# Enhanced catalytic degradation of methylene blue by α-Fe$_2$O$_3$/graphene oxide via heterogeneous photo-Fenton reactions

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## ARTICLE INFO

## ABSTRACT

Novel hybrid nanostructures or nanocomposites are receiving increasing attention due to their newly evolved properties. In this work, α-Fe$_2$O$_3$ anchored to graphene oxide (GO) nanosheet (α-Fe$_2$O$_3$@GO) was synthesized through a facile hydrolysis process and its photo-catalytic performances and durability in heterogeneous Fenton system were fully evaluated. The decolorization rates of methylene blue in α-Fe$_2$O$_3$@GO + H$_2$O$_2$ + UV system within a wide pH range were approximately 2.9-fold that of classical Degussa P25 TiO$_2$ + UV and 2.4-fold that of α-Fe$_2$O$_3$ + H$_2$O$_2$ + UV. This enhanced decolorization of methylene blue (MB) in α-Fe$_2$O$_3$@GO + H$_2$O$_2$ + UV system were attributed to the unique incorporation of GO into the catalyst which not only mediated the morphology of active sites α-Fe$_2$O$_3$ nanoparticles but also offered high electron conductivity and electrostatic attraction between negatively charged GO with positively charged MB. High efficiencies of degradation were achieved on various surface charged organic pollutants (around 96–100%), such as cationic compounds of MB and rhodamine B (RhB), anionic compound Orange II (OII) and Orange G (OG), neutral compounds of phenol, 2-nitrophenol (2-NP) and endocrine disrupting compound 17β-estradiol (E2). The dominant reactive oxygen species (ROS) responsible for decolorization, such as hydroxyl radicals (•OH) and superoxide anion radicals (O$_2$•$^-$) generated by activation of H$_2$O$_2$ on the surface of α-Fe$_2$O$_3$@GO were detected and quantified by free radical quenching methods. The possible degradation mechanism of MB involved the rupture of phenothiazine ring by desulfurization and the rupture of phenyl ring due to the attack of ROS, which was analyzed by LC/MS/MS. The reduction of MB and its intermediates was consistent with the decreasing trend of the acute toxicity towards luminous bacteria with the increasing irradiation time. The results lay a foundation for highly effective and durable photo-Fenton technologies for organic wastewater within wider pH ranges than the conventional photo-Fenton reaction.

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## 1. Introduction

Dye wastewater pollution has been a critical issue in recent years owing to the massive production and applications. For instance, more than 100,000 commercially available dyes are produced at an estimated annual rate of over $7 \times 10^5$ tons globally [1]. Industries, including textile, food, paper, printing, leather and cosmetic, are the main sources of dye wastewater [2]. Because of their toxicity and potentially carcinogenic nature, dyes pose serious threat to the human health and the environment [3]. Therefore, it is important to remove these dye pollutants from wastewater effluents using efficient processes [4,5].

As one of the important advanced oxidation processes (AOPs), the conventional homogeneous Fenton process holds great promise in the treatment of the refractory organic compounds due to power of generating highly reactive hydroxyl radicals (•OH) by activating H$_2$O$_2$ with Fe$^{2+}$ [6–8]. However, the major drawbacks that limit the practical applications of the traditional Fenton process include: (i) a narrow working pH range (pH <3); (ii) high iron concentrations in the final effluent that requires costly removal treatment and generate iron-containing sludge; and (iii) a high demand for H$_2$O$_2$ [9]. To overcome these drawbacks, heterogeneous Fenton processes have emerged as promising alternatives because of their high efficient

activity, wide application pHs and durability [10]. Nevertheless, heterogeneous iron oxide Fenton catalysts (e.g., $Fe_3O_4$ [11], $\alpha$-$Fe_2O_3$ [12], $\gamma$-$Fe_2O_3$ [13], $\alpha$-FeOOH [14,15], $\beta$-FeOOH [16,17], and $\gamma$-FeOOH [18]) usually have lower activities in decomposing $H_2O_2$ than their homogeneous counterparts do, because of the potential diffusion resistance for reactants enter the surface of the catalysts. Moreover, some catalysts have poor durability or stability due to metal leaching in oxidation conditions [19]. Therefore, developing effective and durable catalysts remains a challenge.

To date, nanostructured iron oxides have been widely used as heterogeneous Fenton catalysts, primarily because of their abundance, environmental benign, and the effective generation of surface iron complex and hydroxyl radicals under UV irradiation [20]. Among them, $\alpha$-$Fe_2O_3$ is the most common crystalline polymorph of $Fe_2O_3$ and an n-type semiconductor with small band gap of approximately 2.2 eV that can absorb light with a wavelength up to 560 nm and capable for oxide organic substrates. Besides, $\alpha$-$Fe_2O_3$ is more chemically and thermally stable with low iron release or dissolution when used as a heterogeneous Fenton catalyst in diverse fields [21]. Unfortunately, the reaction activity of $\alpha$-$Fe_2O_3$ in Fenton system is usually lower than that of $\gamma$-$Fe_2O_3$, $\gamma$-FeOOH, $\alpha$-FeOOH and $Fe_3O_4$ due to the high electron-hole recombination rate [21,22]. Practical applications of $\alpha$-$Fe_2O_3$ have also been hampered by aggregation. To improve the photochemical and catalytic properties, different supports were hybridized with $\alpha$-$Fe_2O_3$, such as activated carbon [23], alginate [24], clay [25], bentonite [26], kaolin [27], zeolite [28], and CNTs [29]. Comparing with aforementioned supports, Graphene would endow $\alpha$-$Fe_2O_3$ more improved catalytic activity due to its two dimensional (2D) carbonaceous mono-layered structure, excellent thermal conductivity, electronic properties and high surface area (e.g. 2600 $m^2$/g) [30,31]. The multiple oxygen-containing functional groups (carboxyl, hydroxyl, and epoxy) covalently attach to its layers, resulting in a negatively charged surface [32]. The oxygen functional groups on graphene oxide sheet serve as activation sites for nucleation and growth of iron precursors to form graphene supported metal oxide-containing nanocomposites [33,34] aiming to fabricate $\alpha$-$Fe_2O_3$@graphene composites with unique properties and applications [35,36]. So far, $\alpha$-$Fe_2O_3$@graphene nanocomposites in many past studies are primarily used as anode materials for lithium-ion batteries [37], advanced energy storage devices [38], supercapacity [39], and electrochemical sensor [40,41]. Only a few studies reported the catalytic applications in the treatment of dye pollutants [42]. The previously reported synthesis methods often involved the use of toxic organic chemicals (e.g., hydrazine), high temperatures or high pressures, which may reduce the scalability and cost effectiveness of the applications. For example, Qiu et al. reported that $Fe_2O_3$ nanocrystals were in situ grown on the surface of graphene aerogels by a Stober-like method using ethanol and acetonitrile as cosolvents at a high temperature and a high pressure [43]. Xu et al. reported the fabrication of $Fe_2O_3$@Graphene microsphere through a two-step spray-drying process under 150–280 °C [41]. Zhang et al. used GO, $FeCl_2$, and urea to synthesize $Fe_2O_3$@graphene under microwave heater with $N_2$ protection [44]. Wang et al. synthesized $Fe_2O_3$@graphene by coating ferric on graphene oxide and then reduced via $H_2$ within 12 h [45]. Zhu et al. reported that $Fe_2O_3$@graphene was synthesized involved the precipitation of ferric with urea and then regeneration of GO by hydrazine [46]. Additionally, there is a lack of detailed investigations on the mechanisms of the enhanced degradation efficiency or pathways of dye pollutants [41]. For example, the enhanced heterogeneous Fenton degradation of MB was investigated by nanoscale zero valent iron (nZVI) assembled on magnetic $Fe_3O_4$/reduced graphene oxide (Fe–$Fe_3O_4$@rGO) [33]. In this study, the optimum operation pH was 3, above which the decolorization ratio of MB sharply decreased. Therefore, this new catalyst

was actually able to overcome the drawbacks of homogeneous Fenton reaction. Also, the decolorization ratio of MB catalyzed by Fe–$Fe_3O_4$@rGO decreased from ~93% in first cycle decreased to 69% in fifth cycles [33]. Moreover, MB degradation mechanisms, photodegradation pathways and toxicity of the intermediates were largely overlooked on these novel hybrid catalysts, which is essential to fundamentally understand the unique strength and potential limitations in dye wastewater treatment.

To develop a facile and scalable method for $Fe_2O_3$@graphene with higher durability, this study presented a new synthesis method for the heterogeneous catalyst, $\alpha$-$Fe_2O_3$ anchored on graphene oxide nanosheets ($\alpha$-$Fe_2O_3$@GO). The photodegradation of methylene blue (MB) was studied under ultraviolet light irradiation in presence of $H_2O_2$. MB was chosen as a typical model cationic dye, as it represents a class of non-biodegradable dye and is widely used in the textile industry [47]. We also explored the effectiveness of decolorization and mineralization mechanisms of the MB dye and other typical dye or emerging contaminants (i.e., OII, OG, 2-NP, and E2) with $\alpha$-$Fe_2O_3$@GO in a heterogeneous photo-Fenton process under different experimental variables such as pH, $H_2O_2$ levels, initial MB concentration, various organic structures, repeated use and scaling up experiments.

## 2. Experimental

### 2.1. Reagents and materials

MB with a molecular formula $C_{16}H_{18}ClN_3S \cdot 3H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $H_2O_2$ used in this study was purchased from Runjie Chemical Ltd. (Shanghai, China); Orange II (OII), Orange G (OG), rhodamine B (RhB), 2-nitrophenol (2-NP) and phenol, were all purchased from Sinopharm Chemical Reagent Ltd. (Shanghai, China). 17β-estradiol (E2) was purchased from Eppendorf Company (Hamburg, Germany). Natural graphite was purchased from Guangfu fine chemical research institute (Tianjin, China), and used without further purification. Benzoquinone and methanol were purchased from Lingfeng Chemical Ltd. (Shanghai, China). Coumarin and tetranitromethane (TNM) were obtained from Aladdin Chemical Ltd. (Shanghai, China). All the other chemicals used were analytical grade. 2000 mg/L of MB stock solution was prepared by dissolving MB into deionized water and stored at room temperature. The working solutions were prepared by diluting MB stock solution with deionized water to desired concentrations.

### 2.2. Preparation and characterization of $\alpha$-$Fe_2O_3$@GO catalyst

Graphene oxide (GO) was prepared from graphite powder by a modified Hummers method [48]. The $\alpha$-$Fe_2O_3$@GO catalyst was prepared by gradually adding 0.1 g GO into 100 mL water and sonicated to obtain the GO dispersion. 4.04 g $Fe(NO_3)_3 \cdot 9H_2O$ and 2.4 g urea was added slowly into above GO water solution. After 30 min sonication, the mixture underwent hydrolysis with magnetically stirred for 12 h in water-bath thermometer at 100 °C. After repeat separation by centrifugation and washing with deionized water, the obtained product was dried in vacuum oven at 60 °C and then manual powdered for further use.

The crystal structure of $\alpha$-$Fe_2O_3$@GO was characterized by X-ray diffraction (XRD, Rigaku D/Max-2500, Japan) employing Cu K$\alpha$ as the source of radiation at $\lambda$ = 1.54056 Å over an angular range between 5° and 70°. Surface morphology was characterized by a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). High resolution transmission electron microscope (HRTEM) images were measured on HT7700 electron microscopy with resolution of 0.204 nm and the accelerating voltage of 120 kV.