

Photochemical Preparation of Selenium-rGO Composite for Application in Photocatalytic Degradation

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Abstract. Se-rGO composite photocatalyst was prepared by photochemical method and improved Hummers method. The morphology and structure of the photocatalyst were characterized by SEM and XRD. The photocatalytic properties of the composite were studied by degrading RhB under UV light. The results showed that the composite retained the original morphology of selenium and graphene oxide after compounding, where a large number of spherical Se particles are clustered and loaded on the surface of GO layers; hexagonal phase is observed in the pattern of pure Se, and the crystalline structure remains unchanged after compounding GO. The photocatalytic activity of the composite is more than twice as high as that of the pure Se. Moreover, the photocatalytic activity of the photochemical prepared Se-rGO composite is much higher than that of the mechanically mixed Se/GO. Se-rGO composite has good photocatalytic performance and the degradation process conforms well to the first-order reaction kinetics. The degradation rate of RhB solution can reach 76.8% after 120 minutes of UV irradiation.

1. Introduction

With the continuous development of science, technology and economy, environmental pollution caused by industrial production is becoming more and more serious, especially water pollution. Industrial dyes such as rhodamine B (RhB) and methylene blue (MB), having high content of organic matter and strong toxicity that will cause irreversible damage to the water system if discharged into the water without proper treatment. Therefore, water pollution treatment has become the focus of global pollution control, and the methods that commonly used to treat that mainly including physical adsorption, chemical flocculation and biodegradation, but there are many shortcomings such as long degradation cycle or low efficiency. Since reported by Bard in 1977 [1], photocatalytic degradation of wastewater has attracted wide attention in academic field. Semiconductor materials have good light response and suitable band gap, which enable them to make full use of ultraviolet or visible light. Semiconductor photocatalytic technology have unique advantages such as easy operation, low energy consumption, environmentally friendly and wide application.

Selenium (Se), belongs to chalcogenide elements, is a non-toxic non-metallic semiconductor with narrow band gap (about 1.7eV) that widely used in medicine, chemical industry, electrical and electronic industries, ceramics, metallurgy and glass manufacturing. In 1873, electrical resistance changes under light irradiation were first found in selenium [2]. After that, researchers have carried out a lot of research on the photoelectric properties of selenium. Selenium is also widely used in laser



printing, photovoltaic cells, fuel cells and X-ray instruments. Chen Y [3], Che L [4] and Xie W [5] et. al reported the photocatalytic research of Se. At present, the commonly used methods to synthesize selenium are chemical reduction and laser ablation, which involve strong reductants and complex reaction conditions. Therefore, an easy-to-operate and environmentally friendly approach to synthesize selenium is necessary.

In recent years, graphene (GR) has become one of the most attractive materials in the fields of sensors [6] and photocatalysts [7]. There are abundant π bonds in GR and the π electrons can move freely in two-dimensional plane, so the surface of GR has efficient electron transfer which gives GR good conductivity. As an important derivative, reduced graphene oxide (rGO) has very high specific surface area and a large number of π - π binding sites. It can enrich organic macromolecules on the surface of photocatalysts, which is conducive to the photocatalytic reaction, therefore improved the photocatalytic efficiency. In the past few years, Pd/GO, Au/GO and ZnO/GO [8-10] have been synthesized constantly, and they all showed good photocatalytic activity.

In this work, SeCl_4 solution was used as precursor and GO was used as raw material to prepare the in-situ Se-rGO composite by one-pot photochemical method under mild reaction conditions. Se and rGO were successfully compounded under UV irradiation at room temperature. RhB solution was used to simulate organic wastewater for the measurement of photocatalytic performance. The photocatalytic properties of the Se-rGO composite, pure Se and mechanically mixed Se/GO were compared and the reaction kinetics were also discussed. In the process of photodegradation, most of the photogenerated electrons will be transferred to rGO, which promotes the separation of the photogenerated electrons and holes and greatly inhibits the recombination of them, thus improves the photocatalytic performance of elemental selenium.

2. Experiment Section

2.1. Materials

Selenium dioxide (SeO_2 , AR, 99%), isopropanol (AR, 99%), hydrochloric acid (AR, 7%) and rhodamine B (RhB, AR, $C=1.9 \times 10^{-5} \text{ mol/L}$). Graphene oxide was synthesized by modified Hummers method with the solid content of 0.086 mg/ml.

2.2. Synthesis of Se-rGO Composite

Se-rGO composite is synthesized by one-pot photochemical method. The precursor solution is formed by dissolving selenium dioxide in a mixture of hydrochloric acid and isopropanol, followed by dropping graphene oxide aqueous solution into. The mixture was then irradiated by two ultraviolet lamps (8w, 254nm) for 8 hours under constantly magnetic stirring. The red-grey solid was then collected and washed with deionized water and ethanol several times before drying at room temperature.

2.3. Characterization

The morphologies and size of selenium, graphene oxide and the Se-rGO composite were observed by scanning electron microscopy (SEM, Carl Zeiss Gemini 500). The composition information was characterized via X-ray powder diffraction (XRD, BRUKER D8 ADVANCE D/max2200, with $\text{Cu-K}\alpha$ radiation) and the diffraction peaks and the indices of crystallographic plane were then analyzed by MDI Jade 6.5.

2.4. Measurement of Photocatalytic Activity

The degradation rate of RhB under ultraviolet light within limited time was tested to evaluate the photocatalytic performance of the composite. 12.5 mg of the Se-rGO composite was added to 100 ml RhB aqueous solution and treated ultrasonically for 15 minutes to make the composite disperse evenly. The solution was placed in a dark box under continuously stirring for 30 minutes to achieve the adsorption-desorption equilibrium between the dye and the catalyst. After the photodegradation began, 5 ml solution was taken out every 20 minutes and centrifuged at 4000 rpm for 2 minutes, then the absorbance of supernatant was measured at 553 wavelength. The photodegradation rate is calculated

by the following formula:

$$\eta = \frac{C}{C_0} * 100\%$$

In the formula, η is the photodegradation rate, C_0 is the concentration of RhB after adsorption, and C is the concentration of RhB at photocatalytic reaction reaches time t . The photocatalytic properties of selenium, graphene oxide and mechanically mixed Se/rGO were also tested for comparison.

3. Results and Discussion

3.1. Composition and Morphology

Figure 1 shows the SEM and XRD information of Se, GO and the Se-rGO composite. Figure 1a shows that selenium is presents as spherical particles with diameter ranging from 0.5-1.5 μm , and some of the Se spheres are fused and aggregated. Graphene oxide showed the usual morphology as thin-layer folded structure (Figure 1b). After compounding, the original morphology of selenium spheres and GO are basically retained and GO is coated on the surface of selenium spheres (Figure 1c).

Figure 1d shows the XRD patterns. The prepared GO has a characteristic peak of $2\theta=12.5^\circ$. The broad diffraction peaks of Se observed at $2\theta=23.52^\circ$, 29.70° , and 51.72° correspond to the (100), (101) and (201) planes of hexagonal selenium (JCPDS card NO. 06-0362). No other diffraction peaks are observed in the XRD spectra, which indicates that the as-prepared samples have high purity. The characteristic peaks of composite are almost the same as those of elemental selenium, indicating that combination with graphene oxide does not change the crystalline structure of selenium.

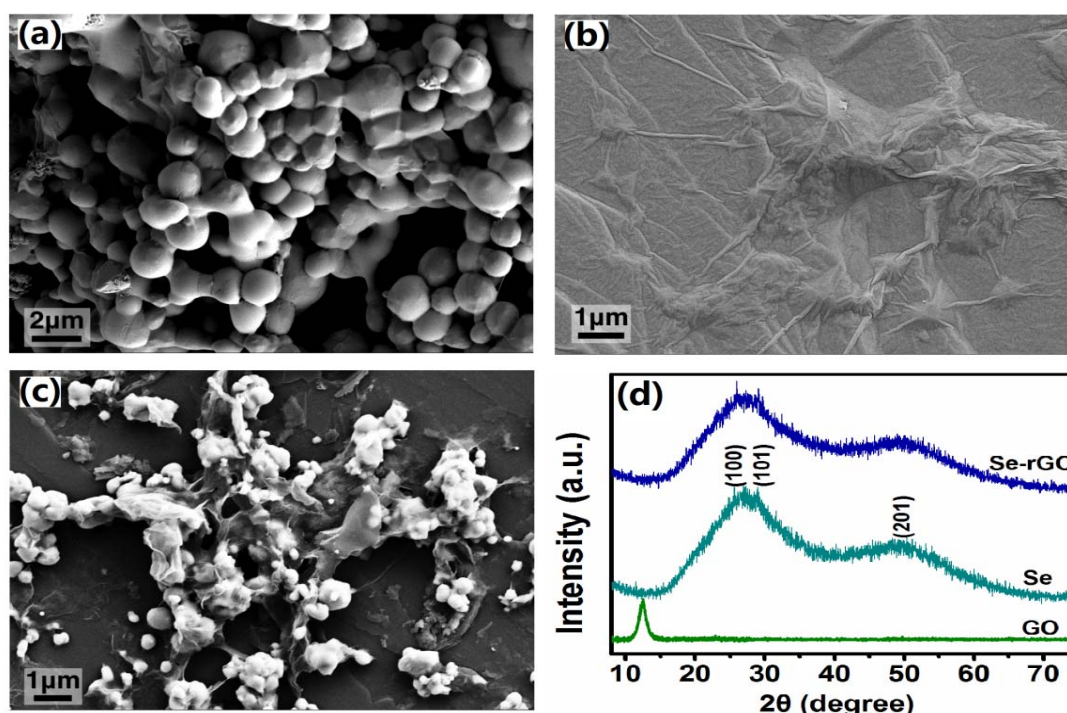
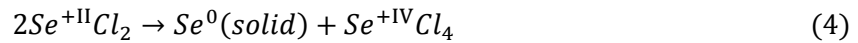
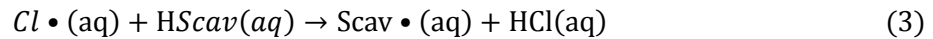
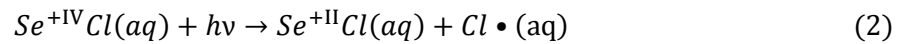


Figure 1. The SEM images of (a) pure Se, (b) pure GO, (c) Se-rGO composite; and (d) XRD patterns of Se, GO and Se-rGO composite.

3.2. Growth Mechanism

Simply put, SeO_2 is dissolved in hydrochloric acid solution to form SeCl_4 , then reacts as follows under the driving of UV light:





Graphene oxide absorbs electrons under ultraviolet radiation and partially reduces to form reduced graphene oxide. Reduced graphene oxide contains abundant hydrophilic oxygen-containing functional groups such as hydroxyl group and epoxy group [11] that can provide sites for the growth of selenium, a tightly bounded in-situ Se-rGO composite was thus prepared. The growth process is shown in Figure 2.

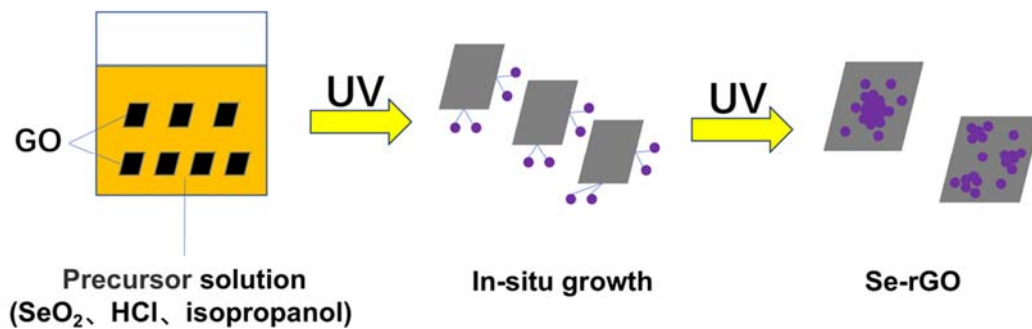


Figure 2. Schematic view of the formation mechanism of the composite Se-rGO.

3.3. Photocatalytic Activity

In order to investigate the photocatalytic properties of the composite, the degradation of RhB by elemental Se, pure GO, Se-rGO composite and mechanically mixed Se/GO was examined, and the reaction rates were calculated and compared. Before the photodegradation started, the catalyst was added to RhB aqueous solution, and the mixture was treated by ultrasound to make the catalyst disperse evenly. The mixture was then stirred in darkness for 30 minutes to achieve an adsorption-desorption equilibrium. The results show that all samples have a certain degree of adsorption on RhB aqueous solution. The degradation rate curves of RhB in 120 minutes are shown in Figure 3a and the corresponding degradation efficiency is summarized in Figure 3b. The photocatalytic degradation rate of RhB with Se-rGO was the highest with 76.8%, and that of pure Se and mechanically mixed Se/GO was 31.1% and 19.5%, respectively. Pure GO did not show degradation ability. Compared with the degradation of RhB by in-situ composite Se-rGO and mechanically mixed Se/GO, it can be concluded that the combination of the two components is tighter and the built-in electric field is more conducive to charge transfer and electron hole separation [12], which makes the higher photocatalytic activity of Se-rGO. In addition, the absorbance of RhB aqueous solution increased when pure GO or mechanically mixed Se/GO was added, indicating that the desorption between dyes and catalysts occurred after illumination, which also contributed to the poor photocatalytic performance. Kinetic analysis of all degradation reactions was carried out (Figure 3c). The corresponding equation was suggested as follows:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad [13]$$

k represents the apparent reaction rate (ARR) constant. It can be seen that the catalytic behavior of all catalysts conforms well to the first order kinetics. The ARR constants of all samples are summarized in Figure 3d, and Se-rGO has the highest value of 0.0218 min^{-1} . The ARR of pure Se, pure GO and mechanically mixed Se/GO are 0.0119 min^{-1} , 0.0100 min^{-1} and 0.00010 min^{-1} , respectively.

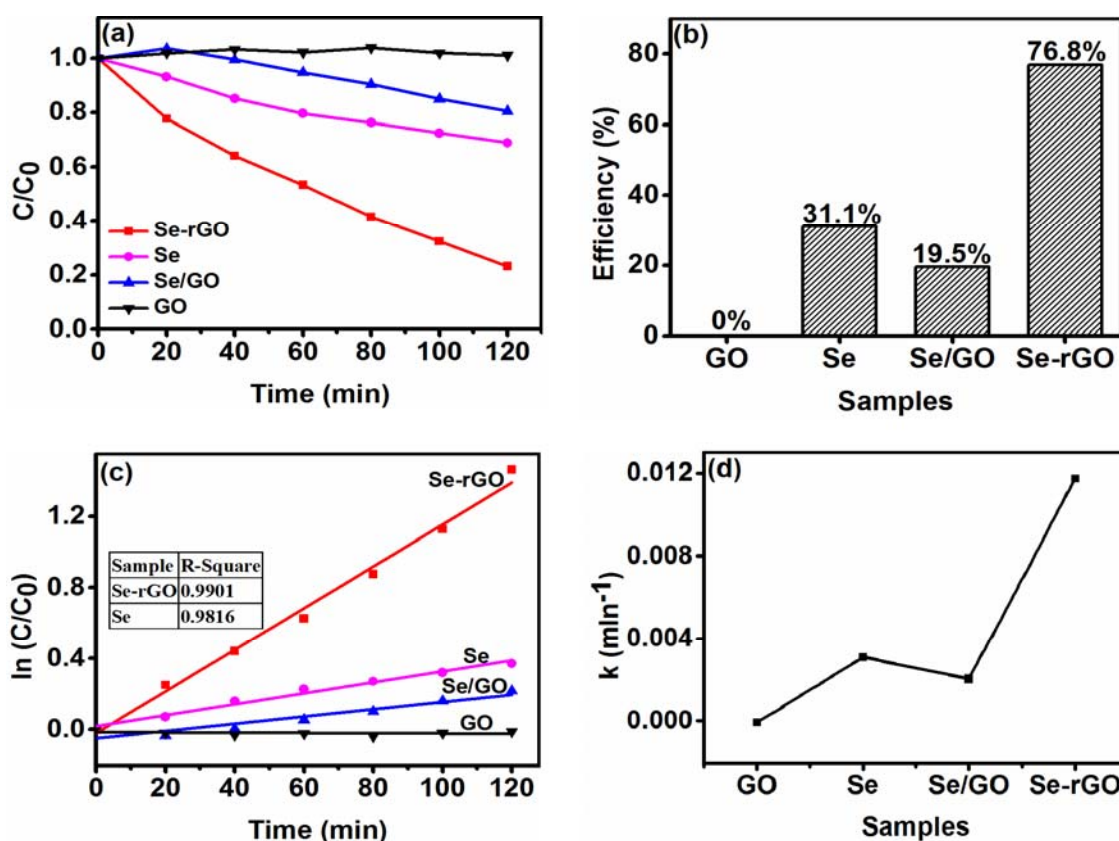


Figure 3. The photocatalytic activities of Se, rGO, Se-rGO and Se/rGO. (a) The degradation rate curves of RhB in 120 minutes; (b) The degradation efficiency of RhB in 120 minutes; (c) First-order kinetic simulations of the degradation processes of different materials; (d) Summary of the ARR constants.

3.4. Photocatalytic Mechanism

The typical photocatalytic mechanism is that the free radicals with photoactivity functioning as the active catalytic species, generally considered as hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$) [14]. In order to verify the existence of these free radicals, free radical scavenging experiments were carried out. Methanol (as h^+ scavenger) and tert-butanol (as $\bullet\text{OH}$ scavenger) were added to RhB aqueous solution respectively in the presence of Se-rGO, and pure nitrogen (as $\bullet\text{O}_2^-$ scavenger) was also bubbled into. The results of controlled photocatalytic experiments are shown in Figure 4a. Compared with the solution without any scavenger, the addition of methanol or nitrogen almost completely inhibited the degradation of RhB, while the degradation rate of RhB decreases significantly when the solution was added with tert-butanol. The results showed that the main active species in the photocatalytic degradation process were $\bullet\text{OH}$ and $\bullet\text{O}_2^-$. Therefore, the catalytic mechanism can be expressed as shown in Figure 4b. When irradiated by ultraviolet or visible light, holes and electrons will be generated in Se-rGO. In the following reaction process, photogenerated electrons react with dissolved oxygen to produce superoxide radicals, which will be further converted into hydroxyl radicals, and H_2O reacts with photogenerated holes h^+ to produce hydroxyl radicals. Hydroxyl radicals possess strong oxidation that can degrade dye molecules into carbon dioxide and water [15]. Due to the good conductivity of graphene, a large number of photogenerated electrons are transferred from Se to rGO, which greatly inhibits the electron-hole recombination rate and enhances the photocatalytic ability.

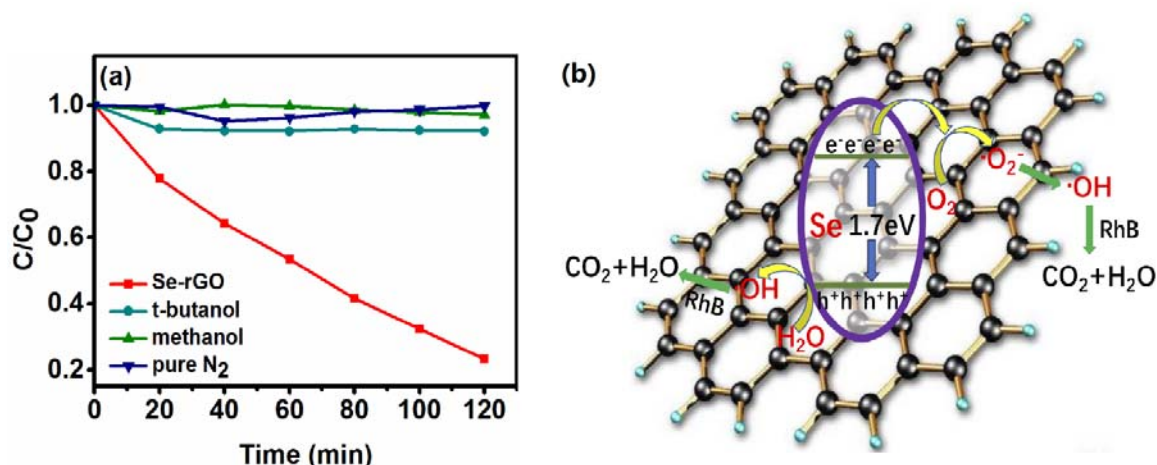


Figure 4. (a) The photodegradation behavior of the RhB aqueous solution in the presence of Se-rGO under varied controlled conditions; (b) The schematic view of proposed mechanism of the RhB degradation in the presence of Se-rGO.

4. Conclusion

In summary, the Se-rGO composite photocatalyst was prepared by a simple photochemical method. After in-situ compounding with graphene, the photogenerated electron-hole recombination rate decreased, which resulting a significant improvement in the photocatalytic performance of the Se-rGO compared with that of pure Se and mechanically mixed Se/GO. The degradation rate of RhB reaches 76.8% within 120 minutes of low-power UV irradiation. The mechanism study reveals that the hydroxyl radicals ($\cdot OH$) and superoxide radicals ($\cdot O_2^-$) are the main active species in degradation. Photochemical method is a promising method in the synthesis of catalysts, and the Se-rGO composite have broad applications in photocatalysis, sensors and batteries.

5. Acknowledgements

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6. References

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