Study on Photocatalytic Ability and Mechanism of Graphene Oxide

Haoqi Zhao, Baoshan Gu* and Peiyan Yang

National Engineering and Research Center of Continuous Casting Technology, China Iron and Steel Research Institute Group, No.76 Xueyuan Nanlu, Beijing 100081, China
E-mail: *gubs@263.net

Abstract. Graphene oxide (GO) was prepared by a modified Hummers method, and the morphology, composition and structure of the graphene were characterized by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and Raman spectroscopy. The refractory organic wastewater was represented by methyl orange (MO). The photocatalytic ability of GO to degrade MO under visible light irradiation was improved by the addition of \( \text{H}_2\text{O}_2 \), aeration, and the increase of illumination, according to the photocatalytic mechanism of GO.

1. Introduction
Graphene is a two-dimensional honeycomb flat film formed by compact accumulation of single-layer carbon atoms. It is the thinnest, strongest, best conductive and heat conducting nanomaterial in the materials currently used. Graphene can be used as a carrier material, which provides attachment sites for photocatalytic materials and transmits photo-generated electrons rapidly, reducing the probability of the combination of electrons and holes and improving the efficiency of photocatalytic materials. Graphene can also reduce the bandgap width of photocatalytic materials, thus improving the photocatalytic efficiency. Graphene oxide (GO) is a derivative of graphene, which can be regarded as graphene decorated with a large number of oxygen-containing functional groups, such as hydroxyl, carboxyl, carbonyl and epoxy groups, on the surface and on the edge. It has high activity, good hydrophilicity and excellent adsorption capacity and is also easier to prepare.

In this work, graphene oxide (GO) was prepared by a modified Hummers method[1] and organic dye methyl orange (MO) solution was used as the target degradation compound, according to the photocatalytic mechanism of GO, the degradation rate of MO degraded by GO under visible light was improved by adding \( \text{H}_2\text{O}_2 \), aeration and increasing light intensity.

2. Experimental Section

2.1. Preparation of GO and Its Dispersions
GO was prepared by the modified Hummer method[1]. 2 g of flake graphite and 2 g of sodium nitrate were added to 100 ml of concentrated sulfuric acid, after stirring at 0 °C, 12 g of potassium permanganate was added slowly, continue stirring for 90 minutes, then heat up to 40 °C and stir for 2 hours, slowly add 80 ml of deionized water and 10 ml of \( \text{H}_2\text{O}_2 \) (mass fraction 30%), take out after stirring for 10 minutes. The obtained GO was washed with deionized water, separated and dried, and then dispersed in water to obtain GO aqueous solution with a concentration of 4 mg/mL.
2.2. Photocatalytic Experiments
The photocatalytic efficiency of GO was evaluated by degrading MO solutions. In the experiment of exploring the effect of H$_2$O$_2$ on GO photocatalysis, 0.6ml of GO (4mg/mL) and a moderate amount of H$_2$O$_2$ was added to the methyl orange solution. In the other experiments, 0.6ml of GO (4mg/mL) and 3mL of H$_2$O$_2$ were added. Shake it to make it evenly distributed. A 200W light source with wavelength of 380-840nm was used to irradiate the solution to generate a photocatalysis reaction and the absorbance of the solution was determined by visible spectrophotometer at a certain interval.

3. Results

3.1. Characterization and Analysis of GO
3.1.1. Scanning electron microscope (SEM) and Energy Dispersive Spectrum (EDS) analysis. The morphology of GO was observed with SEM as Figure 1 (a). The gossamer graphene layer presents a typical graphene wrinkling and crumpling structure and is thin and transparent. EDS result shows that the weight ratio of C and O in GO is about 1.84:1 and the degree of oxidation is high.

3.1.2. Raman spectra. Raman spectra of GO is presented in Figure 1 (b) and typical Raman spectra peaks of GO can be observed. The Raman peak ratio ID/IG is about 1.03, indicating there exists a lot of defects in GO and GO possesses high activity.

![Figure 1. (a) SEM of GO and (b) Raman spectra of GO](image)

3.2. The Effect of H$_2$O$_2$ on GO Photocatalysis
The photocatalytic performance of GO cooperated with H$_2$O$_2$ was studied by photocatalytic degradation of MO solution under visible light irradiation. Figure 2 shows the typical curve of MO solution degradation process degraded by GO cooperated with H$_2$O$_2$. After 6h, the absorbance around 380nm decreases, indicating that MO begins to degrade and generates CO$_2$ and H$_2$O[2].

![Figure 2. Typical curve of MO solution degraded by GO cooperated with H$_2$O$_2$](image)
0.16ml of 4mg/mL GO and different amounts of H$_2$O$_2$ were added into each group for photocatalytic degradation respectively. The absorbance of methyl orange was measured at the maximum absorption wavelength, and the degradation rate was calculated by \((A_0 - A_t) / A_0 \times 100\%\), as shown in Figure 3. When there is no H$_2$O$_2$, the degradation effect of GO is not obvious. When H$_2$O$_2$ is 0.6-1ml, the degradation rate of the three groups can reach more than 80% within 8h. However, large amount of H$_2$O$_2$ does not promote the reaction, but inhibits it, the reasons are as follows.

Under light irradiation, GO alone can absorb photon energy, and the photocatalytic mechanism can be explained by the following formula\([3-5]\):

$$\text{GO} + h\nu \rightarrow h^+ + e^-$$

$$\text{H}_2\text{O} + h^+ \rightarrow \text{OH} + \text{H}^+$$

$$\text{OH}^- + h^+ \rightarrow \cdot \text{OH}$$

$$\text{O}_2 + e^- \rightarrow \cdot \text{O}_2^-$$

$$\cdot \text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \cdot \text{HO}_2$$

$$\cdot \text{HO}_2 + \cdot \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$$

$$\text{H}_2\text{O}_2 + \cdot \text{O}_2^- \rightarrow \text{OH} + \text{OH}^- + \text{O}_2$$

$$\text{H}_2\text{O}_2 + h^+ \rightarrow 2 \cdot \text{OH}$$

$$\text{MO} + \cdot \text{OH} \rightarrow \text{Degradation}$$

In the photocatalysis process, When methyl orange solution is illuminated, electrons(e-)-holes(h+) pairs are produced by \(\pi-\pi^*\) band excitation in the \(\pi\)-conjugated domains of GO after absorbing photon energy\([4]\) and then electrons and holes migrate to the surface of GO and serve as the oxidizing and reducing sites\([5]\). Electrons interact with oxygen to generate \(\cdot \text{O}_2^-\). \(\cdot \text{O}_2^-\) is not stable, H$_2$O$_2$ which is produced in the process will react with \(\cdot \text{O}_2^-\) and H$_2$O to produce \(\cdot \text{OH}\) eventually, H$_2$O$_2$ can also combine with holes and H$_2$O to generate \(\cdot \text{OH}\), which has strong oxidizing to degrade MO easily, so the addition of H$_2$O$_2$ can promote the photocatalytic reaction and improve the photocatalytic efficiency. However, when the concentration of H$_2$O$_2$ in the solution is too high, the \(\cdot \text{OH}\) in the system will be captured to generate \(\cdot \text{O}_2\text{H}\), which will reduce the treatment effect\([6]\).

![Figure 3. MO solution degraded by GO cooperated with different amount of H$_2$O$_2$](image)

The average photocatalytic efficiency is calculated with the following formula,

$$\eta = \frac{m_0^{\text{MO}} - m_t^{\text{MO}}}{m_{\text{cat}} \cdot t}$$

where, \(m_0^{\text{MO}}\) is the mass of MO in the initial solution, \(m_t^{\text{MO}}\) is the mass of MO in the solution after photocatalytic degradation, \(m_{\text{cat}}\) is the mass of GO used, and \(t\) is the photocatalytic treatment time.
The standard curve of concentration C and absorbance A of methyl orange obtained by linear fitting is \[ C = 12.14645A + 0.5262 \], and the average photocatalytic efficiency is calculated at the first 8h, as shown in Table 1. When 0.8ml of H$_2$O$_2$ is added, the average photocatalytic efficiency is high, which is 1.8819 h$^{-1}$, while pure GO is only 0.1482 h$^{-1}$.

**Table 1.** The average photocatalytic efficiency of GO with different amounts of H$_2$O$_2$

| H$_2$O$_2$/ (mL) | 0   | 0.6 | 0.8 | 1   | 2   | 5   | 10  | 15  | 20  |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| η/(h$^{-1}$)    | 0.1482 | 1.8171 | 1.8819 | 1.7877 | 1.3066 | 0.2627 | 0.2529 | 0.3002 | 0.1746 |

In order to explore the optimal input amount of H$_2$O$_2$ and GO, the maximum average photocatalytic efficiency group is scaled up and back to calculate the average photocatalytic efficiency, as shown in Table 2. It can be seen from the Table 2 that when H$_2$O$_2$ is 0.8ml and GO is 0.16ml, the average photocatalytic efficiency is the highest, which is 1.8819h$^{-1}$, and it is much higher than the average photocatalytic efficiency in other literature.

**Table 2.** The average photocatalytic efficiency of different amounts of H$_2$O$_2$ and GO

| Group | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------|---|---|---|---|---|---|---|---|---|
| H$_2$O$_2$/ (mL) | 0.5 | 0.8 | 1 | 1.5 | 2 | 2.5 | 3 | 4 | 5 |
| GO/(mL) | 0.1 | 0.16 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.8 | 1 |
| η/(h$^{-1}$) | 1.0522 | 1.8819 | 1.0918 | 1.2964 | 0.9266 | 0.7226 | 0.6167 | 0.4494 | 0.2880 |

The degradation rate curves of each group are shown in Figure 4. It can be seen that when H$_2$O$_2$ is 4 mL and GO is 0.8mL, the degradation rate is the highest.

![Figure 4. Different amounts of H$_2$O$_2$ and GO to photodegrade MO](image)

Plot methyl orange concentration C versus time t and power function fitting for the fastest groups during the first 8h. The concentration of methyl orange is calculated by the absorbance. The power function fitting results and correlation coefficient are as shown in Table 3.
### Table 3. Power exponent equations of C~t in different groups

| H$_2$O$_2$/mL | GO/(mL) | C~t            | R'(Adj.) |
|-------------|---------|----------------|----------|
| 1.5         | 0.3     | C=-3.50+5.64e$^{-0.058t}$ | 0.9888   |
| 2           | 0.4     | C=-3.07+5.11e$^{-0.060t}$ | 0.9917   |
| 2.5         | 0.5     | C=-3.11+5.17e$^{-0.057t}$ | 0.9943   |
| 3           | 0.6     | C=-2.63+4.70e$^{-0.070t}$ | 0.9923   |
| 4           | 0.8     | C=-1.712+3.68e$^{-0.093t}$ | 0.9937   |

When n = 1, the half-life t1/2 is independent of the initial concentration. When n ≠ 1, the relationship between half-life t1/2 and initial concentration C0 can be expressed as ln t1/2 = lnA + (1-n) ln C0, and A is constant. The half-life t1/2 of methyl orange is obtained under different test conditions. Plot ln t1/2 versus ln C0 and the unitary linear fitting is carried out. The reaction order of the test data of ln t1/2~ln C0 can be obtained, as shown in Table 4. In this experimental condition, the reaction order can be approximately considered as 3/2. The kinetic model can be expressed as

$$\frac{dC}{dt} = -kC^{3/2}$$

, integral both sides and get

$$\frac{1}{\sqrt{C}} = \frac{1}{2}kt + \frac{1}{\sqrt{C_0}}$$


### Table 4. The reaction order of MO degradation reaction by half-life method

| H$_2$O$_2$/mL | GO/(mL) | Int1/2~ln C0 | Reaction order n |
|-------------|---------|----------------|-----------------|
| 1.5         | 0.3     | -0.4456 ln C0+11.1142 | 1.45           |
| 2           | 0.4     | -0.4296 ln C0+11.0116 | 1.43           |
| 2.5         | 0.5     | -0.4630 ln C0+11.1548 | 1.46           |
| 3           | 0.6     | -0.4316 ln C0+10.9927 | 1.43           |
| 4           | 0.8     | -0.4299 ln C0+10.9172 | 1.43           |

### 3.3. Effects of Stirring and Aeration on GO Photocatalysis

As can be seen in Figure 5, there is no significant difference in degradation rate whether stirring, indicating that GO is well dispersed in the solution, and its large specific surface area can absorb the reactants, making the reaction more sufficient. It can be approximately regarded as homogeneous catalysis with high catalytic efficiency.

![Figure 5. Effect of stirring and aeration on GO photocatalysis](image-url)
3.4. Effects of Light intensity on GO Photocatalysis

Light intensity is changed by changing the lighting distance, as shown in Figure 6(a), and the degradation rate increases with the increase of the light intensity. Plot $\frac{1}{\sqrt{C_t}}$ versus t and the unitary linear fitting is carried out, as shown in Figure 6(b). It fits well and the results shows that the degradation reaction of methyl orange is in accordance with the apparent 3/2 order kinetics model. Figure 6(c) shows the relationship between the rate coefficient of 3/2 order of the methyl orange degradation under different light intensity and the light intensity. Rate coefficient increases exponentially with light intensity $E$, $k = 7.5986 \times 10^{-4} e^{6.5237 \times 10^{-5} E} + 0.0298$, and it fits well, $R^2(\text{Adj.})=0.99995$.

![Figure 6](image)

**Figure 6.** (a) Effect of light intensity on GO photocatalysis; (b) Effect of light intensity on degradation rate; (c) The relationship between the rate coefficient and illumination

4. Conclusions

GO was prepared by the modified Hummer method. The degradation rate of MO by GO under visible light was improved by adding $\text{H}_2\text{O}_2$, aerating and increasing light intensity.

1. The average photocatalytic efficiency of GO cooperated with $\text{H}_2\text{O}_2$ is much higher than that of other materials. The reaction order is 3/2 and the kinetic model can be expressed as $\frac{dC}{dt} = -kC^{3/2}$.

2. GO is well dispersed in the solution, and there is no significant difference in degradation rate whether stirring. It can be approximately regarded as homogeneous catalysis with high catalytic efficiency.

3. The degradation rate increases with the increase of light intensity. The reaction conforms to the 3/2 reaction order kinetic model. The degradation rate coefficient $k$ of methyl orange increases with the increase of light intensity $E$, and the relationship between the rate coefficient $k$ and light intensity $E$ is $k = 7.5986 \times 10^{-4} e^{6.5237 \times 10^{-5} E} + 0.0298$. 
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6. **References**
[1] Jr W S H, Offeman R E. Preparation of Graphitic Oxide[J]. Journal of the American Chemical Society, 1958, 80(6): 1339.
[2] Al-Qaradawi S, Salman S R. Photocatalytic degradation of methyl orange as a model compound[J]. Journal of Photochemistry & Photobiology A Chemistry, 2002, 148(1): 161-168.
[3] Krishnamoorthy K, Mohan R, Kim S J. Graphene oxide as a photocatalytic material[J]. Applied Physics Letters, 2011, 98(24): 032107.
[4] Matsumoto Y, Koinuma M, Ida S, et al. Photoreaction of Graphene Oxide Nanosheets in Water[J]. J.phys.chem.c, 2011, 115(39): 19280-19286.
[5] Hsu H C, Shown I, Wei H Y, et al. Graphene oxide as a promising photocatalyst for CO2 to methanol conversion[J]. Nanoscale, 2013, 5(1): 262-8.
[6] Chong M N, Jin B, Chow C W, et al. Recent developments in photocatalytic water treatment technology: a review[J]. Water Research, 2010, 44(10): 2997-3027.