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Facile Synthesize rGO/Ag₃PO₄ with Enhanced Photocatalytic Degradation of organic dye by a Microwave-assisted Method

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ABSTRACT:

To design and synthesis of highly efficient photocatalysts by a facile, environmental friendly, and economical method has become of vital importance in the photocatalytic field. With the assist of a simple microwave treatment for 40 min, the reduced graphene oxide /Ag₃PO₄ (rGO/Ag₃PO₄) visible-light-response photocatalyst can be rapidly synthesized under atmosphere. TEM results show that the irregular Ag₃PO₄ particles are distributed on the surface of rGO sheet. In the photo-degradation process of Methyl Orange (MO), the optimum photocatalytic activity of rGO(1.5 %)/Ag₃PO₄ under simulated daylight is almost 2 times higher than pure Ag₃PO₄. Obviously, this facile method paves a convenient way to prepare visible-light-response Ag₃PO₄-based composites with high photocatalytic efficiency in large scale and also to reduce the high cost of Ag₃PO₄ for practical uses.

Keywords: microwave-assisted method; rGO/Ag₃PO₄; simulate daylight photocatalytic

1. Introduction

Over the past few decades, the design and synthesis of highly efficient photocatalysts have attracted considerable attention because of their potential applications in the water splitting for hydrogen production, removal and degradation of organic pollutants, and reduction of CO_2 into renewable chemical fuels [1-3]. Recently, silver orthophosphate (Ag_3PO_4) has been reported as a new photocatalyst for the oxidation of water and photodecomposition of organic compounds [4-6]. These works demonstrate that Ag_3PO_4 is a suitable candidate for the application in photocatalytic fields. However, pure Ag_3PO_4 is easily photocorroded and decomposed to weakly active silver during the photocatalytic reaction process, which is the main hindrance for the practical application of Ag_3PO_4 as a recyclable and highly efficient photocatalyst. The efficient way to overcome this disadvantage is to combine Ag_3PO_4 with a metal or other semiconductor to form hybrid materials [7, 8].

Graphene have been used in synthesizing semiconductor composite photocatalysts to improve the photocatalytic performance due to the effective separation of the photogenerated electron-hole pair and the increase of the reactive sites in the photocatalytic process [9]. Recently, it is reported that the photocatalytic activity and stability of the Ag_3PO_4 photocatalyst could be further improved by the modification of graphene. Although there have been some reports on $\text{rGO}/\text{Ag}_3\text{PO}_4$ composites [10,11], as a promising hybrid photocatalyst, the exploration of $\text{rGO}/\text{Ag}_3\text{PO}_4$ composites still has a long way to go, especially through a facile, environmentally friendly, and economical method.

Microwave-assisted synthesis is an effective tool in synthetic organic chemistry because of its unique features such as rapid and selective heating, higher reaction rates, increased product yields, and energy saving [12]. In this work, rGO/Ag₃PO₄ has been synthesized via microwave method at the first time. The structures and morphologies of the constructed materials were analyzed by Raman, XRD, SEM, and TEM. Photocatalytic activity was assessed by analyzing the decomposition of MO solution. The significant enhancement of photocatalytic properties was observed. Conspicuously enhanced photocatalytic activity was achieved by comparing with pristine Ag₃PO₄ in the present study. Moreover, the effect of mass ratios of rGO in the rGO/Ag₃PO₄ composites on the photocatalytic activity was explored comparatively. The possible mechanism for enhanced photocatalytic activity was proposed based on the obtained experimental results. The presented method needs no surfactant or post-annealing treatment, which can reduce the cost. Thus, it is suitable for industrial production of rGO/Ag₃PO₄.

2. Experimental

2.1 Preparation of the rGO/Ag₃PO₄ Composite Materials. Graphene oxide was prepared by the improved Hummer method [13]. In a typical synthesis, AgNO₃ aqueous solution (50 mL, 0.1 M) was added to GO aqueous suspension (7.2 mL, 1.8 mg mL⁻¹) with stirring. The acquired mixed suspension was kept stirring for another 30 min to ensure the electrostatically driven assembly of positively charged Ag⁺ on the surface of negatively charged GO sheets. Then, Na₂HPO₄ aqueous solution (50 mL, 0.3 M) was added dropwise to the mixture, and the reaction mixture was kept

stirring for 30 min. Yellow precipitate was observed due to the formation of Ag_3PO_4 ($3\text{Ag}^+ + \text{PO}_4^{3-} = \text{Ag}_3\text{PO}_4$). Ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) was added to adjust pH to 12. The mixture was then placed in a microwave (XH-300UL Beijing Xiang Hu Science and Technology Development Co. LTD). With the assist of microwave, rGO/ Ag_3PO_4 composite is easily acquired in a short time of 40 min with a power of 120 W under atmosphere. The temperature in the synthesized process was 100 °C kept by the microwave radiation. After letting it cool at room temperature, the precipitates were washed three times with distilled water and finally dried in oven at 60°C for 24 h. According to the above method, the rGO/ Ag_3PO_4 samples with different weight ratios of rGO (0 %, 0.5 %, 1 %, 1.5 %, 2 % and 2.5 %) were prepared.

2.2 Analyses of Material Properties. The structures of samples were investigated by X-ray diffraction (XRD, $\text{CuK}\alpha$ Philips PW3710) in 2 θ mode and Raman spectra (Renishaw RM-1000). A scanning electron microscope (SEM, Hitachi S-4200) and transmission electron microscope (TEM, JEOL JEM-2100F) were used to examine the morphologies and the elemental make up of the rGO/ Ag_3PO_4 composites. Room temperature photoluminescence (PL) spectra were recorded by Perkin Elmer Instruments (LS-55). To measure the photocatalytic property of the hybrid, MO has been taken as a representative organic pollutant in water since most of the fabric industries use MO as the coloring agent. The photocatalytic degradation experiment of MO is performed by taking 10 mL of 1×10^{-3} g/L MO solution in a cylindrical vessel. 0.01 g prepared photocatalyst was added to 10 mL MO with a concentration of 10 mg/L. After the dark adsorption for 30 min to ensure absorption-desorption

equilibrium, the measurement was done. The solution was stirred while being irradiated by Xenon lamps of 800W (Xu Jiang Nanjing) (The light intensity of 800 W Xenon lamp is about 4000 lux). After every 1 min for simulate daylight irradiation, the suspensions were collected and then centrifuged (10000 rpm, 5 min) to remove the photocatalyst particles. The absorbance property of the dye-containing solution was measured by UV-vis spectrophotometer.

3. Results and discussion

rGO/Ag₃PO₄ composite has been successfully synthesized via a facile microwave method at the first time. Irregular Ag₃PO₄ particles tightly combine with rGO sheets, which supply an efficient transfer channel for photogenerated electron. It is favorable for improving the photocatalytic degradation of organic dyes.

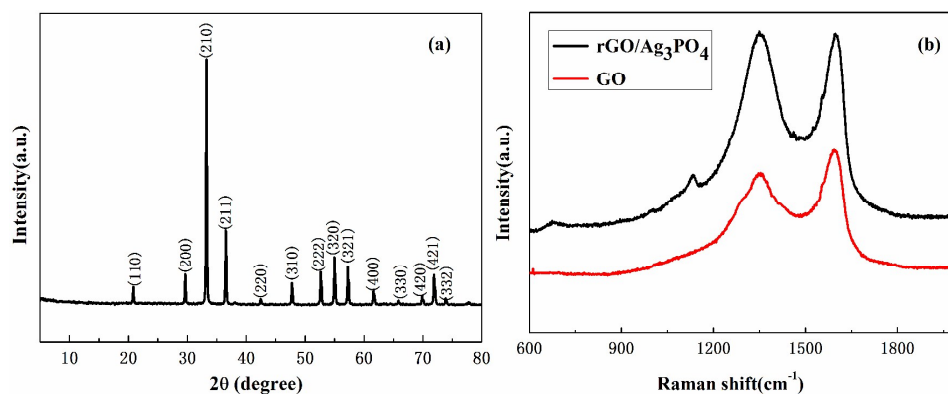


Fig. 1 (a) Typical XRD pattern of rGO/Ag₃PO₄;

(b) Typical Raman spectra of rGO/Ag₃PO₄ and GO powder.

3.1 XRD Analysis. The XRD pattern of rGO/Ag₃PO₄ composite is shown in Fig.1(a). All of the diffraction peaks could be well indexed to the cubic phase of Ag₃PO₄ (JCPDS no. 060505), which is in agreement with the previous reports [14, 15]. No diffraction peaks corresponding to rGO are observed in the rGO/Ag₃PO₄ composite, which may be due to the small amounts and relatively low diffraction

intensity of rGO in the sample [12].

3.2 Raman Spectra. Fig. 1(b) shows the Raman spectra of as-synthesized GO and rGO/Ag₃PO₄. It is well known that GO exhibits two characteristic main peaks of D band at 1350 cm⁻¹ and G bands at 1594 cm⁻¹. The G band is attributed to the in-plane vibration of sp² bonded carbon atoms while the D band suggests the presence of defects within the hexagonal graphite structure [16]. The I_D/I_G value of rGO/Ag₃PO₄ is about 1.009 and the I_D/I_G value of GO is about 0.8583. It is obvious that the composite shows relatively higher intensity of D band compared with GO, which confirms that the GO sheets are restored during microwave treatment [17].

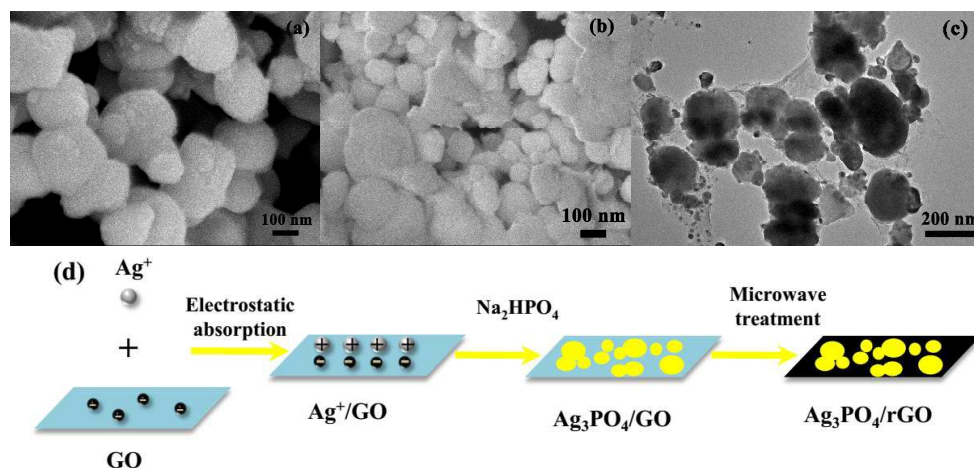


Fig. 2 (a) SEM image of Ag₃PO₄; (b) Typical SEM image of rGO/Ag₃PO₄ composite; (c) TEM image of rGO/Ag₃PO₄ composite; (d) Schematic illustration of the synthesis process.

3.3 Microstructure Analysis and Formation Process. Fig. 2(a) shows the SEM image of Ag₃PO₄. It is composed of irregular Ag₃PO₄ particles. The rGO/Ag₃PO₄ composite (Fig. 2(b)) clearly consists of sphere-like Ag₃PO₄ with different sizes, the size of some particles are less than 10 nm, and others are larger than 200 nm. The SEM observations imply that the presence of rGO causes a slight decrease in the size

of Ag_3PO_4 particles in the $\text{rGO}/\text{Ag}_3\text{PO}_4$ composites. The TEM image of the $\text{rGO}/\text{Ag}_3\text{PO}_4$ composite is shown in Fig. 2(c). The size of Ag_3PO_4 in TEM is consistent with that in SEM. It seems that large amounts of Ag_3PO_4 particles are distributed on the surface of rGO sheets. This structure might provide enough contact surface area between rGO sheets and Ag_3PO_4 particles, and also presumably facilitate charge-carrier transport. According the reaction in the synthesis process and TEM results, a probable synthesis mechanism of $\text{rGO}/\text{Ag}_3\text{PO}_4$ is proposed which is shown in Fig. 2(d). Firstly, The Ag^+ ions are absorbed on the GO surface due to the electrostatic interaction. Then, yellow Ag_3PO_4 precipitate is formed on the surface of GO with the adding of Na_2HPO_4 into to the mixture. Finally, GO is reduced to rGO rapidly in alkaline conditions with microwave treatment and the $\text{rGO}/\text{Ag}_3\text{PO}_4$ composite is formed. Meanwhile, it is thought the crystalline quality of Ag_3PO_4 would be improved.

3.4 Photocatalytic Activity. The photocatalytic activities of as-prepared samples were evaluated by the degradation of MO under simulate daylight irradiation, which is shown in Fig. 3a. Significantly, the $\text{rGO}/\text{Ag}_3\text{PO}_4$ photocatalysts with different rGO concentrations of 0.5 %, 1 %, 1.5 %, 2 % and 2.5 % exhibit much higher photodegradation activities for photodegrading MO than the pure Ag_3PO_4 , and the photocatalytic activity is enhanced remarkably with the increasing of the rGO proportion in the composites. When the rGO content achieves to 1.5 %, the as-prepared photocatalyst exhibits the highest photocatalytic activity and can degrade MO by 93.47% in 6 min. This can be attributed to the formation of the tight

rGO-semiconductor heterojunction which can effectively promotes the transfer of the charge from rGO nanosheets under the simulate daylight irradiation. However, a remarkable decrease in the degradation rate of MO under the same photolysis condition occurs with further increasing the proportion of rGO to 2 %, which may result from that the excess loading of rGO can reduce photon absorption and dye adsorption for Ag_3PO_4 .

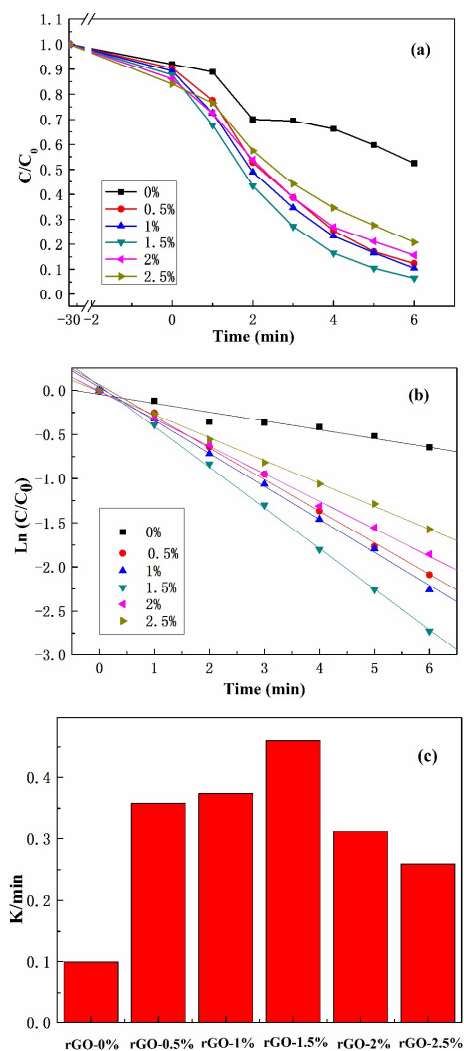


Fig. 3 (a) Degradation rate of MO for pure Ag_3PO_4 and $\text{rGO}/\text{Ag}_3\text{PO}_4$ composites under simulated daylight; (b) First-order kinetics plot for the photodegradation of MO for Ag_3PO_4 and $\text{rGO}/\text{Ag}_3\text{PO}_4$ composites; (c) Degradation rate constant k (min^{-1}) for the photodegradation of MO for Ag_3PO_4 and $\text{rGO}/\text{Ag}_3\text{PO}_4$ composites.

To have a better understanding of the reaction kinetics of the MO degradation by various photocatalysts, the above experimental data are fitted by a first-order model as expressed by Equation (1):

$$-\ln(C/C_0)=kt \quad (1)$$

Where k is the rate constant (min^{-1}) that commonly gives an indication of the activity of the photocatalyst, C_0 and C are the initial concentration and the concentration at different degradation time of MO dye, respectively. Fig. 3b shows a linear relationship between $\ln(C/C_0)$ and the irradiation time for the degradation of MO. As can be seen from Figure 3b, the photocatalytic degradation curves for all samples fit well with pseudo-first-order kinetics. Furthermore, the degradation rate constant k shown in Fig. 3c indicates that the 1.5 % rGO/Ag₃PO₄ composite exhibits the highest degradation rate.

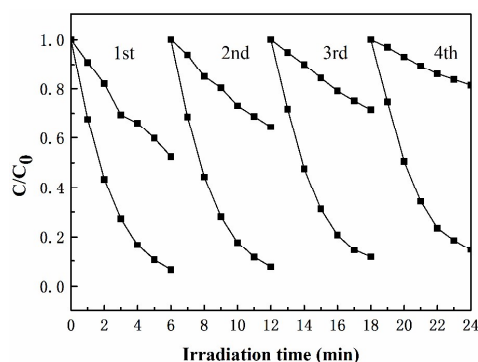


Fig. 4 Cycling runs of pure Ag₃PO₄ and 1.5 % RGO/Ag₃PO₄ composite for the degradation of the MO solution under simulated daylight.

The stability of photocatalysts is important to their practical applications. To further investigate the stability of the prepared rGO/Ag₃PO₄, cycling degradation experiments of MO were performed, as shown in Fig. 4. 1.5% rGO/Ag₃PO₄ maintains

a high photocatalytic activity after four cycles. By contrast, the pure Ag_3PO_4 shows a significant reduction in its photocatalytic degradation activity, which already decreased by about 30% in the fourth cycling. The possible reason for the great improvement of the photocatalytic stability of 1.5% $\text{rGO}/\text{Ag}_3\text{PO}_4$ is that the introduction of graphene can facilitate the electron transfer of Ag_3PO_4 , which promoted the effective separation of photoexcited electron-hole pairs and decrease the photocorrosion of Ag_3PO_4 .

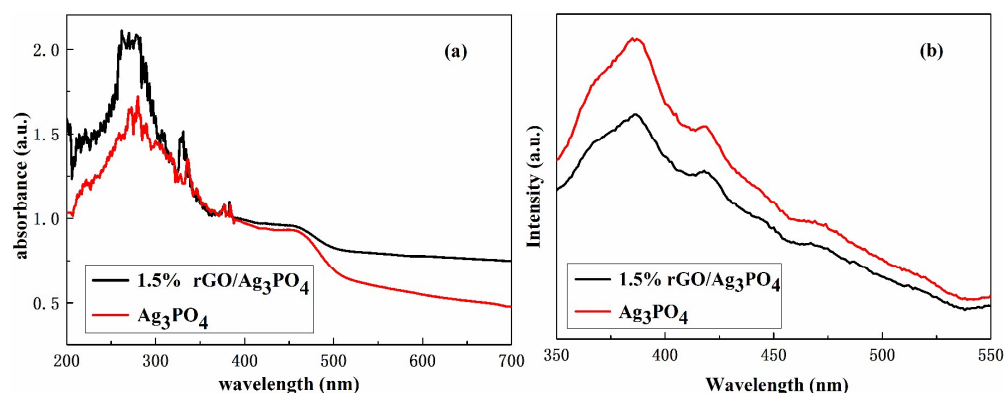


Fig. 5 UV-Vis and PL spectra of Ag_3PO_4 and 1.5 % $\text{rGO}/\text{Ag}_3\text{PO}_4$ composite.

Fig. 5a shows UV-Vis absorption spectra of Ag_3PO_4 and 1.5 % $\text{rGO}/\text{Ag}_3\text{PO}_4$. Pure Ag_3PO_4 shows the characteristic absorption edge at 561 nm. The wavelength threshold is corresponding to a band gap of 2.21 eV. Compared with Ag_3PO_4 , the slope of the absorption edge for 1.5 % $\text{rGO}/\text{Ag}_3\text{PO}_4$ becomes small, which is different from the almost unchanged of the slope reported by Chai et al. [10]. This indicates the interaction between rGO and Ag_3PO_4 . Moreover, stronger absorption in the visible range occurs. The accurate bandgap of $\text{rGO}/\text{Ag}_3\text{PO}_4$ could not get from the plotting of the absorption edge due to the strong absorption resulting from the addition of the rGO . However, a decrease of the bandgap could be inferred by a redshift of the

absorption edge. Both the decrease of the bandgap and the stronger absorption should be attributed to the combination Ag_3PO_4 particles and rGO sheets. Thus, it is expected that rGO/ Ag_3PO_4 should have enhanced photoactivities than the pure Ag_3PO_4 sample.

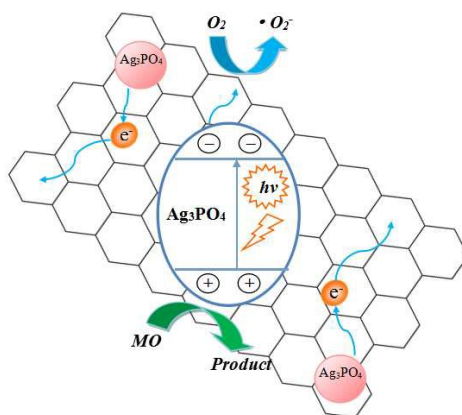


Fig. 6 Schematics of the band diagram and charge transfer mechanism between Ag_3PO_4 and rGO.

The effective separation of photogenerated electrons and holes in the rGO/ Ag_3PO_4 composite is confirmed by PL emission spectra of pure Ag_3PO_4 and 1.5 % rGO/ Ag_3PO_4 composite. It is well-known that the PL spectra of semiconductor materials result from the recombination of photo-induced charge carriers. In general, the lower PL intensity indicates a decrease in the recombination rate of photogenerated charge carriers. As shown in Fig. 5b, the strong emission peak is located at about 380 nm for the bare Ag_3PO_4 , which could be attributed to the recombination of the charge transfer transition between the O 2p orbital and the empty d orbital of central Ag^+ . Compared with pure Ag_3PO_4 , the emission peak intensity of the rGO/ Ag_3PO_4 composite decreases moderately, which indicates that the recombination of photogenerated electron-hole pairs is inhibited by the electron conductive channel between Ag_3PO_4 and rGO. It is verified that the photogenerated

electron-hole pairs could be effectively separated due to combination of rGO and Ag_3PO_4 .

The photocatalytic mechanism was shown in Fig. 6. Firstly, Ag_3PO_4 was excited when the composite photocatalyst was irradiated. Electrons in valence band was excited to conduction band, then the electron could be migrated to the rGO under the effect of electricfield in the composite body, and subsequently retransferred to the surface of the rGO to participate in the photocatalytic reaction. The efficient transfer of the electron could be ascribed to the rGO with the ability to efficiently separate electron-hole pairs. The holes were left in the valence band. Therefore, the photocatalytic performance of the $\text{rGO}/\text{Ag}_3\text{PO}_4$ was improved.

4. Conclusions

In summary, we have demonstrated a simple method for rapid synthesis of the reduced graphene oxide/ Ag_3PO_4 ($\text{rGO}/\text{Ag}_3\text{PO}_4$) composite. With a simple microwave treatment for 40 min, the formation of $\text{rGO}/\text{Ag}_3\text{PO}_4$ composite by the combination of rGO and Ag_3PO_4 with high crystalline quality and the transformation of graphene oxide (GO) to rGO can be achieved simultaneously in one step under atmosphere. According to the results of the Uv-vis absorption spectra and PL measurements, the enhanced photocatalytic activity and stability is attributed to the excellent separation of photogenerated electrons and holes resulting from the combination of the rGO and Ag_3PO_4 . Accordingly, a transfer mechanism of photoninduced electrons is proposed between Ag_3PO_4 and rGO. Obviously, this method paves a convenient and economical way to prepare visible-light-response Ag_3PO_4 -based composites with high

photocatalytic efficiency in large scale.

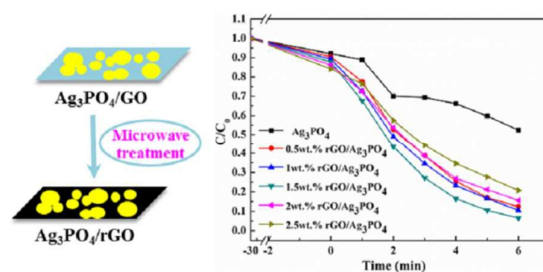
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A facile and rapid microwave-assisted method was developed to synthesize high efficient $\text{rGO}/\text{Ag}_3\text{PO}_4$ photocatalyst.