

Preparation of TiO₂/RGO Composite and Application in Photocatalytic Degradation of Unsymmetrical Dimethylhydrazine Wastewater

Xiaomeng Lv¹, Xuanjun Wang¹, Ying Jia¹, Zhiyong Huang¹ and Qilong Han¹
¹Rocket Force University Of Engineering, Xi ' an, P.R. China

Keywords: TiO₂/RGO, Preparation, UDMH wastewater, Photocatalytic Degradation.

Abstract: The TiO₂/reduced graphene oxide composite was prepared with graphene oxide and titanium dioxide by hydrothermal reduction method. Surface morphologies were collected by scanning electron microscopy and ultraviolet-visible absorption performance was studied by ultraviolet-visible spectrophotometer. The TiO₂/RGO composites were used as catalysts for photocatalytic degradation of unsymmetrical dimethylhydrazine wastewater with a concentration of 120 mg·l⁻¹. The optimum condition of catalyst dosage, pH value and reaction time were 1g·l⁻¹, 7 and 120 min respectively and the optimum photocatalytic degradation rate of UDMH wastewater was 72.1%.

1 INTRODUCTION

Unsymmetrical dimethylhydrazine (UDMH) is an important liquid propellant used in aerospace and military field. It is difficult to achieve completely photocatalytic degradation of UDMH in wastewater disposal with single catalyst owing to its complicated molecular structure. Thus, searching for composite catalytic materials for the photocatalytic degradation of UDMH wastewater is important. New carbon materials such as graphene and reduced graphene oxide (RGO) et al. have a promising application prospects in flexible graphite, thermal energy storage materials, sorbents, conductive resin composites and catalyst[1-2]. As a wide-band gap semiconductor material, TiO₂ particle has good chemical stability, thermal conductivity, and ultraviolet absorption that be applied in photoelectron apparatus and photocatalyst[3-4]. Hybridization reaction of TiO₂ particle and RGO was conducted easily owing to a few oxygen-containing function groups on the surface of RGO.

In the present study, TiO₂/RGO composites were prepared with graphene oxide and titanium dioxide as raw materials by hydrothermal reduction method. Then, TiO₂/RGO applied in the photocatalytic degradation experiment on UDMH wastewater was carried out and the influence of reaction condition on the optimum photocatalytic degradation rate was also discussed.

2 EXPERIMENTAL

2.1 Preparation of TiO₂/RGO

An appropriate amount of 50 mg (to the accuracy of 0.1 mg) graphene oxide (GO) sample was placed into a with 50 ml NaOH solution of 10 mol·l⁻¹. After 2 hours dispersion treatment of the beaker in ultrasonic processor, a certain amount of TiO₂ particle was added and then another 2 hours dispersion treatment was conducted. Dispersed solution was placed into a high pressure resistant reaction container, magnetic stirred in room temperature for 4 hours, heated in 150 °C for 24 hours, removed and washed with dilute hydrochloric acid and ultrapure water successively, and then placed into a vacuum drier of 60 °C for 12 hours and a vacuum tube furnace of 600 °C (pure nitrogen environment) for 1 hour. Then, TiO₂/RGO composites were obtained.

2.2 Characterization

Surface morphologies of TiO₂/RGO composites were collected by scanning electron microscopy (Czech, TESCAN, VEGA II XMUINCN). Ultraviolet-visible (UV-vis) absorption spectrum was collected by UV-vis spectrophotometer (Japan, SHIMADZU, UV-2700, 200 nm ~ 900 nm).

2.3 Photocatalytic Degradation of UDMH Wastewater

TiO₂ particles and TiO₂/RGO composites were used as catalysts for photocatalytic degradation experiment of 120 mg•l⁻¹ UDMH wastewater. A self-made ultraviolet light photocatalytic device as shown in Figure 1 was constituted of ultraviolet light lamp, sealed wooded cases and strong magnetic stirrer. The beaker containing UDMH wastewater was placed under the UV lamp and the liquid level of UDMH wastewater was 10 cm far away from the UV lamp. The experiment of influence of catalyst dosage, pH and reaction time on the photocatalytic degradation rate was carried out.

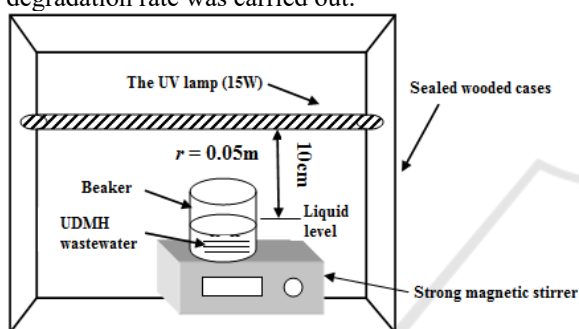


Figure 1: A self-made UV light photocatalytic device.

3 RESULTS AND DISCUSSION

3.1 SEM Analysis

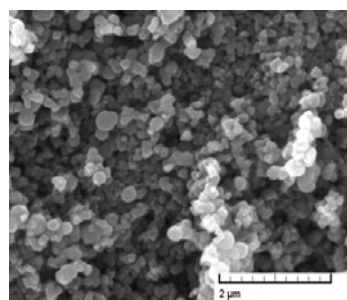
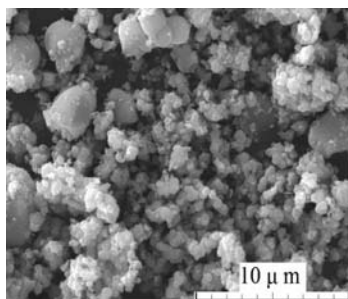


Figure 2: SEM images of TiO₂/RGO.

Figure 2 shows SEM images of TiO₂/RGO composites prepared that with high purity have well-proportioned size in the range from 5 μm to 30 μm. Surface of TiO₂/RGO composites appearing spherical particles was covered with fold thin RGO film. As shown in Figure 2, TiO₂/RGO composites with small agglomeration were clearly observed. This result indicates that the oxygen-containing function groups on the surface RGO attained become fewer after reduction and the hydrophilicity of RGO become lower. After Hybridization reaction of TiO₂ particle and RGO, agglomeration of TiO₂/RGO could be restrained effectively owing to its own nanostructure.

3.2 UV-vis Analysis

A comparative study of UV-vis absorption spectrum analysis between TiO₂ particles and TiO₂/RGO composites were studied by UV-2700 ultraviolet-visible spectrophotometer as shown in Figure 3. The result shows a marked growing of UV-vis absorption intensity of TiO₂/RGO in the range from 200 nm to 400 nm. The UV-vis absorption intensity of TiO₂/RGO-1 was 80% stronger than that of TiO₂. Owing to sufficient electron transfer from valence band to conduction band, most transfer electrons were accepted by RGO and few electrons back was recombined with hole. The more the electron holes mount exist on the surface of TiO₂/RGO, the stronger the catalytic oxidation will be.

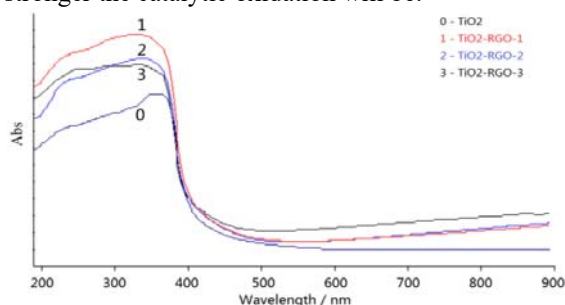


Figure 3: UV-vis absorption spectrum of TiO₂/RGO.

3.3 Photocatalytic Property Analysis

Figure 4 shows the result of influence of catalyst dosage on photocatalytic degradation rate of $120\text{mg}\cdot\text{l}^{-1}$ UDMH wastewater with TiO_2 and TiO_2/RGO samples. The increase in catalyst dosage from $0.25\text{ g}\cdot\text{l}^{-1}$ to $0.75\text{ g}\cdot\text{l}^{-1}$ resulted in an accelerated photocatalytic degradation rate of UDMH wastewater. The photocatalytic degradation rate increased to its maximum at about catalyst dosage of $1\text{ g}\cdot\text{l}^{-1}$, and then decreased slowly because of more catalyst dosage, possibly resulting in reducing UV-vis absorption of TiO_2 and TiO_2/RGO .

The degradation rate of UDMH wastewater with TiO_2/RGO catalyst can achieve 70.2% that was approximately 50% higher than that of TiO_2 particle. This result indicates that Hybridization reaction is advantageous to increase of the specific area and absorption of TiO_2/RGO . This condition could result in improving surface chemical mobility and broadening energy band gap of TiO_2/RGO , and in favor of the increase of degradation rate.

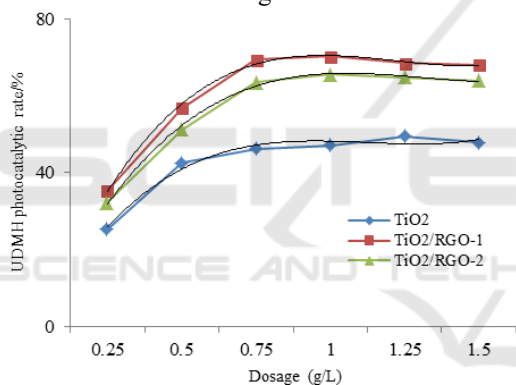


Figure 4: Influence of catalyst dosage on photocatalytic degradation rates of UDMH wastewater.

The results of influence of pH value on photocatalytic degradation rate of $120\text{ mg}\cdot\text{l}^{-1}$ UDMH wastewater with TiO_2 and TiO_2/RGO samples were shown in Figure 5. The increase in pH value from 2 to 8 resulted in a gradual growing photocatalytic degradation rate of UDMH wastewater from 27.5% to 72.1%. The photocatalytic degradation rate increased to its maximum at about pH value of 7, and then decreased gradually.

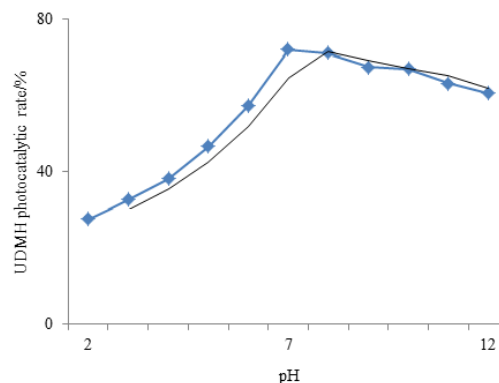


Figure 5: Influence of pH value on photocatalytic degradation rates of UDMH wastewater.

Because of physicochemical property of UDMH, the solution pH value is a very important factor for photocatalytic degradation experiment. A neutralization reaction with unsymmetrical dimethylhydrazine and hydrogen ion occurred and UDMH-salt compounds were generated in acid condition. TiO_2/RGO was photocatalytic-insensitive to UDMH-salt compounds, which resulting in a lower photocatalytic degradation rate. In neutral and alkaline condition, UDMH existed in molecular form that could be benefit to photocatalytic degradation. The pH value above 9 is advantageous for electron transfer due to high concentration of hydroxide and the photocatalytic reaction with TiO_2/RGO and UDMH could be restrained partly due to decrease of electron-hole pair amount.

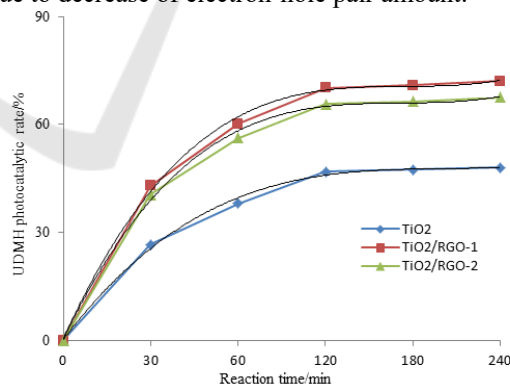


Figure 6: Influence of reaction time on photocatalytic degradation rates of UDMH wastewater.

Figure 6 shows the result of influence of reaction time on photocatalytic degradation rate of $120\text{ mg}\cdot\text{l}^{-1}$ UDMH wastewater with TiO_2 and TiO_2/RGO samples. As the reaction time increased, the photocatalytic degradation rate increased at the initial reaction and became closer to its maximum 72.1% at 120 min. This result indicates that

photocatalytic reaction was completed after 120 min. In the initial reaction time from 0 min to 60 min, a significant increase of photocatalytic degradation rate occurred owing to large specific area of TiO₂/RGO and rapidly absorption to UDMH molecular that was benefit to photocatalytic reaction. The reaction time longer than 120 min is disadvantageous for the increase in photocatalytic degradation rate because of absorption-degradation saturation balance between TiO₂/RGO and UDMH molecular.

4 CONCLUSIONS

The TiO₂/RGO composite was prepared with graphene oxide and titanium dioxide as raw materials by hydrothermal reduction method. The TiO₂/RGO composites were used as catalysts for photocatalytic degradation of unsymmetrical dimethylhydrazine wastewater with a concentration of 120 mg·l⁻¹. The optimum condition of catalyst dosage, pH value and reaction time were 1g·l⁻¹, 7 and 120 min respectively and the optimum photocatalytic degradation rate of UDMH wastewater was 72.1%.

REFERENCES

1. XIAO X Y, LI Y C, LIU Z P. Graphene commercialization [J]. *Nat Mater*, 2016, 15: 697-698.
2. Li J H, Li J Y, Li L F, et al. Flexible graphene fibers prepared by chemical reduction induced self-assembly [J]. *Journal of Materials Chemistry A*, 2014, 2(18): 6359-6362.
3. J.S. Lee, K.H. You, C.B. Park, Highly Photoactive, Low Band gap TiO₂ Nanoparticles Wrapped by Graphene [J]. *Advanced Materials* 24 (2012): 1084-1088.
4. Y.Y. Gao, X.P. Pu, D.F. Zhang, G.Q. Ding, X. Shao, J. Ma, Combustion synthesis of grapheneoxide-TiO₂ hybrid materials for photodegradation of methyl orange, *Carbon* 50 (2012):4093-4101.