Photocatalytic Degradation of Coking Wastewater by Ce-Ti-Graphene Composite

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Abstract. Photocatalytic technology has bright prospects in the field of coking wastewater treatment. UV spectrophotometer is used to test the photodegradation of 10 mol/L rhodamine B solution on the self-built photocatalytic platform. The photocatalytic properties of 7 kinds of catalysts are compared and analyzed. The results show that after the 30min simulation of sunlight, the photocatalytic effect from the best to the worst is 10% CeO2-TiO2/10% RGO > 5% CeO2-TiO2/10% RGO > 1% CeO2-TiO2/10% RGO > TiO2/10% RGO > 10% CeO2-TiO2. In the case of the TiO2 composite with single modified materials of the same mass, the composite with graphene has better photocatalytic properties than the composite with CeO2 while the TiO2 composite with two modified materials shows better photocatalytic effect than that with only one single material, and the samples with more CeO2 have more excellent photocatalytic properties in the case of the same mass of graphene. And the photocatalytic performance of 10% CeO2-TiO2/10% RGO composites is the best, whose photocatalytic degradation is 6.71 times that of pure TiO2. The results show that the composite of graphene and CeO2 effectively improves the photocatalytic efficiency and improves the defects of TiO2 to a certain extent.

1. Introduction
Components of coking wastewater are extremely complex, besides containing inorganic pollutants in high concentration like ammonia, cyanide, sulfur, cyanide, fluoride and other outside, still contain difficult degradable organic pollutants such as phenols, pyridine, quinoline, polycyclic aromatic hydrocarbons (PAHs) which are poisonous and harmful [1]. Although the traditional sewage disposal method can alleviate the impact of the coking wastewater on the environment to a certain extent, it is ineffective to deal with refractory organic compounds in coking wastewater, which consequently exists secondary pollution. Photocatalytic technology under the condition of light can make the light catalyst to generate strong oxidizing free radicals, so that organic matter which is hard to be degraded in waste water pollution can effectively be removed [3]. Compared with the traditional water treatment technology, photocatalytic technology has obvious advantages including energy saving, high efficiency and complete degradation of pollutants and it’s easy to operate with no secondary pollution, which is suitable for advanced treatment of coking wastewater system with low turbidity and good transparency [3].

The core of photocatalysis technology is the selection and preparation of photocatalysts, whose composition, structure and related properties directly influence the overall catalytic effect of photocatalysis. Due to high stability of photochemistry, strong corrosion resistance with non-toxicity and harmlessness, TiO2 has become the most widely used, the most common form of photocatalyst, which is hardly a burden to the environment with lower cost of industrialization. XiaoJun-xia [4] with
the use of TiO$_2$ or its compounds as catalyst photocatalytic to treat coking wastewater, have achieved good effects, in which kinds of organic matter reduced from 66 kinds before processing to 23, and the order for degradation rate of organic matter is petroleum hydrocarbon $>$ alcohol, acid, aldehyde, etc $>$ organic phenol $>$ benzene content $>$ nitrogen heterocyclic organic matter $>$ polycyclic aromatic hydrocarbons.

However, due to the high recombination rate of hole and photoelectron, the wide band gap results in a narrow range of light response, which can only absorb ultraviolet light accounting for a small part in sunlight, and the characteristics of the recycling difficult and difficult to recycle, the photocatalytic efficiency of titanium dioxide photocatalyst is restricted by a lot of $^{[5-9]}$. In order to improve the defects of TiO$_2$ itself, scientists have made various attempts such as doping metal ions or nonmetal ions, surface photosensitive treatment (oxidizing agent of photosensitization formed by activated carbon, alginate, methylene blue), compounding semiconductor (sulfur sensitization, oxide sensitizing), precious metal deposition (Ru, Tb, Ce, Th, etc.), the immobilization of the semiconductor (should be fixed on the carrier surface or be fixed in the reactor wall), acidic modulation (adding CH$_3$OH, AgNO$_3$ and other sacrificial agent), field coupling treatment (electric field, magnetic field, thermal field, microwave field) as well as some measures such as mixture with carbon based materials $^{[10-13]}$. Graphene has received much attention from public due to its unique structure and excellent properties.

People have had a deep understanding of graphene/TiO$_2$ composite photocatalyst. The introduction of graphene in a certain extent reduces energy gap width of TiO$_2$, increases its light absorption efficiency, and improves the efficiency of its electronic conduction, causing photon-generated carriers transfer from the surface of TiO$_2$ to the surface of graphene, which reduces composite efficiency of electron–hole pairs in the TiO$_2$. In the meanwhile, the graphene itself has great specific surface area and strong adsorption ability, so organic molecules can be largely adsorbed on the surface of graphene, making response more efficiently and rapidly, so as to improve the photocatalytic efficiency $^{[14-18]}$. Graeme Williams et al. $^{[19]}$, for the first time in 2008 manufactured graphene oxide-titanium dioxide composite material by adopting the method of ultraviolet irradiation and reduction for suspended graphite oxide in ethanol, which has opened the door to the designing and construction of graphene/semiconductor composite. In 2010, Zhang H $^{[20]}$ by using of graphite oxide and commercial P25 through a simple hydrothermal method mixed with water and ethanol as the solvent to obtain the graphene/composite photocatalyst P25, which shows that the scope of light absorption of TiO$_2$ / graphene composites expands to the visible light region and under the condition of visible light it still has higher photocatalytic activity. Xu $^{[21]}$ by use of hydrothermal method with TiF$_4$ and P25 respectively manufactures the different TiO$_2$ /graphene photocatalyst, which by comparing with TiO$_2$/carbon nanotubes indicates that preparation methods has an important influence on graphene photocatalytic performance of TiO$_2$ light catalyst, and photocatalytic performance of TiO$_2$ / graphene light catalyst composed by liquid titanium instead of solid TiO$_2$ powder has more obvious improvements, because compound composed by the liquid titanium as the titanium source can make the TiO$_2$ load on the surface of graphene more uniformly, and thus strengthen the interaction between TiO$_2$ and graphene.

From this perspective, the compound formed by graphene and TiO$_2$ shows better photocatalytic performance than the individual TiO$_2$. Despite the titanium dioxide/graphene composites is very promising, it’s far from the practical application. Therefore, it is necessary to develop a new type of highly active photocatalyst based on graphene/TiO$_2$ composite photocatalyst.

Because of its unique optical and catalytic properties rare earth oxides has wide application in the field of photocatalysis. As a kind of highly active rare earth oxides, cerium oxide due to the strong oxygen storage, optical performance stability, high thermal stability and electrical conductivity and the diffusion performance, arouses people’s great attention. Therefore, it has good theoretical and practical significance for getting efficient and stable graphene-based photocatalyst and solving the problem of coking wastewater pollution by introducing cerium oxide to graphene-based photocatalyst so as to develop a new type of photocatalyst and exploring its microscopic structure and the change of the physical and chemical properties.
2. Experimental method

2.1. Preparation of CeO₂-TiO₂/RGO composite photocatalyst

TiO₂-CeO₂/RGO composite is synthesized by two-step hydrothermal method. The specific process is as follows:

A certain amount of six water nitrate cerium (Ce(NO₃)₃•6H₂O) is weighed up to dissolve in anhydrous ethanol and 2 mL tetrabutyl titanate (C₁₆H₃₆O₄Ti) is dissolved in mixed solution containing water and ethanol. The above solution is blended and then mixed with ammonia adjusting PH to 10. The solution obtained which has been stirred well is moved to the high pressure reaction kettle to react 24 hours under 120 °C then to cool to the normal room temperature. The product finally obtained will be washed and dried with deionized water and alcohol to get a CeO₂-TiO₂ composites. A certain quality of graphite oxide is added to mixture of ethanol and deionized water and then treated under ultrasonic dispersion for 60 minutes. Subsequently, a certain amount of CeO₂-TiO₂ particles is added to the above solution, and then, the solution was mixed for 30 minutes. Successively, the solution was transferred into the high-pressure reaction kettle and kept under 120 °C for 24 hours. The product finally obtained will be washed and dried to finally get graphene composite catalyst. Specific sample components are as follows in Table 1.

| Sample | TiO₂(mol) | CeO₂ (wt %) | GO (wt %) |
|--------|-----------|-------------|-----------|
| 1      | 5.86*10⁻³ | 10          | 0         |
| 2      | 5.86*10⁻³ | 10          | 10        |
| 3      | 5.86*10⁻³ | 5           | 10        |
| 4      | 5.86*10⁻³ | 1           | 10        |
| 5      | 5.86*10⁻³ | 0           | 10        |
| 6      | 0         | 0           | 10        |
| 7      | 5.86*10⁻³ | 0           | 0         |

The source of TiO₂ in the above samples is tetrabutyl titanate, whose content is 2 mL, while the amount of CeO₂ and RGO is added into it with the corresponding mass ratio of TiO₂.

2.2. Experimental equipment and principle of photocatalytic degradation of organic wastewater

According to the photocatalysis principle, rhodamine B (Rh B) solution is used as the degradation substance to simulate the photocatalytic performance test of organic matter in degraded sewage. The homemade photocatalytic experimental platform is used for the experiment and the schematic diagram of the experimental device is shown in Figure 1. The rhodamine B solution is placed in the glass reactor of PR22-25 PYREX, in which QW220 quartz cold trap through circulating water cooling is installed. 500 w xenon arc lamp light is placed in this cold trap. The glass reactor coated with a layer of foil paper to prevent light-leaking to some extent is placed in the mixer to ensure the solution uniform when it’s sampled. The whole reactor is put in a homemade sealed iron box to ensure that no other light source is involved in the reaction. The specific methods are as follows:
The 50 mg photocatalyst prepared in advance is taken first, and meanwhile the 250 mL solution of 10 mol/L rhodamine B is prepared. These two types of solutions are mixed into a homemade photocatalytic experimental device, supplemented by dark field conditions. The dark adsorption equilibrium of dark field is confirmed after 30 minutes. Then the switch of the xenon light source is turned on. Within the next 30 minutes, samples are taken every 5 minutes and every time 5 mL of the sample is taken during the sampling process. The sample is centrifuged in a centrifuge of 5500 r/min for 5 min, and the absorption spectrum of the solution is measured by ultraviolet spectrophotometer to obtain the concentration of rhodamine B in the supernatant. According to the linear regression equation corresponding to rhodamine B curves, the corresponding concentration of rhodamine B solution is obtained. According to the experimental data photocatalytic efficiency diagram is obtained and the degradation efficiency of these 6 kinds of catalyst is compared.

The standard curve of rhodamine B is drawn as follows: the absorbance of rhodamine B at different concentration is tested as shown in Table 2 below. The standard curve of rhodamine B can be made according to the following data (Figure. 2).

The linear regression equation corresponding to the curve is: $\text{Abs}=0.09581c-0.00613$, and the correlation coefficient $R^2=0.9999$. According to this formula, the corresponding concentration of rhodamine B solution can be obtained, and then the photocatalytic degradation rate is calculated according to the following equation.

| Table 2. Absorbance of rhodamine B solution at different concentrations |
|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Concentration (mg/L)     | 0               | 1               | 2               | 4               | 6               | 8               | 10              |
| Absorbance (A)           | 0.087           | 0.187           | 0.381           | 0.570           | 0.753           | 0.956           |
Figure 2. Standard curve of rhodamine B solution

\[ \text{Abs} = 0.09581 - 0.00615x \quad R^2 = 0.99978 \]

In the equation:
- P—Degradation rate of rhodamine B;
- \( C_0 \)—initial mass concentration of rhodamine B;
- \( C_t \)—mass concentration of rhodamine B when the photocatalytic time is t;
- \( A_0 \)—initial absorbance of rhodamine B;
- \( A_t \)—the absorbance of rhodamine B when the photocatalytic time is t

3. Analysis and Discussion

Figure 3 shows that the photocatalytic degradation curve of organic compounds in the photocatalytic experiments of 7 different composite catalyst samples in Table 1. The detailed data are shown in Table 3.
The end point of 30 min dark adsorption is selected as the starting point. The concentration of rhodamine B at this time is set as C\(_0\). The horizontal coordinate is time, and the vertical coordinate is C/ C\(_0\). It is evidently seen from Fig.3 that the photocatalytic effect of the composite materials is much better than that of the pure TiO\(_2\) samples and the degradation rate of the worst photocatalytic effect materials, 10% CeO\(_2\)-TiO\(_2\), is 4.36 times that of the TiO\(_2\) samples under 30 min illumination, and the best photocatalytic effect materials, 10%CeO\(_2\)-TiO\(_2\)/10% RGO, is 6.71 times that of the TiO\(_2\) samples, indicating that the composite materials prepared in the experiment have effectively improved the photocatalytic efficiency. The combination of graphene and CeO\(_2\) does improve the defects of TiO\(_2\) to some extent, and the modification of TiO\(_2\) is successful.

In addition, although loaded with CeO\(_2\), the photocatalytic effect of 10%CeO\(_2\)-TiO\(_2\) catalyst is not obvious in the first 5 minutes. The photocatalytic effect is basically the same as that of TiO\(_2\) catalyst, but in the subsequent time, the photocatalytic effect exceeds that of TiO\(_2\)/10% RGO catalyst loaded with graphene only. The photocatalytic effect of TiO\(_2\)/10% RGO catalyst in the first five minutes is basically the same as that of the ternary composite photocatalyst loaded with a small amount of CeO\(_2\), and the photocatalytic effect of 10%CeO\(_2\)-TiO\(_2\)/10% RGO samples at each time point is ahead of other
composite materials.

Overall, after the 30 min simulation of sunlight, the photocatalytic effect from the best to the worst is 10% CeO$_2$-TiO$_2$/10% RGO > 5% CeO$_2$-TiO$_2$/10% RGO > 1% CeO$_2$-TiO$_2$/10% RGO > TiO$_2$/10% RGO > 10% CeO$_2$-TiO$_2$. In the binary system of either CeO$_2$-TiO$_2$ or TiO$_2$-RGO composite photocatalysts, by loading the same mass, the effect of graphene on the increase of photocatalytic degradation of rhodamine B organic solution is better than that of CeO$_2$. The effect of the ternary system of CeO$_2$-TiO$_2$-RGO composite photocatalysts on the increase of photocatalytic degradation of rhodamine B organic solution is better than that of the binary system of CeO$_2$-TiO$_2$ or TiO$_2$-RGO composite photocatalysts. By loading the same mass of RGO, the photocatalytic performance of the ternary system of CeO$_2$-TiO$_2$-RGO composite photocatalysts increased with the increase of the CeO$_2$ concentration.

4. Conclusion

Uv spectrophotometer is used to test the photodegradation of 10 mol/L rhodamine B solution on the self-built photocatalytic platform. The results show that in the case of TiO$_2$ composite of only one material, the photocatalytic effect of the composite graphene with the same mass is better than that of the composite CeO$_2$. The effect of the ternary system of CeO$_2$-TiO$_2$-RGO composite photocatalysts on the increase of photocatalytic degradation of Rhodamine B organic solution is better than that of the binary system of CeO$_2$-TiO$_2$ or TiO$_2$-RGO composite photocatalysts. By loading the same mass of RGO, the photocatalytic performance of the ternary system of CeO$_2$-TiO$_2$-RGO composite photocatalysts increased with the increase of the CeO$_2$ concentration. The photocatalytic performance of 10% TiO$_2$-CeO$_2$/10% RGO composites is the best, whose photocatalytic degradation is 6.71 times that of pure TiO$_2$. It shows that the composite of graphene and CeO$_2$ effectively improves the photocatalytic efficiency and improves the defects of TiO$_2$ to a certain extent.

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