

Supporting Information

Synergistic Effect of Co₃O₄ Nanoparticles and Graphene as Catalysts for Peroxymonosulfate-based Orange II Degradation with High Oxidant Utilization Efficiency

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1. The specific preparation methods of the PMEs.

A platinum wire was inserted ($r = 500$ μm diameter, 3–4 cm long) into a cylindrical glass tube and then was connected to a copper wire by spot welding or by adding graphite powder. The platinum wire was heat-sealed by an alcohol lamp flame. The exposed platinum wire was polished by emery papers (800-2400-4000 mesh) and then ultrasound in water and alcohol several times. The tip of Pt microdisk electrode was put into plenty of boiling aqua regia solution ($V(\text{HNO}_3):V(\text{HCl})=3:1$) to control a suitable corrosion depth ($L = 30\text{--}50$ μm). Subsequently, prepared power materials were filled tightly into the cavity electrode. Therefore, the powder microelectrode was obtained.

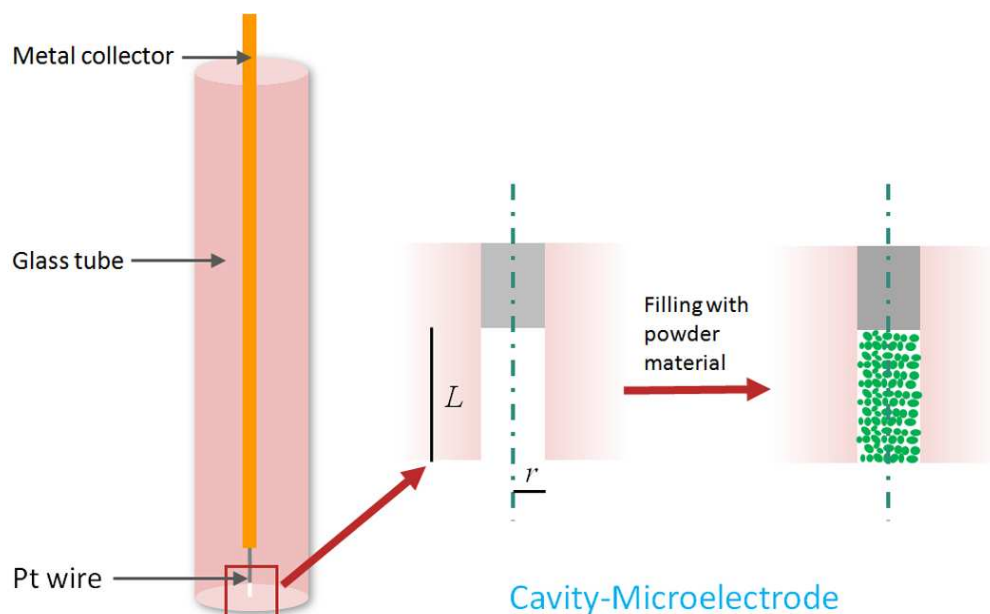


Fig. S1. The schematic diagram of the powder microelectrodes (PMEs).

2. The effect of operating factors.

The effects of various operating factors including initial solution pH, Oxone dosage, catalyst dosage and reaction temperature were investigated. The solution pH can remarkably influence pollutant degradation rate as presented in Fig. S2a in a range of 4.0–10.0, the degradation rate of Orange II accelerated with increasing pH because of the formation of Co–OH on the surface of as-prepared Co₃O₄/Graphene composites was enhanced at the higher pH value which promoted heterogeneous PMS activation.⁴² The best catalytic activity was obtained at a pH value of 10, but there is a weak changes that the solution pH at 7.0, 8.5 and 10.0. Hence, controlling pH could be considered as one approach to regulate the degradation of pollutants in the SO₄^{•-} existing system. Consequently, the proper pH value is 7.0 because of the easier formation of SO₄^{•-} at a neutral pH. The degradation of Orange II system was further

studied at varying amounts of Oxone (Figure. S2b) and catalyst (Figure. S2c). Obviously, with an increase in Oxone dose (0.5, 1.0, and 1.5mM), the decomposition rate of Orange II was increasing. Increased doses of Oxone led to the degradation rate of Orange II decomposition increasing from 40% (at 0.5mM) to 100% (at 1.0mM) during 6 min. The increase in Oxone dose would provide more chance to the reaction with $\text{Co}_3\text{O}_4/\text{graphene}$, which enhances the rate of activation of PMS to generate $\text{SO}_4^{\cdot-}$, resulting in an increase in Orange II removal. With the increase of catalyst dosage (25, 50 and 75 mg/L), the catalytic efficiency rises due to more catalyst, which provides a greater possibility for the generation of $\text{SO}_4^{\cdot-}$. However, the increase of degradation is inconspicuous that the dosage is 0.050g/L compared with 0.025g/L. And there is a slight improve in the removal of Orange II in the 0.075g/L of sample. Therefore, 2.0 mM of PMS and 0.050g/L of catalyst is the suitable dosage experimentally. Temperature is taken as an important means to control the degradation of pollutants in the $\text{Co}_3\text{O}_4/\text{G}/\text{PMS}$ system. The degradation of Orange II system was further investigated at varying temperature (25, 35, 45 and 55 °C), and the results are shown in Fig. S2d. The results suggest that increased temperature could significantly increase the Orange II removal rate because of it is easier for the production of $\text{SO}_4^{\cdot-}$ at higher temperatures. High temperature is a dangerous element in industrial production and wastewater treatment. Therefore, 25 °C is applied in degradation.

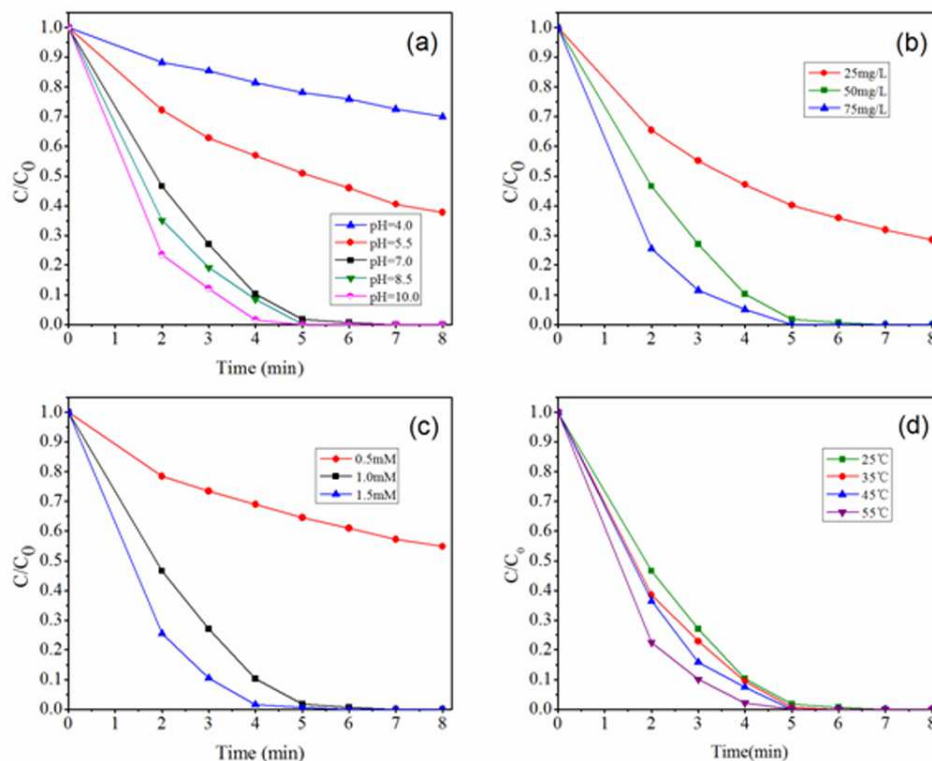


Fig. S2. Factorial effects of heterogeneous reaction on Orange II degradation: (a) pH value, (b) Oxone dosage, (c) catalyst dosage, and (d) reaction temperature. Apart from the experimental parameter, other factors were fixed: pH = 7.0, [Oxone] = 2 mM, [Orange II] = 0.3 mM, [Co₃O₄/graphene] = 50 mg/L and $T = 25\text{ }^{\circ}\text{C}$.

3. The effect of the compositions of Co₃O₄/graphene

3.1 Preparation of different mass ratio composites. Co(NO₃)₂·6H₂O (0.29 g), NH₄F (0.12 g), and urea (0.30 g) were dissolved in deionized water (10 mL). Dispersed GO (5 g/L) was sonicated for 30 min and dropped into the resulting solution; the mass ratio of Co(NO₃)₂·6H₂O and GO was maintained at 1:1, 3:1, 5:1, 10:1, 20:1. Afterward, the solution was stirred for 1 h and then transferred to a Teflon-lined autoclave (25 mL) at 120 °C for 5 h. The precipitate was collected through

centrifugation, washed thoroughly with water and ethanol to remove any impurities, and dried at 60 °C for 12 h. The solid was heated to 300 °C for 3 h at a rate of 1 °C/min in a N₂ atmosphere. According to the different ratio, the products were labeled as (1:1)Co₃O₄/grapheme, (3:1)Co₃O₄/grapheme, (5:1)Co₃O₄/grapheme, (10:1)Co₃O₄/grapheme and (20:1)Co₃O₄/graphene. Pure Co₃O₄ and pure graphene were synthesized in the same manner but in the absence of Co(NO₃)₂·6H₂O or GO, respectively.

3.2 Orange II degradation performances. The degradation curves of Orange II with different mass ratio as catalysts are shown in Fig. S3. As shown in Fig. S3, the degradation efficiency of Orange II in water via advanced oxidation technology based on sulfate radicals by using Co₃O₄/graphene composites as catalysts follows the order (5:1)Co₃O₄/graphene > (3:1)Co₃O₄/graphene > (10:1)Co₃O₄/graphene > (1:1)Co₃O₄/graphene > (20:1)Co₃O₄/graphene > pure Co₃O₄ > bare graphene. The activity of the catalyst increased and then declined with increasing Co₃O₄ loading. Co₃O₄/graphene expressed enhanced catalytic property compared with pure Co₃O₄ thanks to that the rates of the electron transfer from Co²⁺ to HSO₅⁻ between Co₃O₄/graphene and PMS are higher and faster than those in Co₃O₄ alone. The degradation rate of dyes accelerated with decreasing Co₃O₄ content because of more graphene leads to a efficient electrical conductivity which improve the catalytic activity. At (5:1)Co₃O₄/graphene, the degradation of Orange II was accomplished within 7 min, which indicates that this concentration produced the best catalysis. Further increasing the Co₃O₄ loading results in a significant decrease of degradation activity. The results are probably due to that overmuch graphene covered the active

site on the surface of some cobalt particles, thereby affect the property of composites. Bare Co_3O_4 has a lower degradation activity than Co_3O_4 and graphene nanocomposite but was better than bare graphene for the degradation of Orange II. In addition, the nanocomposite shows different catalytic activities with different Co_3O_4 loadings. This phenomenon shows that a synergistic catalysis exists between Co_3O_4 and graphene. And, (5:1) Co_3O_4 /graphene is the suitable composition for activation of PMS to degrade Orange II in aqueous solutions.

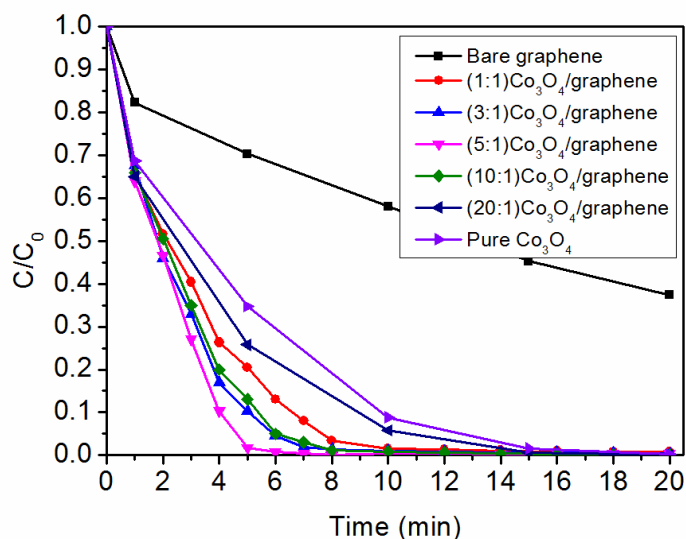


Fig. S3. Degradation curves of Orange II by using different ratio Co_3O_4 /grapheme.

Figure Captions

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