.1, 0.2, 0.3, 0.4, 0.5 or 0.6 g/L and doping ratio was 0.25. 0.3 g/L hydrogen peroxide 1 mL was added and stirred for 2 hours under ultraviolet light. The degradation efficiency was calculated to obtain the effect of different dosage on the removal of oil from seawater, as shown in Figure 8.

![Figure 8. Effects of dosage on the reaction](image)

4.7 Effect of initial oil concentration on degradation of marine diesel pollutant

10mg of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g/L simulated oil seawater was taken in six 100mL beakers and 50mL of seawater was added. The calcination temperature of nanometer composite photocatalyst was 500 °C, the dosage was 0.2 g/L and doping ratio was 0.25. 0.3 g/L hydrogen peroxide 1 mL was added and stirred for 2 hours under ultraviolet light. The degradation efficiency was calculated to obtain the effect of different dosage on the removal of oil from seawater, as shown in Figure 9.

![Figure 9. Effects of the initial concentration of diesel on the reaction](image)

It can be seen from Figure 8 that at the beginning of the reaction, the removal rate of oil would increase with the increase of the dosage of nanometer tin dioxide composite photocatalyst. When the dosage of composite photocatalyst is more than 0.3g/L, the removal rate began to decline slowly. The reason for the decrease in the removal rate may be that when the concentration of catalyst in seawater increases to a certain extent, the addition of the catalyst will result in enhanced scattering of light by the tin dioxide, which may result in a decrease in the utilization of solar energy and a reduction in electrons.

It can be seen from Figure 9: at the beginning of the reaction, the oil removal rate would increase with the increase of the concentration of diesel oil. But when the diesel concentration exceeds 0.15 g/L, the seawater oil removal rate began to decline slowly. The reason for the decrease in the removal rate may be that the oil concentration is too high and the degradation rate is reduced.
5. Orthogonal experiment

In order to determine the optimal reaction conditions of nano-SnO\textsubscript{2} composite photocatalyst for oil degradation in seawater, the factors such as the doping ratio and dosage of catalyst, the initial concentration of diesel, the pH value of solution, the time of ultraviolet light and the concentration of H\textsubscript{2}O\textsubscript{2} solution were selected. Six factors five levels of orthogonal verification experiments was designed. And the effect of these six factors on the catalytic oxidation rate of nano-SnO\textsubscript{2} composite photocatalyst was analyzed according to the orthogonal test table.

Table 1 Orthogonal experiment table

| No. | Reaction time (h) | Concentration of diesel (g/L) | Doping ratio (g/L) | Dosage of H\textsubscript{2}O\textsubscript{2} (g/L) | pH value | Removal rate |
|-----|------------------|------------------------------|-------------------|---------------------------------|---------|--------------|
| 1   | 0.5              | 0.05                         | 0.2               | 0.1                             | 0.1     | 6            | 86.05%       |
| 2   | 0.5              | 0.1                          | 0.25              | 0.4                             | 0.5     | 7            | 85.71%       |
| 3   | 0.5              | 0.15                         | 0.3               | 0.5                             | 0.4     | 8            | 75.25%       |
| 4   | 0.5              | 0.2                          | 0.35              | 0.3                             | 0.2     | 10           | 78.06%       |
| 5   | 0.5              | 0.25                         | 0.4               | 0.2                             | 0.3     | 9            | 73.76%       |
| 6   | 1                | 0.05                         | 0.25              | 0.2                             | 0.2     | 7            | 80.00%       |
| 7   | 1                | 0.1                          | 0.3               | 0.3                             | 0.4     | 10           | 78.14%       |
| 8   | 1                | 0.15                         | 0.2               | 0.1                             | 0.5     | 9            | 76.83%       |
| 9   | 1                | 0.2                          | 0.4               | 0.4                             | 0.3     | 6            | 70.12%       |
| 10  | 1                | 0.25                         | 0.35              | 0.5                             | 0.1     | 8            | 77.17%       |
| 11  | 1.5              | 0.05                         | 0.3               | 0.3                             | 0.3     | 8            | 83.08%       |
| 12  | 1.5              | 0.1                          | 0.35              | 0.1                             | 0.5     | 9            | 90.89%       |
| 13  | 1.5              | 0.15                         | 0.25              | 0.2                             | 0.2     | 7            | 75.68%       |
| 14  | 1.5              | 0.2                          | 0.4               | 0.5                             | 0.1     | 6            | 78.06%       |
| 15  | 1.5              | 0.25                         | 0.2               | 0.4                             | 0.4     | 10           | 72.69%       |
| 16  | 2                | 0.05                         | 0.35              | 0.4                             | 0.4     | 9            | 89.97%       |
| 17  | 2                | 0.1                          | 0.3               | 0.2                             | 0.5     | 6            | 77.93%       |
| 18  | 2                | 0.15                         | 0.25              | 0.5                             | 0.3     | 7            | 84.65%       |
| 19  | 2                | 0.2                          | 0.4               | 0.1                             | 0.2     | 8            | 84.44%       |
| 20  | 2                | 0.25                         | 0.2               | 0.3                             | 0.1     | 10           | 78.64%       |
| 21  | 2.5              | 0.05                         | 0.4               | 0.5                             | 0.5     | 10           | 74.74%       |
| 22  | 2.5              | 0.1                          | 0.35              | 0.3                             | 0.1     | 7            | 91.54%       |
| 23  | 2.5              | 0.15                         | 0.2               | 0.4                             | 0.2     | 6            | 79.11%       |
| 24  | 2.5              | 0.2                          | 0.3               | 0.2                             | 0.4     | 8            | 79.22%       |
| 25  | 2.5              | 0.25                         | 0.25              | 0.1                             | 0.3     | 9            | 77.68%       |

k1 398.83 413.84 393.32 415.89 411.47 391.28
k2 382.27 424.22 403.71 386.58 397.29 417.58
k3 400.40 391.52 393.63 409.48 389.29 399.17
k4 415.64 389.91 427.64 397.60 395.27 409.12
k5 402.29 379.93 381.12 389.88 406.10 382.27
R 33.37 44.29 46.52 29.31 22.18 35.30

One of the best reaction conditions for the determination of oil pollution in seawater by orthogonal test is that the doping ratio of nanometer tin dioxide composite photocatalyst is 0.35. The dosage of catalyst is 0.3g/L, the initial concentration of diesel is 0.1g/L, the pH value of the solution is 7, the time of ultraviolet light is 2.5 hours and the oil removal rate in seawater is 91.54%.

In addition, the orthogonal test table can also be obtained that the effect of catalyst doping ratio. The catalyst dosage, the initial concentration of diesel, the concentration of hydrogen peroxide, the pH value of the solution and the UV irradiation time on the degradation rate are as follows: catalyst
doping ratio, initial concentration of diesel, solution pH, UV light time, catalyst dosage, hydrogen peroxide concentration.

In order to verify whether the removal rate was stable under the best experimental conditions in orthogonal experiments, three sets of parallel experiments were carried out as follows:

| No. | Concentration of diesel (g/L) | Removal rate |
|-----|-----------------------------|--------------|
| 1   | 0.102                       | 92.98%       |
| 2   | 0.102                       | 92.34%       |
| 3   | 0.098                       | 92.69%       |

From the validation test data, it can be obtained that the removal efficiency is relatively stable and the effect is good, the average removal effect can reach 92.67%.

6. Conclusions
(1) ZnO/SnO$_2$ composite nanometer photocatalyst prepared by chemical precipitation method was characterized by XRD and SEM. The results show that the composite nano-tin dioxide is an irregular sphere with uniform size.
(2) ZnO/SnO$_2$ composite nanometer photocatalyst can effectively photocatalytically oxidize diesel pollutant in seawater under ultraviolet light.
(3) When the doping ratio of ZnO/SnO$_2$ composite nanometer photocatalyst is 0.35, the dosage of catalyst is 0.3 g/L, the initial concentration of diesel is 0.1 g/L, the concentration of hydrogen peroxide solution is 0.1 g/L, the pH value of solution is 7, UV light time was 2.5 hours, the seawater oil removal rate can reach 91.54%.
(4) The influence degree of each factor on the catalytic degradation rate of nano-tin dioxide composite photocatalyst is: catalyst doping ratio > initial concentration of diesel oil > pH value > UV irradiation time > catalyst dosage > hydrogen peroxide concentration.

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