Evaluation of Photocatalytic Activity of Co_3O_4/Graphene Composite

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Abstract. Cobalt oxide/graphene (Co_3O_4/rGO) was successfully prepared using hydrothermal method. The major aim of the study is to investigate the photocatalytic activities on the removal of methyl orange (MO). These as-prepared catalysts (Co_3O_4, rGO and Co_3O_4/rGO) were investigated for the degradation of MO via photocatalysis process and were successfully achieved. The photocatalysts were compared with the corresponding bare Co_3O_4 and rGO respectively and demonstrated for the photo-degradation activity for MO. One of the significant findings emerged from this study was that Co_3O_4/rGO exhibits a very high photocatalytic activity in degradation of MO solution under visible or UV-visible light irradiation compare with UV and in darkness. The Co_3O_4/rGO exhibits better photocatalytic activity in a low concentration of MO compared to the highest concentration. The higher loading amount of Co3O4 on Co3O4/rGO contributes more on the activity.

Introduction

Environmental pollution is a global concern and its magnitude is increasing rapidly due to urbanization, industrialization and changing lifestyles of people consumption. Synthetic textile dyes and other industrial dyestuffs is one of the major water pollutants. The dyes are not only affecting the light irradiation in water, which is important for the delicate balance of the ecosystem of the waterways, many of these dyestuffs are toxic and some of them are carcinogenic and mutagenic, resulting in adverse impact on human and animal health.[1]

Photocatalysis is a highly attractive method for removing organic pollutants because it eventually decomposes the organic molecules into CO_2 and H_2O causing no additional waste. [2] Some types of semiconductors are considered as an ideal photocatalyst, which are stable, inexpensive, non-toxic and highly photoactive, including TiO_2, ZnO and other metal oxides. However these semiconductors with wide band gaps mainly absorb ultraviolet (UV), which only accounts for about 4% of the solar radiation energy, while the visible light (Vis) contributes to about 43%.[3, 4] The development of an effective photocatalyst using visible light irradiation to response for wastewater treatment remains a challenge. Recently, cobalt oxide (Co_3O_4) has attracted enormous research interest in many fields, including gas sensors, catalysts, supercapacitor and lithium-ion batteries.[5] The Co_3O_4 is a kind of p-type semiconductor, which has higher hole concentration than electrons, and is sensitive to visible light. Various Co_3O_4-graphene hybrid materials have been synthesized for oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and catalytic oxidation of methylene blue (MB), [6, 7] indicating excellent catalytic property of Co_3O_4-graphene. Therefore, the main purpose of this study is to investigate the performance of Co_3O_4/reduced graphene oxide (rGO) for the degradation of methyl orange (MO).

Experimental

Pure Cobalt Oxide (Co_3O_4) was prepared through chemical method and synthesized via hydrothermal treatment process, with detailed procedure as described by Dai et al.[6] The

Co_3O_4/rGO composite can be synthesized as described below: 0.432g of graphene oxide was dispersed in to 24 ml of Ethyl Alcohol, sonicating for 60min in ultrasonic cleaner (220 V, 50/60 Hz) to achieve homogenous solution. After sonication, 1.2 ml of 0.2 M of $Co(Ac)_2$ was added to the mixture followed by 1.2ml of water and continued to stirred for 10 hours at a temperature of 80 ^oC. The resulting solution was then transferred into a 40 ml autoclave for hydrothermal reaction at 150 ^oC for 3 h. After cooling to room temperature, the solution was collected and separated through centrifugation, followed with drying in vacuum oven at 65 ^oC for 24 hours.[8]

The photocatalytic activity of Co_3O_4, rGO and Co_3O_4/rGO was measured by the photodegradation of MO under visible light irradiation. In each test, 10 mg of catalyst was added into 25ml of MO solution with magnetic stirring in darkness for 30 minutes to achieve an adsorption/desorption equilibrium of MO on the catalyst. Then, the solution was exposed under visible light or UV-vis light (Xenon lamp). The samples were drawn every 30 minutes from the reactor for the analysis of MO concentration, which is measured by the absorbance at 464 nm using a UV-Vis spectrometer (LKB Biochrom Novaspec II).

Results and discussion

Photocatalytic evaluation of different materials (Co_3O_4, rGO and Co_3O_4/rGO). The synthesized Co_3O_4/rGO nanomaterials were applied in the photodegradation of MO. As Co_3O_4 is p-type semiconductor that works under visible light irradiation, the photodegradation reactions were performed under visible light. The comparison of the photocatalytic activity of Co_3O_4, rGO and Co_3O_4/rGO were investigated first, as shown in Figure 1A. MO was degraded in the presence of Co3O4 , rGO and Co3O4/rGO, which suggested that the degradation of MO results from the photocatalyst under visible light irradiation. Compared with pure Co3O4 , the concentration of MO decreases rapidly for both pure rGO and Co3O4/rGO composites. This result showed that the photocatalytic reaction performed well in the degradation of MO. Co3O4/rGO composites showed a remarkable photocatalytic *degradation* efficiency compared with pure Co3O4. Under visible light irradiation for 180 min, 70% of the initial MO dyes were decomposed using the Co3O4/rGO composites; in contrast, only 49% of the initial dyes were decomposed for pure Co3O4 under the same condition. The photodegradation activity of the organic dyes with the presence of Co3O4/rGO composites as catalyst was higher than that with the presence of only Co3O4 or only rGO. The enhanced photocatalytic performance was mainly ascribed to the efficient charge transportation and separation from Co3O4 to rGO.

The effect of Co_3O_4 loading amount on Co_3O_4/rGO composite. In order to investigate the enhanced photocatalytic function of Co_3O_4/rGO, we varied the loading of Co_3O_4 in Co_3O_4/rGO composite in the range of 0.01g – 0.05g. As shown in Figure 1 B, an increase in Co_3O_4 results in a consistent increase of photo-degradation of MO. A 0.01g loading of Co_3O_4 only resulted in about 20% photodegradation of MO, whilst an increase to 0.05 g loading resulted in 60% MO degradation. This demonstrates that Co_3O_4 plays a critical role in this photocatalytic reaction, further confirming that the photodegradation of MO are mainly caused by the Co_3O_4, while rGO plays a role as additive to enhance the charge separation process for MO degradation due to its excellent conductivity.

The effect of different MO concentration. The effect of concentration was investigated by varying the MO concentration in range of 10ppm, 30ppm, 50ppm, 80ppm and100ppm. The photocatalytic performance of the Co_3O_4/rGO composite in terms of photo-degradation of MO via visible light irradiation was shown in at Figure 1C. The result indicates that MO in the solution was slightly removed within 180mins. The effectiveness of the materials varies with different amount of MO concentration. In a low concentration like 10ppm could only remove about 70% of the dye from the solution compared to the high concentration, which could only degrade less than 15% of MO solution. So based on the result, it was found that this Co_3O_4/rGO was able to degrade MO at low concentration compared to high concentration. On the 30ppm the photocatalytic performance dropped slightly and remains uniformed for certain duration of 180 min. This indicates that only 25%

of the MO was degraded and more than 70% remains in the solution. This behavior is likely due to the competing light absorption between MO and Co3O4/rGO.

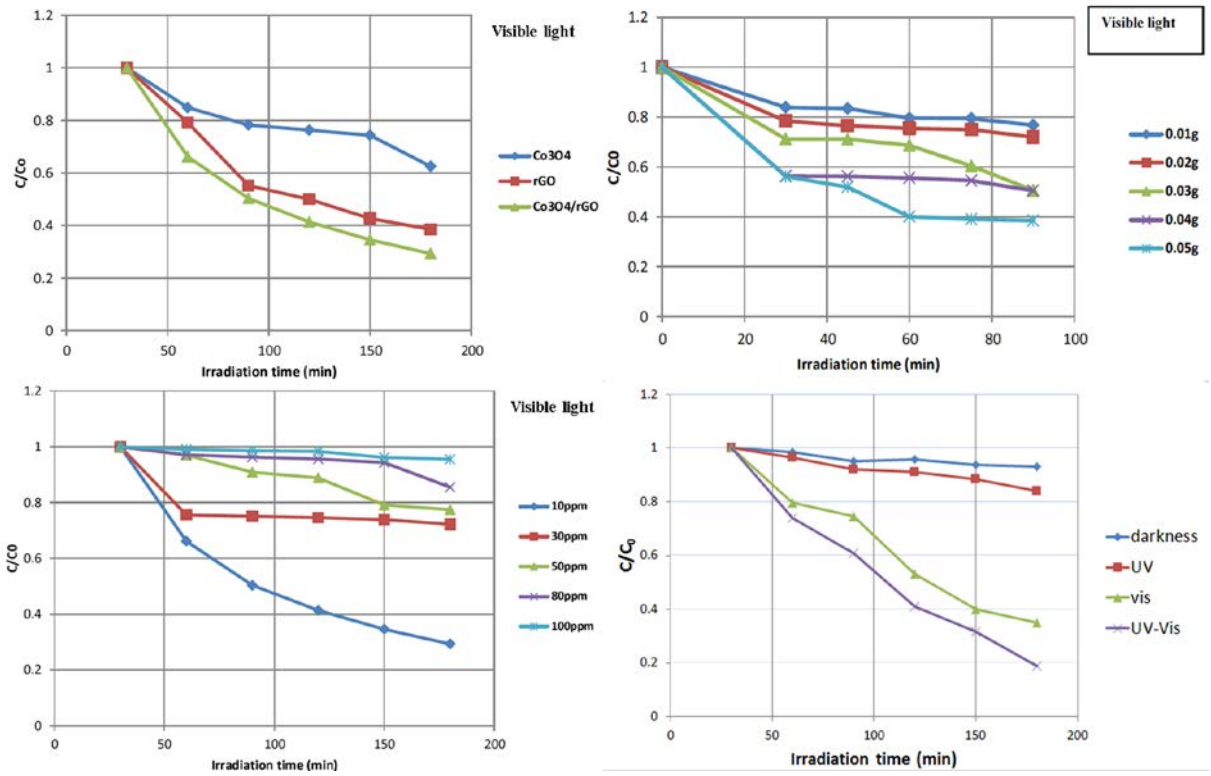

Fig.1 A) Photocatalytic activity of different materials (Co_3O_4, rGO and Co_3O_4/rGO) under irradiation of visible light; B) The effect of Co_3O_4 loading amount on Co_3O_4/rGO composite; C) The effect of different MO concentration; D) The comparison of photocatalytic activity under different light source.

Comparison via darkness, UV, visible light and UV-vis light irradiation. The results of this study will also be compared to the findings through different light source irradiation for photocatalysis including in darkness, UV light, visible light, and UV-vis light irradiation. The removal efficiency of MO in darkness indicates the Co_3O_4/rGO composite can only remove 5% of the MO through physical adsorption. The UV light irradiation was found having no obvious enhancement on the degradation performance of MO on Co_3O_4/rGO composite as Co_3O_4 is a p-type semiconductor that does not work under UV light. The Co_3O_4/rGO composite under visible light shows higher photocatalytic activity conparing with irradiating under darkness and UV. The photodegradation rate was increased when the system is shone under the full Xenon light spectrum. The sped-up reaction appears to be the additive effects of UV and visible light.

Conclusion

The following conclusions can be drawn from the present study. The most significant findings emerged from this study is that the photocatalytic activity of Co_3O_4/rGO composites is higher than Co_3O_4 and rGO on their own. Co_3O_4/rGO exhibits a very high photocatalytic activity in degradation of MO solution under visible light irradiation compare with under UV and in darkness. In addition, the Co_3O_4/rGO exhibits better photocatalytic activity in a low concentration of MO compared to the highest concentration. The higher loading of Co_3O_4 in Co_3O_4/rGO results in higher photocatalytic activity. The increase in the photocatalytic degradation efficiency can be attributed to the fact that rGO acts not only as a charge acceptor to promote the separation and transfer of photo-generated carriers but also as a support to stabilize Co_3O_4 and adsorb MO molecules in the aqueous solution.

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