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Magnetic Cobalt-Graphene Nanocomposite derived from Self-Assembly of MOFs with Graphene Oxide as an Activator for Peroxymonosulfate

Kun-Yi Andrew Lin^{*}, Fu-Kong Hsu, and Wei-Der Lee

Department of Environmental Engineering, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan, R.O.C.

*Corresponding Author. Tel: +886-4-22854709, E-mail address: linky@nchu.edu.tw

(Kun-Yi Andrew Lin)

Abstract

While Metal Organic Frameworks (MOFs) have been extensively explored as a platform for developing porous metal oxides, another intriguing direction is to use MOFs as precursors to prepare carbonaceous materials. By simple one-step carbonization, MOFs can be turned into promising hierarchical carbon materials. Such a technique can be also used to convert MOF-composites to carbon-based composites with task-specific functionality other than the precursors. In this study, this strategy is adopted to prepare a magnetic cobalt-graphene (MCG) nanocomposite from carbonizing a self-assembly of a cobalt-based MOF, ZIF-67, and graphene oxide (GO). The preparation of MCG represents a simple alternative route to synthesize magnetic graphene materials and graphene-supported cobalt materials. By combining cobalt and reduced graphene oxide (RGO), the as-prepared MCG can be an effective catalyst to activate peroxymonosulfate (PMS) in the advanced oxidation process. Thus, the activation capability of

MCG is evaluated by decolorizing Acid Yellow (AY) dye in water. MCG exhibited an enhanced catalytic activity to activate PMS compared to the carbonized ZIF-67 because RGO also activated PMS and improved electron transport ability. The kinetics of the decolorization of AY (10 mg L^{-1}) was 0.0119 min⁻¹ with PMS = 200 mg L⁻¹ and MCG = 500 mg L⁻¹. The activation energy of the decolorization using PMS activated by MCG was found to be 12 kJ mol⁻¹. Factors influencing the PMS activation were also investigated including temperature, pH, UV, ultrasonication and inhibitors. To evaluate the long-term catalytic activity of MCG, a 50-cycle decolorization test was performed and the regeneration efficiency remained at 97.6% over 50 cycles, showing its stable and effective catalytic activity. These features make MCG a promising catalyst to activate PMS.

Keywords: MOFs, ZIFs, Cobalt, Graphene, Peroxymonosulfate, Acid yellow

1. Introduction

Metal organic frameworks (MOFs) represent one of the most interesting and widely-studied materials nowadays¹⁻⁴. As a type of crystalline inorganic-organic hybrid materials, MOFs can be tuned to possess various superior characteristics including versatile functionalities, high chemical resistance, large pore volume and high surface area, etc.⁵⁻⁷ These properties enable MOFs attractive materials for catalysis^{3, 8, 9}, gas adsorption/storage¹⁰⁻¹³, analytical chemistry¹⁴, drug delivery^{13, 15}, and photoluminescence¹⁶.

While fundamentals and applications of MOFs are continuingly explored, many studies have used MOFs as a platform to develop composites including MOF/metal oxide composites¹⁷⁻¹⁹, MOF/silica composites^{20, 21}, MOF/organic polymer composites²², MOF/quantum dot composites²³, MOF/polyoxometalate composites^{24, 25} as well as MOF/carbon composites²⁶⁻²⁹. These composites have been proven to be promising materials in various applications such as protective coatings³⁰, gas separation and storage³¹, heterogeneous catalysis³², biomedicine³³ as well as analytic chemistry³⁴.

Aside from using MOFs as a platform for preparing composites, another technique of using MOFs as precursors to prepare carbonaceous materials has also drawn enormous attention.

Considering MOFs' unique structures, MOFs can be turned into hierarchically-structured carbon materials. Recently, Xu *et al.* had prepared porous carbon materials based on MOF-5³⁵ with the addition of furfuryl alcohol as a carbon source. Several studies also successfully prepare metal-containing carbonaceous materials using MOFs as precursors via the direct carbonization of MOFs without the addition of carbon source³⁶⁻⁴⁰. These MOF-derived carbon composites, as a combination of metal oxides and carbon, have revealed superior potential in catalysis³⁹, sensing⁴¹, batteries³⁶, adsorption⁴⁰, and energy storage^{42, 43}

MOF-derived carbonaceous materials can be conveniently prepared via one-step carbonization of MOFs, so the above-mentioned MOF-hybrid composites can also be precursors for preparing various carbon-based composite materials. Such carbonaceous composite materials may exhibit other functionalities than the precursors. This technique may also become a new and versatile route to prepare carbon-based composite materials. In this study, we aim to use this strategy to obtain a carbon-based composite material based on a self-assembly of zeolitic imidazole framework (ZIF)-67 and graphene oxide (GO) via the electrostatic attraction. Although a few examples have combined MOFs with graphene-related materials, these MOF/graphene composites are utilized based on the resulting porosity⁴, visible-light photo-catalytic property⁴⁴, etc. The ZIF-67/GO composite in this study is specifically designed to turn this cobalt-containing ZIF-67/GO into a magnetic carbon-graphene (MCG) nanocomposite. By simple carbonization of ZIF-67/GO, this provides an alternative route to prepare a magnetic graphene material and a graphene-supported cobalt material, which can be used in several applications involving magnetically-controllable graphene or cobalt-based materials⁴⁰. Particularly, it has been reported that cobalt oxide (e.g., Co_3O_4) is an effective catalyst to activate peroxymonosulfate (PMS)⁴⁵⁻⁴⁸ to produce radical for the advanced oxidation process in wastewater treatment. The combination of Co₃O₄ and carbonaceous materials (e.g., reduced GO (RGO)) is also found to have synergic effects to improve this PMS activation reaction⁴⁹⁻⁵². This MCG nanocomposite can be an effective activator for PMS. The as-prepared MCG is characterized by scanning electronic

microscopy (SEM), transmission electronic microscopy (TEM), zeta potential analyzer, X-ray diffraction (XRD), X-photoelectron spectroscopy (XPS), Raman and IR spectroscopies, SQUID magnetometer, thermogravimetric analyzer and volumetric sorption analyzer. The MCG-activated PMS process was evaluated by decolorizing an acidic dye, Acid yellow 17 (AY), in water. Factors influencing the PMS activation were examined including decolorization, including temperature, pH, UV, ultrasonication, and inhibitors. MCG was reused for 50 cycles to study its recyclability to activate PMS for the dye decolorization.

2. Experimental

2.1 Materials

The chemicals in this study are all commercially available reagents and used directly without purification. 2-methylimidazole (2-MIM) was from Acros Organics (USA). Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) was from Choneye Pure Chemicals (Taiwan). Acid yellow 17 (AY), potassium iodide (KI), ascorbic acid, methanol, *tert*-butyl alcohol (TBA) and peroxymonosulfate were purchased from Sigma Aldrich (USA). Deionized (D.I.) water was prepared to exhibit less than 18 MOhm-cm. Graphene oxide (GO) was prepared by oxidizing graphite powder according to the modified Hummers' method⁵³.

2.1 Preparation of Magnetic Cobalt-Graphene (MCG) Nanocomposite

The preparation of the magnetic cobalt-graphene (MCG) nanocomposite is illustrated in Fig. 1. First, 0.9 g of Co(NO₃)₂·6H₂O was dissolved in 6 ml of D.I. water, while 11 g of 2-MIM was added to 40 ml of D.I. water. The cobalt solution was slowly added to the 2-MIM solution and the resultant mixture was stirred at ambient temperature for 4 hours. Meanwhile, 0.18 g of GO was added to 50 ml of D.I. water and sonicated for 1 hour to form a well-dispersed GO solution. The GO solution was slowly poured into the former mixture and the resultant mixture was stirred at ambient temperature for 24 hours. The self-assembled product was then collected via centrifugation, washed with D.I. thoroughly and dried at 85 °C to yield the ZIF-67/GO

nanocomposite. The ZIF-67/GO was then carbonized in nitrogen at 600 °C for 6 hours, and subsequently washed with water and ethanol thoroughly to obtain the final product, MCG. The carbonization process converted ZIF-67 and GO of the ZIF-67/GO nanocomposite to cobalt-bearing carbonaceous nanoparticles (or called carbonized ZIF-67 (cZIF-67)) and RGO, respectively. In addition to 600 °C, MCG were also prepared by carbonization at 400 and 800 °C to examine the effect of carbonization temperature on the activation of PMS.

2.2 Characterization of Magnetic Cobalt-Graphene (MCG) Nanocomposite

MCG was first characterized by a Field Emission SEM (JEOL JSM-6700, Japan) and Transmission Electronic Microscopy (TEM) (JEOL JEM-2010, Japan) to observe the morphology of MCG. The crystalline structure of MCG was analyzed using an X-ray diffractometer (PANalytical, the Netherlands) with copper as an anode material (40 mA, 45 kV) to obtain the powder X-ray diffraction (XRD) patterns. The absorption infrared (IR) spectrum of ZIF-67 was obtained by a Fourier-Transform Infrared spectrometer (Jasco 4100, Japan) with KBr pellets as sample holders. Raman spectrum of MCG was also used to determine cobalt and carbon in MCG by a Raman spectrometer (Tokyo Instruments Inc. Nanofinder 30 R, Japan). Thermogravimetric (TG) curve of MCG was obtained by a thermogravimetric (TG) analyzer (Instrument Specialists Incorporated i1000, USA) at a heating rate of 20 °C min⁻¹ from 25 to 800 °C in nitrogen or air. Magnetization of MCG was measured using a Superconducting Quantum Interference Device (SQUID) Vibrating Sample Magnetometer (Quantum Design MPMS SQUID VSM, USA) at 27 °C. To characterize surface area and pore volume, N₂ sorption/desorption isotherms were measured at a relative pressure (P/P_0) ranging from 0.0001–0.99 using a volumetric sorption analyzer (Micromeritics ASAP 2020, USA). Zeta potentials were measured in water with pH values ranging from 3-11 using a zetasizer (Nano-ZS, Malvern Instruments Ltd, Malvern, UK).

Journal of Materials Chemistry A 2.3 Tests for MCG as the activator for PMS

To evaluate MCG as the activator for PMS, batch-type experiments of dye (i.e., AY) decolorization in water were conducted as a model test. In a typical dye decolorization test, a certain amount of PMS powder was first added to a 500 ml of AY solution with an initial concentration (C_0) of 100 mg L⁻¹. The solution was stirred for at least 20 min to completely dissolve PMS powder and also to allow the reaction between PMS and AY to reach equilibrium. A certain amount of MCG (e.g., 0.25 g) was subsequently added to the AY solution to activate PMS. The decolorization efficiency was monitored by withdrawing aliquot samples from the reactor at pre-set times and the residual PMS was quenched with KI. The remaining concentration of AY (C_t) was then immediately analyzed using a UV-Vis spectrophotometer at 418 nm (e-ChromTech CT-2000, Taiwan). Since MCG could also remove AY from water via adsorption, the AY adsorption to MCG was also measured. To investigate effects of MCG dosage and PMS loading, the MCG dosage was varied from 250 to 750 mg L^{-1} , whereas the PMS loading was changed from 100 to 400 mg L^{-1} . The effects of pH, UV irradiation and ultrasonication on the PMS activation by MCG were also investigated in this study. The pH of solution was varied by adding 0.1 M HCl and NaOH to AY solutions. The PMS activation by MCG in the presence of UV irradiation was performed by placing a 9W UVA lamp (Philips PL-S9W, Netherland) into the afore-mentioned batch-type reactor. For the experiment in the presence of ultrasonication, the batch-type reactor was directly placed in an ultrasonication bath with temperature-controllable function (Yeong-Hsin LEO-1002S, Taiwan). Total organic carbon (TOC) concentration of aliquot samples was analyzed using a total carbon analyzer (Shimadzu TOC-V, Japan). All decolorization experiments were performed in duplicate and repeated at least twice.

Journal of Materials Chemistry A 2.4 Effects of inhibitors and recyclability of MCG as the activator of PMS

Several inhibitors, including ascorbic acid, KI, methanol and TBA were used to investigate the effects of inhibitors and to provide insights into the potential mechanism of PMS activated by MCG. As a catalytic activator of PMS, MCG's long-term activity was an important aspect. Thus, a 50-cycle AY decolorization test was performed to examine MCG's recyclability. The spent MCG was collected via centrifugation and used as it was without any treatments in the subsequent AY decolorization experiment.

3. Results and Discussion

3.1 Characterization of magnetic cobalt-graphene nanocomposite

As shown in Fig. 1, the self-assembled ZIF-67/GO nanocomposite was first synthesized and carbonized to yield MCG. The ZIF-67/GO nanocomposite can be observed in Fig. 2(a) and ZIF-67 nanoparticle was found to assemble with GO sheets. Such an assembly between ZIF-67 and GO could be attributed to two mechanisms. First, as shown in Fig. 3, ZIF-67 exhibits positive surface charge under a wide range of pH, while GO sheets are negatively-charged. In the typical preparation, pH of the mixture of ZIF-67 and GO sheets was found to be 8.5, at which the electrostatic attraction between ZIF-67 and GO sheets facilitated the assembly of ZIF-67/GO composite. Thus, the zeta potential is found to become much more positive in ZIF-67/GO compared to that of GO. Such an electrostatic attraction between MOFs and GO has been also proven effective for preparing a self-assembled composite of zirconium-based MOF, UiO-66-NH2 and GO⁴⁴. Second, since ZIF-67 consists of imidazole rings, ZIF-67 could be attracted to GO sheets via the π - π stacking interaction between the imidazole rings and the benzene rings of GO ⁵⁴⁻⁵⁶. Fig. 3 also reveals the zeta potential of the as-synthesized MCG, which spans a wide range of zeta potential under pH=3–11.

The as-synthesized ZIF-67 nanoparticle is also found to exhibit obvious porosity, which is not observed in the conventional ZIF-67 prepared in the absence of GO. To validate the formation of

ZIF-67 on GO sheets, the XRD pattern of the as-prepared ZIF-67/GO was analyzed and compared with that of the conventional ZIF-67 (Fig. S1, see ESI[†]). The as-prepared ZIF-67 in the self-assembled ZIF-67/GO exhibits almost identical pattern to the conventional ZIF-67, validating the formation of ZIF-67 in the self-assembled hybrid. The special morphology of the as-prepared ZIF-67 could result from the presence of GO which interfered the crystalline growth of ZIF-67. After carbonizing this ZIF-67/GO at 600 °C, the resulting MCG can be seen in Fig. 2(b). The cZIF-67 or called the cobalt-bearing nanoparticle (NP) was still found to assemble with the reduced GO (RGO) sheets. Fig 2(c) reveals a closer view on the surface of the cobalt-bearing NPs which still exhibit porosity as seen on the ZIF-67 in Fig. 2(a). Although Fig. 2(b) shows that MCG seems to be an aggregate of the cobalt-bearing NPs and RGO sheets, MCG in fact can be a single sheet after dispersion in water by ultrasonication. Fig. 2(d) shows a TEM image of a single sheet of MCG, consisting of a RGO sheet assembled with cobalt-bearing NPs and the size range of cobalt-bearing NPs was ranging from 200 to 1000 nm. The range agrees with the reported size of ZIF-67⁵⁷, suggesting that even though ZIF-67 was prepared in the presence of GO and carbonized at a high temperature, its size remained similar.

The crystalline structure of MCG is shown in Fig. 4(a); the intensity of XRD signal was relatively low probably due to the amorphous carbonaceous part of MCG. However, the XRD pattern can be still analyzed and indexed to the typical crystalline structure of Co_3O_4 based on JCPDS file# 42-1467, indicating that the cobalt existing in the cobalt-bearing NPs was in the form of cobalt oxide. The existence of Co_3O_4 is also detected by the IR spectroscopic analysis (Fig. 4(b)). It is worth mentioning that strong bands at 570 and 661 cm⁻¹ are found in the spectrum of MCG, corresponding to the stretching vibrations of the cobalt-oxygen bond. Specifically, the band at 661 cm⁻¹ can be assigned to the A-B-O₃, where A denotes cobalt cations in the tetrahedral position and B represents cobalt cations in an octahedral position. Moreover, the band at 570 cm⁻¹ is attributed to the B-O-B₃ vibrations in the spinel lattice⁵⁸. We also observe the same bands in the spectrum of cZIF-67, validating the existence of Co₃O₄ in MCG.

Additionally, the band at 1585 cm⁻¹ can be assigned to the C-N bonding derived from 2-MIM. To investigate the carbonaceous part of MCG, the Raman spectroscopy was also used and the Raman spectrum of MCG can be found in Fig. 4(c). The D and G bands can be easily detected at 1350 and 1590 Raman shift $(cm^{-1})^{59}$, respectively, in the Raman spectrum of MCG, confirming the existence of carbonaceous content of MCG, which was derived from cZIF-67 and RGO sheets. A few strong bands can be also observed in the low Raman shift range at 192, 470, 510, 608 and 682 Raman shift (cm^{-1}) , corresponding to the existence of Co_3O_4 ⁵⁸. The features of the Raman spectrum of MCG are almost identical to those of cZIF-67, demonstrating that MCG primarily consists of cobalt oxide and carbonaceous content. However, we found that the intensity ratio of the D band over the G band of MCG (i.e., 0.91) was higher than that of cZIF-67 (i.e., 0.76). This is because a part of MCG was RGO which exhibit much more defect structures, resulting in a high intensity of the D band.

Since MCG was derived from carbonizing the self-assembled ZIF-67/GO nanocomposite, it is necessary to determine the yield from turning ZIF-67/GO to MCG. Thermogravimetric (TG) curve of ZIF-67/GO is displayed in Fig. 4(d). ZIF-67/GO begins exhibiting dramatic weight loss starting at 300 °C where the organic matters of ZIF-67/GO were decomposed, possibly owing to the decomposition of the ligand. The TG curve of ZIF-67/GO subsequently remained steady at 27% until 800 °C. This residual weight percentage reveals that the conversion rate of ZIF-67/GO to MCG was 27 wt%. Fig. 4(d) also displays the TG curve of MCG which remains almost unchanged from ambient temperature to 800 °C, exhibiting its high thermal stability. By comparing the residual weights of ZIF-67/GO and ZIF-67 in N₂, the fraction of graphene in MCG was estimated to be 26 wt%. The fractions of Co₃O₄ and ZIF-derived carbon in MCG were also found to be 36 and 38 wt%, respectively, based on the residual weight of cZIF-67 in air (Fig. S2, see **ESI**†).

In addition to the chemical properties, the physical properties of MCG were also characterized including the surface area and the saturation magnetization. Fig. 4(e)

shows the N₂ sorption/desorption isotherms of MCG which can be considered as a combination of the type II and III sorption isotherms. The BET surface area and the total pore volume were found to be 168 m² g⁻¹ and 1.36 cm³ g⁻¹, respectively. The magnetic property of MCG is shown in Fig. 4(f) and the saturation magnetization of MCG reached 15 emu g⁻¹. This is quite comparable to other reported magnetic graphene-based composites and Co₃O₄ nanoparticle that exhibit saturation magnetization of 15–20 emu g^{-1 60, 61}.

3.2 Decolorization of AY using PMS activated by MCG

The decolorization of AY (as seen in Fig. S3) using PMS activated by MCG can be demonstrated in a sequence of pictures shown in Fig. S4 (see **ESI**[†]). Fig. S4(a) reveals the AY solution (50 mg L^{-1}) after addition of PMS (200 mg L^{-1}) and the solution is still yellow, indicating that PMS alone could not sufficiently degrade AY. Subsequently, MCG nanocomposite was added to the vial and black MCG nanocomposite was dispersed and settled down as seen in Fig. S4(b). However, the solution is still yellow and no decolorization is observed. This picture suggests that the instantaneous adsorption of AY to MCG was not significant. To increase the contact between MCG and AY dye to facilitate the PMS activation, the vial was then placed in the temperature-controllable orbital shaker at 300 rpm for 30 min at 25 °C. The resulting mixture can be found in Fig. S4(c), in which the solution becomes transparent, indicating the complete decolorization of AY in the presence of PMS and MCG. MCG nanocomposites are also drawn by a permanent magnet to the left, confirming that MCG can be easily recovered from aqueous solutions.

Prior to the quantitative investigation of the decolorization of AY using PMS activated by MCG, it is essential to determine the decolorization of AY by MCG via the adsorption. As seen in Fig. S4(b), the instantaneous adsorption of AY to MCG was not detectable visually. Fig. 5(a) shows the decolorization of AY by MCG via the adsorption as a function of time. Even though a longer adsorption time was given, the decolorization of AY to MCG via the adsorption was still

insignificant (< 10%). This indicates that the decolorization of AY seen in Fig. S4(c) was not from the adsorption. Besides, the decolorization of AY using PMS alone was also obtained as a baseline to clarify the role of MCG in the activation of PMS. It is found that PMS alone was ineffective to degrade AY in water and less than 10% of AY was decolorized after 120 min (Fig. 5(b)). After MCG was added to the AY solution in the presence of PMS, the AY concentration dramatically plummeted to approximately 20% of its initial concentration (C_0) after 120-min mixing. As we have found that the adsorption of AY to MCG was little, this significant decolorization should be owing to the activation of PMS by MCG. To further determine the activation mechanism, the surface properties of MCG was explored using XPS. Fig. 6 shows the Co 2p core-level spectrum of MCG which is deconvoluted to display peaks of potential species. It has been reported that peaks at 780.2 ± 0.6 and 781.8 ± 0.6 eV can be assigned to Co³⁺ and Co²⁺ ions^{62, 63}, respectively. Relatively small peaks at 786.3 and 804.8 eV are considered as the shake-up satellite peaks of CO^{2+ 63}. These cobalt cations have been proven to react with PMS to generate sulfate radicals as illustrated in Fig. 7 according to the following equations (Eq. (1))^{38, 45, 46, 49-51, 64.}

$$\operatorname{Co}^{2^{+}} + \operatorname{HSO}_{5}^{-} \to \operatorname{Co}^{3^{+}} + \operatorname{SO}_{4}^{\bullet^{-}} + \operatorname{OH}^{-} \quad (1-a)$$
$$\operatorname{Co}^{3^{+}} + \operatorname{HSO}_{5}^{-} \to \operatorname{Co}^{2^{+}} + \operatorname{SO}_{5}^{\bullet^{-}} + \operatorname{H}^{+} \quad (1-b)$$

The sulfate radical possesses powerful oxidizing potential which can degrade chromophoric groups of AY to decolorize the dye solution. The radical can also further degrade a part of AY to CO_2 and H_2O as observed in the TOC result (Fig. S5, see **ESI**⁺).

Additionally, similar results were noticed when cZIF-67 (without RGO) was used to activate PMS; most of AY in water had been removed. This validates that Co_3O_4 in cZIF-67 catalytically activated PMS to degrade AY. Interestingly, the decolorization efficiency of AY using MCG-activated PMS was noticeably higher than using cZIF-67 activated PMS. This could be owing to the existence of RGO in MCG, which has been proven to be an activator for PMS⁶⁵. It has been found that small amount of oxygen-containing groups, such as ketones, could still remain in the

chemically reduced GO. The oxygen-containing groups are electron-rich and therefore involved in redox processes which may initiate the catalytic activation of PMS⁶⁵. This can be also observed in Fig. 5(b) that RGO alone was able to activate PMS. Besides, several studies also reported that the interfacial interaction between RGO and Co₃O₄ could improve electron transport ability and chemical reaction sites ^{52, 66, 67}. Therefore, MCG can exhibit an enhanced capability to decolorize AY in water compared to cZIF-67 alone. A few previous studies that used graphene-supported Co₃O₄ to activate PMS also reported the similar enhanced dyedecolorization results^{49, 51, 52, 68}.

While cobalt ions of MCG can activate PMS to generate the radicals, we also investigated whether the PMS activation was induced by the dissolution of cobalt ions from MCG. Thus, the leaching-out experiment of MCG during the decolorization was conducted and Fig. S6(a) shows the dissolved form of cobalt ions as a function of time. In the presence of PMS, about 0.71 mg L^{-1} of MCG was leached out in the end of the decolorization. To evaluate the contribution from the dissolved cobalt ions, the equivalent amount of cobalt ion (i.e., Co^{2+}) from cobalt nitrate was used to activate PMS for the decolorization of AY. The result (Fig. S6(b), see **ESI**[†]) reveals that the decolorization using PMS activated by the dissolved Co^{2+} was significantly lower and slower than the heterogeneous PMS activation by MCG. Thus, the main process of PMS activation is considered to be the heterogeneous activation using MCG.

3.3 Effects of carbonization temperature of MCG, PMS loading and MCG dosage on the decolorization of AY

Since MCG was obtained by carbonizing the ZIF-67/GO composite at high temperatures, different carbonization temperatures might influence the activation activity of MCG. Thus, we first investigated the effect of carbonization temperature of MCG and the result of decolorization using MCG prepared at 400, 600 and 800 °C was shown in Fig. S7 (**ESI**[†]). Although the MCG prepared at 400 °C reaches slightly lower C_t/C_0 than the MCG prepared at 600 and 800 °C, the

carbonization temperature was found to be insignificant to the activation performance of MCG.

During the AY decolorization, both PMS and MCG, representing oxidant and catalyst respectively, play critical roles. Thus, the effects of PMS loading and MCG dosage were investigated. In Fig. 8(a), it is observed that as the PMS loading increased from 100 to 400 mg L^{-1} , the C_t/C_0 was lowered from 35% to 5%, showing the enhancement with a higher PMS loading. To quantitatively analyze the effect of PMS loading, the pseudo first order rate law was used as follows (Eq. (2)):

$$C_t = C_0 \exp(-kt) \qquad (2)$$

where k is the apparent first order rate constant of AY decolorization. The k values of AY decolorization using various PMS loadings are listed in Table 1. When the PMS loading increased from 100 to 400 mg L⁻¹, the k value noticeably changed from 0.0069 to 0.0131 min⁻¹. This validates that the PMS loading was an important factor to facilitate the kinetics of decolorization. On the other side, the MCG dosage was also varied from 250 to 750 mg L⁻¹, and Fig. 8(b) reveals that a higher dosage of MCG indeed improved the decolorization efficiency. The kinetic constants of various MCG dosages are also listed in Table 1, in which the k value was also found to increase significantly as more MCG presented in the reaction.

3.4 Effects of temperature and pH on the decolorization of AY in water

Temperature is also considered as an important factor influencing the PMS activation. Consequently, 25, 40 and 60 °C were selected in this study to examine the temperature effect which is shown in Fig. 9(a). When the temperature varied from 25 to 40 °C, the C_t/C_0 of AY was remarkably decreased from 27% to 10%. At 60 °C, the C_t/C_0 was even reduced to 5%, indicating that the decolorization efficiency of AY by PMS was greatly improved at a higher temperature. Besides, the *k* value at each temperature is also determined and summarized in Table 1. The higher temperature was found not only to improve the decolorization efficiency but also to increase the reaction kinetics. The *k* value at 60 °C (i.e., 0.0243 min⁻¹) is almost two times of the

k value at 25 °C (i.e., 0.0119 min⁻¹), revealing the significant effect of temperature on the PMS activation. The *k* values at the tested temperatures are also found to be comparable to those of decolorization of acid dye using PMS activated by transition metals/RGO ⁶⁷. The *k* values at the different temperatures actually can be used to determine the activation energy using the Arrhenius equation as follows (Eq. 3):

$$\ln k = \ln k_0 - \frac{E_a}{R} \frac{1}{T} \qquad (3)$$

where k_0 is the temperature-independent factor (g mg⁻¹ min⁻¹); E_a represents the activation energy (KJ mol⁻¹); *R* is the universal gas constant and *T* is the solution temperature in Kelvin (K). The Arrhenius plot (i.e., ln *k* versus 1/*T*) is shown in Fig. S8 (see **ESI**[†]) and E_a is 12 kJ mol⁻¹. The kinetics and E_a of this study are also compared with other metal oxides/graphene composites used to activate PMS (Table S1, see **ESI**[†]). It can be seen that the composites prepared by Yao *et al.* both contained more than 50% of metal oxides in the corresponding composites, while the composite from Shi *et al.* possessed a similar fraction of metal oxide to that of MCG.

Compared to the study of Yao *et al.* for degrading Orange II, the initial concentration of dye in our study was much higher and PMS loading was significantly lower. However, the kinetics obtained in the present study (0.0119 min⁻¹) is still comparable to that in their study $(0.019 \text{ min}^{-1})^{67}$. In addition, the E_a obtained in the present study was also relatively low compared to the E_a obtained in their study (25.7 kJ mol⁻¹)⁶⁷.

In addition to the temperature, the effect of pH on the PMS activation to decolorize AY has been also investigated as displayed in Fig. 9(b). In a typical decolorization test, the initial pH of the mixture of AY, PMS and MCG was 3.8, which gradually increased to 5.5 in the end (Fig. S9). The solution pH has been found to be a critical factor to the activation of PMS^{46, 69}. Therefore, the effect of initial pH was also investigated by comparing C_t/C_0 under various initial pH from 3 to 11. Fig. 9(b) shows C_t/C_0 at the initial pH = 3–11. One can see that C_t/C_0 decreases gradually as pH varies from 3 to 7, showing that the neutral condition is more favorable for the

decolorization of AY than the acidic condition. This may be attributed to the relatively high stability of PMS at low pH values and therefore reduce the decolorization efficiency⁴⁶. On the other hand, when pH is higher than 7, the C_t/C_0 was found to increase, revealing that the alkaline condition was not favorable either for the decolorization of AY using PMS. This is because PMS may undergo the self-decomposition under basic conditions and consequently the decolorization efficiency was noticeably lowered^{46, 69, 70}. In Fig. 9(b), the optimal pH for the decolorization of AY using PMS activated by MCG is found to be 7.0, at which the C_t/C_0 could reach ~2%, showing the highest decolorization efficiency among all pH values.

3.5 Effects of UV, ultrasonication and inhibitors on the decolorization of AY in water

The activation of PMS can also be facilitated under irradiation of UV light as well as ultrasonication^{46-48, 71}. Therefore, the effects of these facilitators on the decolorization of AY using PMS have been also analyzed. Fig. 10(a) reveals the decolorization kinetics of the test with UV irradiation, with ultrasonication and without any additional facilitators. It is noted that the test with UV irradiation exhibits a higher decolorization efficiency compared to the test without facilitators, indicating the positive effect of UV irradiation on the decolorization of AY using PMS. This improvement could be mainly attributed to that the UV irradiation facilitated the generation of radicals including sulfate as well as hydroxyl radicals^{47, 48, 71}. The corresponding k value is also determined and found to be comparable to that of the test without facilitators (Table 1). The decolorization kinetics of the test with ultrasonication is also displayed in Fig. 10(a), and the kinetics and decolorization efficiency are much higher than that of the test without facilitators (Table 1). This reveals that the ultrasonication appears to an effective facilitator to enhance the PMS activation for the decolorization. The ultrasonication has been reported that the energy derived from the ultrasonication can effectively promote the generation of free radicals and consequently improve the oxidation $\operatorname{process}^{46}$.

In addition to the facilitators, we also particularly investigated various inhibitors which may hinder the activation of PMS for the dve decolorization. The inhibitors include ascorbic acid, KI, TBA and methanol and each concentration is 2 mmol L^{-1} . At first, ascorbic acid, as a common radical scavenger, was examined and the C_{l}/C_{0} became around 85% (Fig. 10(b)), which was close to the C_t/C_0 simply by the dye adsorption to MCG. This indicates that ascorbic acid almost completely inhibited the PMS activation from decolorizing of AY. Since the PMS activation may generate two types of radicals, i.e., hydroxyl and sulfate radicals, the contribution of these two radicals was distinguished using methanol and TBA as scavengers. It can be seen that when methanol was added, the decolorization efficiency was remarkably reduced (i.e., higher C_l/C_0), while the decolorization efficiency was only slightly affected in the presence of TBA. Methanol. containing α -hydrogen, is considered as a probe chemical to account for the contribution of hydroxyl and sulfate radicals. However, TBA is primarily used as a probe compound to determine the hydroxyl radical. Thus, this comparison result suggests that the main contribution for the decolorization using MCG-activated PMS was sulfate radicals and small amount of hydroxyl radicals existed. Besides, another inhibitor, KI, was also examined and the decolorization efficiency was dramatically lowered. KI has been used to scavenger all the surface-bound radicals (hydroxyl and sulfate ones), which are produced at the surface of activators. Thus, this result suggests that the decolorization was mainly attributed to the radicals on the surface of MCG instead of free radicals in the solution 72 .

3.6 The long-term recyclability of MCG

As a catalytic activator, MCG has to be recovered and re-used for multiple times. Thus, the recyclability of MCG for the activation of PMS is evaluated by re-using MCG for multi-cycle decolorization tests without additional treatment of the spent MCG. Fig. S10 shows a 5-cycle decolorization test, in which the decolorization kinetics remains almost the same from the first cycle to the fifth cycle, indicating the stable catalytic activity of MCG through the multiple-cycle

operation. In order to evaluate MCG for a long-term operation, we further extended the cyclic test of MCG to 50 cycles as shown in Fig. 11. Even though no additional regeneration treatment was applied on the spent MCG, MCG exhibits high and stable regeneration efficiency (i.e., 97.6%) over 50 cycles, validating the promising potential of MCG as an effective and re-usable catalyst to activate PMS. Fig. S11 reveals a XPS spectrum of the spent MCG recovered from the 50-cycle decolorization test, in which Co^{3+} and Co^{2+} can be still observed, showing the high stability of cobalt oxide in MCG. On the other hand, the spent MCG recovered from the 50-cycle decolorization test was found to possess a higher fraction of the defect-derived D band (Fig. S12) which might be derived from the long-term oxidation of the graphitic structure of RGO. However, such a variation was found not to cause any activity change of MCG considering the stable and effective regeneration efficiency of MCG.

4. Conclusion

In this study, the magnetic cobalt-graphene (MCG) nanocomposite was prepared directly from carbonizing the electrostatically self-assembled ZIF-67/GO composite. MCG was used as a heterogeneous catalyst to activate PMS for the decolorization of AY in water. MCG exhibited the unique morphology and porous structure and sufficient saturation magnetization also allowed MCG to be readily collected from water after the decolorization reaction. MCG also exhibited an enhanced catalytic activity to activate PMS compared to cZIF-67 possibly owing to the interfacial interaction between cZIF-67/RGO. Factors influencing the PMS activation were also investigated including temperature, pH, facilitators (i.e., UV and ultrasound) and inhibitors. The recyclability test also revealed that MCG can be continuously used with stable and effective catalytic activity. These features make MCG a promising catalyst to activate PMS.

Acknowledgment

The authors are grateful for Mr. Spyros Schismenos' assistance on proofreading and editing of the manuscript. The authors also want to acknowledge the assistance from Research Center for

Sustainable Energy and Nanotechnology at National Chung Hsing University on the material characterization.

†Electronic Supporting Information (ESI) is available free of charge via the Internet.

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Fig. 1. Scheme of synthesis of magnetic cobalt-graphene (MCG) nanocomposite



Fig. 2. The SEM images of (a) the self-assemble ZIF-67/GO nanocomposite, (b) MCG nanocomposite and (d) closer-view of cobalt-bearing NPs (cZIF-67) and (d) TEM image of single-sheet MCG.



Fig. 3. Zeta potentials of ZIF-67, GO, ZIF-67/GO composite and MCG under various pH at 25 $\,$



Fig. 4. Characterization of MCG: (a) XRD pattern, (b) FT-IR, (c) Raman, (d) TGA, (e) N₂ sorption/desorption and (f) saturation magnetization



Fig. 5. Decolorization of AY using (a) MCG and RGO via the adsorption with $pH_{in} = 7.0 \pm 0.1$, and (b) PMS activated by RGO, cZIF-67 and MCG at 25 °C (AY solution = 100 mg L⁻¹; PMS = 90 mg L⁻¹; MCG = 500 mg L⁻¹; RGO = 500 mg L⁻¹; cZIF-67 = 500 mg L⁻¹; $pH_{in} = 3.8$)





Fig. 6. XPS spectrum of the as-synthesized MCG



Fig. 7. A proposed mechanism of MCG to activate PMS to generate sulfate radicals.



Fig. 8. Effects of (a) PMS loading (MCG = 500 mg L^{-1}) and (b) MCG dosage (PMS = 90 mg L^{-1}) on the decolorization of AY (100 mg L^{-1}) with pH_{in} = 3.8 at 25 °C



Fig. 9. Effects of (a) temperature with $pH_{in} = 3.8$ and (b) pH_{in} on the decolorization of AY at 25 °C. (AY solution = 100 mg L⁻¹; PMS = 90 mg L⁻¹; MCG = 500 mg L⁻¹)





Fig. 10. Effects of (a) UV and ultrasonication, and (b) inhibitors on the degradation of AY at 25 °C. (AY solution = 100 mg L^{-1} ; PMS = 90 mg L^{-1} ; MCG = 500 mg L^{-1} ; pH_{in} = 3.8



Fig. 11. 50-cycle test of MCG to activate PMS to degrade AY. (AY solution = 100 mg L^{-1} ; PMS = 90 mg L^{-1} ; MCG = 500 mg L^{-1} ; pH_{in} =

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Table 1. The pseudo first order rate constant (k) of the decolorization of AY under different conditions using PMS activated by MCG.

$\frac{\text{PMS}}{(\text{mg } \text{L}^{-1})}$	$\begin{array}{c} MCG\\ (mg L^{-1}) \end{array}$	T (°C)	Inhibitor	$k (\min^{-1})$	R^2
45	500	25	—	0.0069	0.999
90	500	25	—	0.0119	0.988
180	500	25	—	0.0131	0.989
90	250	25	—	0.0044	0.985
90	750	25	—	0.0146	0.974
90	500	40	—	0.0170	0.974
90	500	60	—	0.0243	0.999
90 + UV	500	25	_	0.0107	0.982
irradiation					
90 +	500	25	_	0.0202	0.983
ultrasonication					
90	500	25	ascorbic acid	0.0047	0.901
90	500	25	KI	0.0005	0.995
90	500	25	<i>tert</i> -butyl	0.0018	0.941
			alcohol		
90	500	25	methanol	0.0012	0.993