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A magnetic CoFe₂O₄–CNS nanocomposite as an efficient, recyclable catalyst for peroxymonosulfate activation and pollutant degradation†

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Sulfate radical (SO₄^{•−}) based advanced oxidation processes allow efficient degradation of refractory organics, but efficient, low-cost, and robust catalysts for such processes are still lacking. In this work, a magnetically recoverable heterogeneous catalyst was fabricated by immobilizing spinel cobalt-ferrite (CoFe₂O₄) particles on graphitic carbon nitride nanosheets (CNS) using a low-cost, one-step solvothermal method. In the CoFe₂O₄–CNS nanocomposite, the CoFe₂O₄ particles were evenly-distributed on the CNS surface, giving the nanocomposite a high specific surface area and significantly raised activity for peroxymonosulfate (PMS) activation and sulfonamide degradation compared to the bare CoFe₂O₄ NPs, which were considerably aggregated. In addition, the CoFe₂O₄–CNS could be more efficiently separated under magnetic field and resuspended compared with the bare CoFe₂O₄ due its larger sizes and no agglomeration. A stable activity of the nanocomposite catalyst during repeated use was also demonstrated. Our results imply high potential of CoFe₂O₄–CNS for sustainable water treatment and environmental remediation applications.

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1. Introduction

Advanced oxidation processes (AOP) based on the sulfate radical (SO₄^{•−}) are promising alternatives to those based on hydroxyl radicals for water treatment and environmental remediation applications, with advantages such as high redox potential (2.5–3.1 V),¹ relatively long lifetime and wide pH range.² SO₄^{•−} can be efficiently generated from peroxymonosulfate (PMS)³ or persulfate (PS)^{4,5} by using transition metals as catalysts. Cobalt (Co)-based materials are the most efficient catalysts for PMS activation so far.^{6,7} In particular, heterogeneous Co catalysts are gaining growing interest because they can be reused and are environmentally-benign.^{8–10} To facilitate their recovery after use, spinel-type Co-bearing ferrite nanoparticles (CoFe₂O₄ NPs) have been recently developed, which show high catalytic activity and good adaptability to magnetic separation.¹¹ However, such nanoparticles are difficult to magnetically separate from the water phase due to their small sizes.^{12,13} Another challenge is the easy agglomeration of the NPs, which leads to poor re-suspension and reduced performance with repeated use.¹¹ One strategy to address the

NPs separation and agglomeration issue is to disperse the NPs on various support materials, including reduced graphene oxide (rGO),¹⁴ carbon nanotube,¹⁵ titanate nanotubes.^{16,17} Recently, the combination of CoFe₂O₄ with graphitic carbon nitride (g-C₃N₄, a low-cost, highly-stable, and porous 2D materials with unique photocatalytic activity^{18–21}) has also been proposed. The CoFe₂O₄/g-C₃N₄ showed high photocatalytic activity for degradation Rhodamine B,^{22,23} but has not been used for SO₄^{•−}-based AOP so far. In addition, the synthesis process of the composite (involving precipitation, ultrasonic mixing and calcining) is complicated, and bulk g-C₃N₄ (ref. 22 and 23) with large size and low specific surface area was typically used.^{24,25}

Inspired by the above studies, here we investigated the feasibility of using CoFe₂O₄/g-C₃N₄ as a catalyst for activation of PMS. To improve its catalysis and recovery performances, we adopted a simple, one-step solvothermal method for the material fabrication, and used ultrathin g-C₃N₄ nanosheet (CNS) as the support for CoFe₂O₄.¹⁸ The catalytic activities of the resulting CoFe₂O₄–CNS nanocomposite and the CoFe₂O₄/g-C₃N₄ obtained by conventional method were evaluated by using sulfonamide (SA) as a model pollutant. SA is a ubiquitous, persistent contaminant, with high risks to aquatic ecosystem and human health.^{26–30} In addition, SA is a rich-electronic compound, which is suitable for SO₄^{•−}-based AOP.^{3,31,32} The magnetic separation and re-suspension performances and the stability of the materials during repeated use were also investigated. Lastly, the catalytic mechanisms of the nanocomposite for PMS activation were elucidated.

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2. Experimental

2.1. Materials

Iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), cobalt dichloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), sodium acetate (NaAc), and ethylene glycol, ethanol, melamine, sulfanilamide, methanol, *tert*-butyl alcohol (TBA), all of analytical grade, were purchased from Sinapharm Chemical Reagent Co., Ltd. Peroxymonosulfate (PMS, Oxone) was purchased from J&K Scientific LTD. All the solutions were prepared with deionized (DI) water.

2.2. Synthesis of CoFe_2O_4 -CNS catalyst

The CNS were synthesized according to the method described in a previous report.²¹ Melamine (5 g) was calcined at 520°C for 4 h with the heating rate of 5°C min^{-1} to obtain yellow bulk $\text{g-C}_3\text{N}_4$. Then, the bulk $\text{g-C}_3\text{N}_4$ was milled into powder, transferred into a combustion boat without any cover, and heated at 550°C for 3 h to obtain CNS. The resulting CNS (200 mg) was added into 30 mL ethylene glycol solution under ultrasonication, followed by adding 2 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Then, 15 mmol sodium acetate, as a protective agent to control the shape of synthesized nanomaterials, was added into the solution under vigorous stirring at room temperature. The mixture was subsequently autoclaved in a 50 mL Teflon lined stainless steel autoclave at 180°C for 24 h, and then naturally cooled down to room temperature. The resulting black precipitate was collected by filtration and washed with absolute ethanol and DI water in sequence for several times. The final product was dried in a vacuum box at 60°C for 6 h prior to use. For comparison, the bare CoFe_2O_4 was fabricated without the addition of $\text{g-C}_3\text{N}_4$ following the same procedures.^{33,34} In addition, graphene oxide-supported CoFe_2O_4 (CoFe_2O_4 -GO) was prepared following a reported method.³⁵

2.3. Catalytic activity test

The catalytic activities of different materials for PMS activation and SA degradation was examined. The bare CoFe_2O_4 NPs and $\text{g-C}_3\text{N}_4$ were used as the controls. Before the degradation test, SA was added into 100 mL DI water under constant stirring to an initial concentration of 10 mg L^{-1} . Then, 100 mg L^{-1} catalyst and 100 mg L^{-1} PMS were added to initiate the degradation reactions. During the test, 1 mL mixed liquor was collected each time at given time intervals, immediately quenched with excess pure methanol (1 mL), and then centrifuged before analysis. All the experiment was conducted in duplicate at ambient temperature ($25 \pm 2^\circ\text{C}$).

2.4. Analysis

The SA concentration was measured by a liquid chromatograph (Alliance, water 2695) equipped with Waters 2487 dual λ absorbance detector and Agilent 5 TC-C18 $150 \times 4.6\text{ mm}$ column. A mixture of methanol and 0.1% formic acid solution (20 : 80, v/v) at a flow rate of 0.5 mL min^{-1} was used as the mobile phase. The column temperature was 30°C . The detection wavelength was set at 268 nm.

The morphology and structure of the materials were examined by scanning electron microscopy (SEM, QUSNTA FEG 250) and transmission electronic microscopy (TEM, HT7700). X-ray diffraction (XRD) patterns were obtained on a Bruker D8 diffractometer using filtered $\text{Cu K}\alpha$ radiation ($\alpha = 1.54178\text{ \AA}$). The Brunauer-Emmett-Teller (BET) specific surface area of sample was determined on an Autosorb iQ Station 3 system at liquid-nitrogen temperature of 77.35 K. The chemical species of Co, Fe, O, C and N were determined by X-ray photoelectron spectroscopy (XPS). Magnetic properties of the samples were examined using a MPMS (SQUID)-vibrating sample magnetometer at 300 K.

3. Results

3.1. Catalysts characterization

The morphologies of the CNS, bare CoFe_2O_4 and CoFe_2O_4 -CNS composite are shown in Fig. 1. The CNS had large sizes ranging from hundreds of nanometer to several micrometer (Fig. 1(a)) but a small thickness of around 10 nm (Fig. 1(d)). The bare CoFe_2O_4 was mainly in the shape of spherical particles that aggregated together (Fig. 1(b) and (e)). In comparison, for the CoFe_2O_4 -CNS composites, the particles were evenly distributed on the CNS (Fig. 1(c) and (f)). The particles did not peel off from the CNS after ultrasonic processing for 30 min due to the formation of heterostructured material. The high resolution TEM (HRTEM) image of CoFe_2O_4 -CNS showed lattice fringe spacing of 0.24 nm, 0.25 nm, 0.29 nm and 0.487 nm (Fig. 1(g) and (h)), consistent with the (2 2 2) (3 1 1) (2 2 0) and (1 1 1) planes of CoFe_2O_4 crystals, respectively.^{36,37} No clear lattice was observed for the CNS due to its low crystallinity. The two components were tightly bonded together, as indicated by the clear interface between them. In addition, the EDX spectra confirm the presence of Co, Fe, C, O, and N elements in the CoFe_2O_4 -CNS (Fig. 1(i)). The Si signal observed here was derived from the silicon substrate.

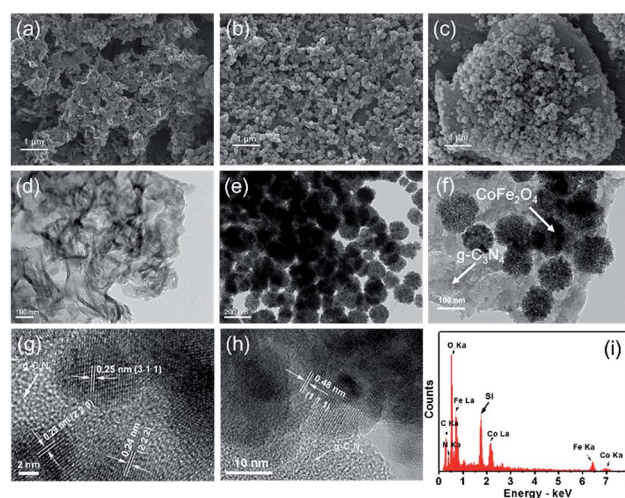


Fig. 1 SEM (a–c) and TEM (d–f) images of (a and d) $\text{g-C}_3\text{N}_4$, (b and e) bare CoFe_2O_4 , (c and f) CoFe_2O_4 -CNS; (g and h) HRTEM images and (i) EDX pattern of CoFe_2O_4 -CNS.



The synthesis of the CoFe_2O_4 and CoFe_2O_4 -CNS composites was also confirmed by the XRD and XPS spectra. The CoFe_2O_4 showed a typical pattern of spinel ferrite with six well-defined peaks at $2\theta = 18.29^\circ$, 30.08° , 35.44° , 43.06° , 56.97° , and 62.58° (Fig. 2(a)), corresponding to the Bragg planes of (1 1 1), (2 2 0), (3 1 1), (4 0 0), (5 1 1), and (4 4 0), respectively.^{38,39} The major crystal phase of CoFe_2O_4 was in a good agreement with JCPDS: 22-1086. For the CoFe_2O_4 -CNS, besides the above six peaks, a characteristic peak at 27.6° corresponding to the (0 0 2) diffraction plane of the CNS was also detected, and no other peaks occurred (Fig. S1†). These results indicate a high purity of the synthesized products. In addition, the XPS survey scan spectra of both materials showed the characteristic peaks of Co, Fe and O, and the extra signal of C (284 eV) and N (400 eV) in the CoFe_2O_4 -CNS, further confirming the formation of CoFe_2O_4 and CoFe_2O_4 -CNS with high purity (Fig. 2(b)).

The surface properties of the synthesized materials were also evaluated. Despite of the similar ordered mesoporous structure and pore sizes of the two materials (Fig. 3), the CoFe_2O_4 -CNS had larger specific surface area ($89.484 \text{ m}^2 \text{ g}^{-1}$ versus $81.253 \text{ m}^2 \text{ g}^{-1}$) and larger pore volume ($0.163 \text{ cm}^3 \text{ g}^{-1}$ versus $0.108 \text{ cm}^3 \text{ g}^{-1}$) than CoFe_2O_4 .

3.2. Catalytic activity for $\text{SO}_4^{\cdot-}$ generation and SA degradation

The CoFe_2O_4 -CNS showed significantly higher activity for PMS activation and SA degradation than the CoFe_2O_4 NPs (Fig. 4(a)) and the CoFe_2O_4 -GO (Fig. S2(a)†). Consistent result was also obtained by the TOC analysis (Fig. 4(b)). In light of the negligible SA removal in the PMS- or catalyst-free controls, this result also implies the critical involvement of $\text{SO}_4^{\cdot-}$ in the process. Here, the higher catalytic activity of CoFe_2O_4 -CNS than CoFe_2O_4 -GO is likely associated with a better dispersion of the CoFe_2O_4 on the CNS with large surface area (Fig. S2(b)†).

The predominant contribution of $\text{SO}_4^{\cdot-}$ to the SA degradation in the CoFe_2O_4 -CNS/PMS system was further confirmed by radicals quenching tests using ethanol or *tert*-butyl alcohol (TBA) as the quencher.⁴⁰ Ethanol is commonly used as a scavenger to quickly react with both hydroxyl and sulfate radical species, whereas TBA mainly quenches OH^{\cdot} .⁴¹ Our results show that the SA degradation was almost completely inhibited in the presence of excess ethanol (Fig. 5(a)), but was decreased only by 22% (within 5 min) with TBA addition. Therefore, the key role of $\text{SO}_4^{\cdot-}$ in the SA degradation can be confirmed.

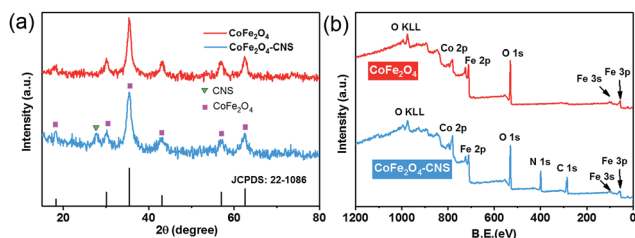


Fig. 2 (a) XRD patterns of CoFe_2O_4 and CoFe_2O_4 -CNS, (b) XPS survey spectra of CoFe_2O_4 and CoFe_2O_4 -CNS.

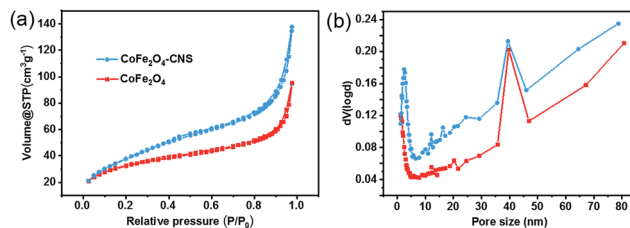
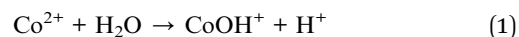


Fig. 3 (a) Nitrogen sorption isotherms and (b) pore size distribution of CoFe_2O_4 and CoFe_2O_4 -CNS.

The SA degradation performances varied under different catalyst dosage, PMS dosage, and the initial pH conditions. The SA removal increased markedly with catalyst dosage from 0.05 to 0.1 g L^{-1} , but increased only slightly when further increasing catalyst dosage to 0.15 g L^{-1} (Fig. 5(b)), indicating that 0.1 g L^{-1} catalyst is sufficient in our reaction system. Increasing PMS concentration also significantly raised the SA removal initially but the removal ratio became relatively stable at high PMS dosage (Fig. 5(c)), likely resulting from self-quenching of the generated $\text{SO}_4^{\cdot-}$ by excess PMS.⁴² In addition, the catalyst showed stable activity over a wide pH range of 5–10 (Fig. 5(d)). The best performance at initial pH of 10.0 was consistent with previous studies.⁴³ Here, the significant performance decline at pH 11.0 might be due to a competitive conversion of PMS to less-active dianion (SO_5^{2-}) and OH^{\cdot} under alkaline condition⁴⁴ and increased electrostatic compelling between the negatively-charged catalyst and PMS species,⁴¹ whereas the suppression at pH 3.0 should be associated with the deactivation of catalyst with protonation of the surface hydroxyl groups.³



3.3. Magnetic separation and reuse performances

The magnetic properties of the CoFe_2O_4 and CoFe_2O_4 -CNS composites were evaluated, and the magnetic hysteresis loops are shown in Fig. 6. The CoFe_2O_4 -CNS showed a lower saturation magnetization value ($M_s = 56.1 \text{ emu g}^{-1}$) than CoFe_2O_4 ($M_s = 88.7 \text{ emu g}^{-1}$), which should be due to magnetic property dilution by the nonmagnetic CNS component.

Nevertheless, the CoFe_2O_4 was more difficult to be attracted by the magnet, due to smaller sizes of the particles (average size

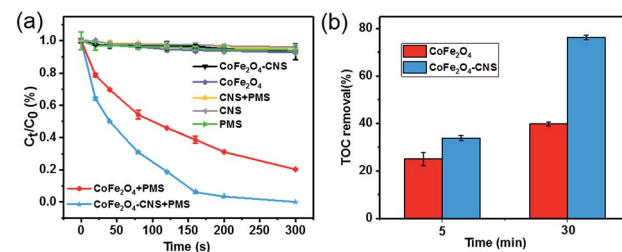


Fig. 4 (a) Removal of SA in different processes. (b) TOC removal of SA at different reaction times. Reaction conditions: $[\text{SA}] = 10 \text{ mg L}^{-1}$, $[\text{PMS}] = 0.10 \text{ g L}^{-1}$, $[\text{catalyst}] = 0.10 \text{ g L}^{-1}$.



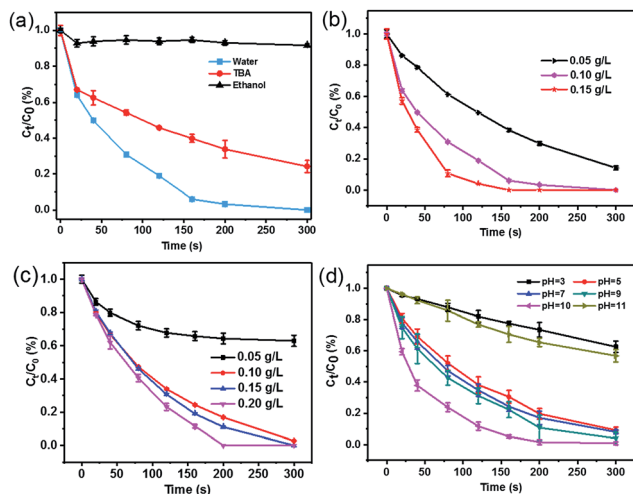


Fig. 5 (a) Effects of radical scavengers on SA degradation in the CoFe₂O₄-CNS/PMS system. SA removal efficiencies under different reaction conditions: (b) different catalyst dosage, initial pH = 6.3, [SA] = 10 mg L⁻¹, [PMS] = 0.10 g L⁻¹. (c) Effect of PMS concentration, initial pH = 6.3, [SA] = 10 mg L⁻¹, [catalyst] = 0.10 g L⁻¹. (d) Effect of initial pH, [SA] = 10 mg L⁻¹, [PMS] = 0.10 g L⁻¹, [catalyst] = 0.10 g L⁻¹.

176 nm for CoFe₂O₄ versus 1.38 μm for CoFe₂O₄-CNS (Fig. S3†). According to the literature,^{12,13,45} the smaller nanoparticles are more difficult to recover than larger ones under magnetic field. Therefore, a more effective, rapid magnetical separation of CoFe₂O₄-CNS than CoFe₂O₄ was achieved in our study (Fig. 6 Inset). Furthermore, for the small-sized CoFe₂O₄ particles, an agglomeration would occur during their magnetic separation, and the resulting aggregates are difficult to re-disperse even with intense ultrasonication.^{13,46} This explains the much poorer re-suspension of CoFe₂O₄ than the larger-sized yet well-dispersed CoFe₂O₄-CNS (Fig. 6 Inset).

The CoFe₂O₄-CNS also showed good stability during repeated use. After five successive reaction cycles, the system still maintained 94.8% SA removal within 30 min (Fig. S4†). In comparison, the SA removal ratio was 98.6% for the CoFe₂O₄ in first cycle and gradually decreased to 69.5% by the fifth cycle (Fig. S4†). The leaching of Co(II) was also more serious in

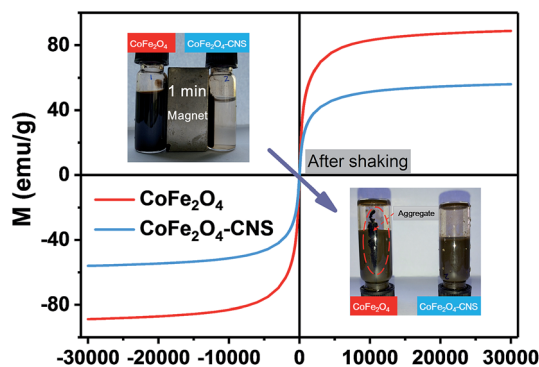


Fig. 6 Magnetic hysteresis loops of CoFe₂O₄ and CoFe₂O₄-CNS composites at room temperature. Inset: separation and resuspension performance of the synthesized materials.

CoFe₂O₄ (Fig. S5†). These results indicate a good repeatability and robustness of the CoFe₂O₄-CNS far exceeding existing CoFe₂O₄ catalysts.

3.4. Mechanism of PMS activation by CoFe₂O₄-CNS

The XPS spectra of CoFe₂O₄-CNS and CoFe₂O₄ before and after reaction were measured to show the possible changes of the catalysts. The high resolution XPS spectra of the Co 2p_{3/2} show three peaks at 779.9, 781.2 and 782.8 eV for all the samples (Fig. 7). These peaks were attributed to the Co^{II} in octahedral (B-site Co^{II}) and tetrahedral sites (A-site Co^{II}) and Co^{III} in tetrahedral (B-site Co^{III}), respectively. It is suggested that during the catalysis the B-site Co^{II} would provide electrons to PMS, leading to SO₄^{•-} production and increase of Co^{III} in B-site (eqn (2)). The latter can also accept electrons from PMS to regenerate Co^{II} with concomitant production of SO₅^{•-} (eqn (3)), thus maintaining the Co^{II}-Co^{III}-Co^{II} redox cycles for the continuous catalysis.^{11,47,48} Our results show that the proportion of B-site Co^{II} in CoFe₂O₄-CNS slightly decreased from 58% to 50% after reaction, while B-site Co^{II} in CoFe₂O₄ drastically decreased from 63% to 32%. Accordingly, the Co^{III} in tetrahedral of CoFe₂O₄-CNS showed less increase (11%) than that of CoFe₂O₄ (17%), indicating a more efficient regeneration of B-site Co^{II} in CoFe₂O₄-CNS. In addition, the high resolution XPS spectra of Fe 2p (Fig. S6†) showed two major peaks assigned to Fe^{II} (710.6 eV) and Fe^{III} (712.6 eV). The catalytic activity of the Fe^{II}/Fe^{III} redox pair (eqn (4) and (5)) for PMS activation has been demonstrated previously.^{11,14,48,49} The CoFe₂O₄-CNS showed less decrease in Fe^{II} content than CoFe₂O₄ after the reaction. Such an improved Fe^{II} regeneration also contributed to the better sustained activity of CoFe₂O₄-CNS in repeated use.

High resolution N 1s spectra (Fig. S7a†) could be fitted into three peaks at 399.1 eV (C-N=C groups, denoted as N1), 399.9 eV (amino groups ((C)₂-N-H) connecting with structural defects and incomplete condensation, denoted as N2), 401.2 eV (N-(C)₃ in the aromatic ring, denoted as N3). For the CoFe₂O₄-CNS, the intensity of N1 peak decreased by 2% after the reaction

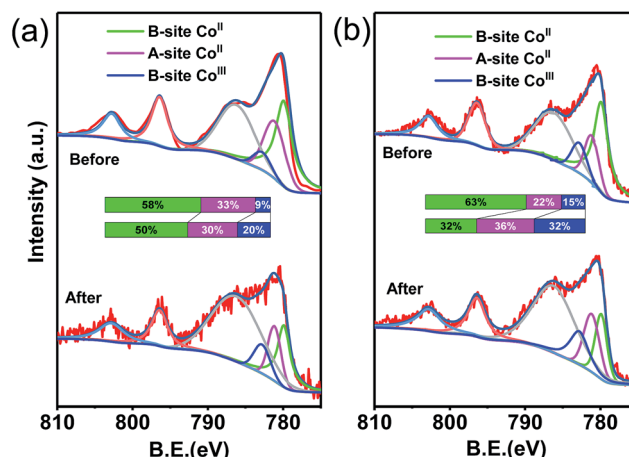
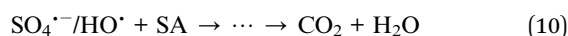
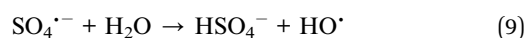
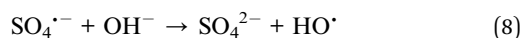
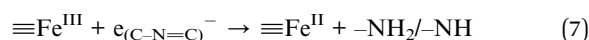
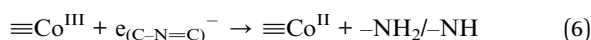
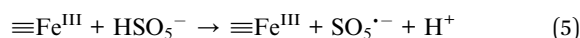
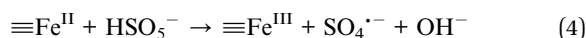
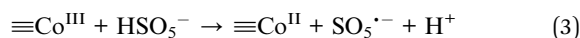
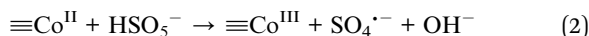


Fig. 7 XPS of Co 2p spectra of (a) CoFe₂O₄-CNS composites and (b) CoFe₂O₄ before and after the reaction with PMS.



while that of N2 peak increased by 2%. The g-C₃N₄ contains abundant graphitic N corresponding to the sp²-bonded N that are involved in the triazine rings (N1)⁵⁰ and can induce electron transfer from adjacent carbon atoms to nitrogen. Such a feature renders the sp² carbon layer of the g-C₃N₄ a high chemical activity.^{51–54} Therefore, it is possible that the delocalized electrons from grapheme N on the zigzag edges of CNS might also contributed to the reduction of M^{III} (M = Co or Fe) species, thus the C=N=C groups would be disrupted to form –NH₂ or –NH groups (eqn (6) and (7)) (Fig. S7(c)†). This was verified by the FT-IR spectra of CoFe₂O₄–CNS which showed increased –NH₂ or –NH groups (absorption centred at 3184 cm^{–1})¹⁷ and decreased C=N=C groups after the reaction (Fig. S7(b)†).



In addition, SO₄^{·–} can react with OH[–] or water to produce HO[·] (eqn (8) and (9)). Therefore, the following mechanism of PMS activation by CoFe₂O₄–CNS can be proposed (Fig. 8). In the CoFe₂O₄ catalyst, the bi-valent metals (≡Co^{II} and ≡Fe^{II}) play a centre role in converting PMS into SO₄^{·–}, with themselves being oxidized into ≡Co^{III} and ≡Fe^{III}. The latter can be reduced back to bi-valent metals by PMS, generating less active SO₅^{·–}. However, this step is relatively slow, leading to decreased content of ≡Co^{II} and ≡Fe^{II} during the catalytic reaction. Here, the introduction of CNS allowed an improved dispersion of the CoFe₂O₄ particles, thus more active sites of ≡Co^{II} and ≡Fe^{II} could be exposed. In addition, the regeneration of ≡Co^{II} and

≡Fe^{II} was reinforced by graphitic N on the zigzag edges of CNS. Such a synergy between CoFe₂O₄ and CNS significantly raised the catalytic activity and stability for PMS activation.

The above results indicate that CoFe₂O₄–CNS could be used as an attractive heterogenous catalyst for sustainable pollutant control application, but issues such as Co^{II} leaching and robustness in real environment are still to be addressed in future studies. In addition, the photocatalytic activity of g-C₃N₄ may also be taken advantage of to further strengthen the performance of such SO₄^{·–}-based treatment processes.^{55,56}

4. Conclusions

A novel CoFe₂O₄–CNS nanocomposite was fabricated for PMS activation and SA degradation. It showed obvious advantage over conventional CoFe₂O₄ catalyst in terms of catalytic activity, stability, and magnetic separation performance. The superior performance of the CoFe₂O₄–CNS was mainly ascribed to a good synergy between the CoFe₂O₄ and CNS: the CNS with large specific surface area significantly improved the dispersion of CoFe₂O₄ particles, not only enabling the exposure of more active sites to favor PMS activation but also allowing more efficient magnetic separation and resuspension of the material; the CNS also directly contributed to the regeneration of ≡Co^{II} and ≡Fe^{II}, thereby further improving the catalyst stability during repeated use. This material has the potential for more sustainable water treatment and environmental remediation applications.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 J. Zou, J. Ma, L. Chen, X. Li, Y. Guan, P. Xie and C. Pan, *Environ. Sci. Technol.*, 2013, **47**, 11685–11691.
- 2 W. D. Oh, Z. Dong, Z. T. Hu and T. T. Lim, *J. Mater. Chem. A*, 2015, **3**, 22208–22217.
- 3 F. Ghanbari and M. Moradi, *Chem. Eng. J.*, 2017, **310**, 41–62.
- 4 H. Chen and K. C. Carroll, *Environ. Pollut.*, 2016, **215**, 96–102.
- 5 J. Wang, Z. Yao, Y. Wang, Q. Xia, H. Chu and Z. Jiang, *Environ. Pollut.*, 2017, **224**, 552–558.
- 6 G. P. Anipsitakis and D. D. Dionysiou, *Environ. Sci. Technol.*, 2004, **38**, 3705–3712.
- 7 Y. Fan, W. Ma, J. He and Y. Du, *RSC Adv.*, 2017, **7**, 36193–36200.
- 8 W. Chu, W. K. Choy and C. Y. Kwan, *J. Agric. Food Chem.*, 2007, **55**, 5708–5713.

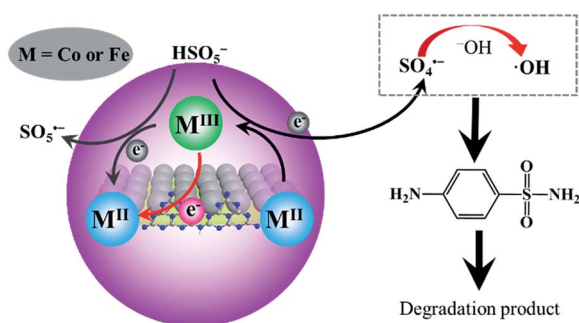


Fig. 8 Mechanisms of PMS activation by CoFe₂O₄–CNS for oxidative degradation of SA.



- 9 Q. Yang, H. Choi and D. D. Dionysiou, *Appl. Catal., B*, 2007, **74**, 170–178.
- 10 W. Zhang, H. L. Tay, S. S. Lim, Y. Wang, Z. Zhong and R. Xu, *Appl. Catal., B*, 2010, **95**, 93–99.
- 11 Y. Ren, L. Lin, J. Ma, J. Yang, J. Feng and Z. Fan, *Appl. Catal., B*, 2015, **165**, 572–578.
- 12 L. M. Rossi, N. J. S. Costa, F. P. Silva and R. Wojcieszak, *Green Chem.*, 2014, **16**, 2906–2933.
- 13 Y. C. Kim, S. Han and S. Hong, *Water Sci. Technol.*, 2011, **64**, 469–476.
- 14 Y. Yao, Y. Cai, F. Lu, F. Wei, X. Wang and S. Wang, *J. Hazard. Mater.*, 2014, **270**, 61–70.
- 15 X. Qi, Q. Hu, J. Xu, R. Xie, Y. Jiang, W. Zhong and Y. Du, *RSC Adv.*, 2016, **6**, 11382–11387.
- 16 B. Buchholz, H. Haspel, A. Oszko, A. Kukovec and Z. Konya, *RSC Adv.*, 2017, **7**, 16410–16422.
- 17 M. Wei, L. Gao, J. Li, J. Fang, W. Cai, X. Li and A. Xu, *J. Hazard. Mater.*, 2016, **316**, 60–68.
- 18 P. Niu, L. Zhang, G. Liu and H.-M. Cheng, *Adv. Funct. Mater.*, 2012, **22**, 4763–4770.
- 19 J. Xu, Y. Wang and Y. Zhu, *Langmuir*, 2013, **29**, 10566–10572.
- 20 J. Xiao, J. Rabeah, J. Yang, Y. Xie, H. Cao and A. Brückner, *ACS Catal.*, 2017, **7**, 6198–6206.
- 21 H. Zhao, H. Yu, X. Quan, S. Chen, Y. Zhang, H. Zhao and H. Wang, *Appl. Catal., B*, 2014, **152–153**, 46–50.
- 22 S. Huang, Y. Xu, M. Xie, H. Xu, M. He, J. Xia, L. Huang and H. Li, *Colloids Surf., A*, 2015, **478**, 71–80.
- 23 Y. Yao, G. Wu, F. Lu, S. Wang, Y. Hu, J. Zhang, W. Huang and F. Wei, *Environ. Sci. Pollut. Res.*, 2016, **23**, 21833–21845.
- 24 K. L. Corp and C. W. Schlenker, *J. Am. Chem. Soc.*, 2017, **139**, 7904–7912.
- 25 X. Zhang, X. Xie, H. Wang, J. Zhang, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2013, **135**, 18–21.
- 26 S. G. Dmitrienko, E. V. Kochuk, V. V. Apyari, V. V. Tolmacheva and Y. A. Zolotov, *Anal. Chim. Acta*, 2014, **850**, 6–25.
- 27 S. Dong, Y. Pi, Q. Li, L. Hu, Y. Li, X. Han, J. Wang and J. Sun, *J. Alloys Compd.*, 2016, **663**, 1–9.
- 28 W. Zhu, J. Liu, S. Yu, Y. Zhou and X. Yan, *J. Hazard. Mater.*, 2016, **318**, 407–416.
- 29 A. A. Ahmed, S. Thiele-Bruhn, P. Leinweber and O. Kühn, *Sci. Total Environ.*, 2016, **559**, 347–355.
- 30 S. T. Khankhasaeva, D. V. Dambueva, E. T. Dashinamzhilova, A. Gil, M. A. Vicente and M. N. Timofeeva, *J. Hazard. Mater.*, 2015, **293**, 21–29.
- 31 J. Giménez, B. Bayarri, Ó. González, S. Malato, J. Peral and S. Esplugas, *ACS Sustainable Chem. Eng.*, 2015, **3**, 3188–3196.
- 32 E. Saputra, S. Muhammad, H. Sun, H. M. Ang, M. O. Tade and S. Wang, *Environ. Sci. Technol.*, 2013, **47**, 5882–5887.
- 33 A. Yan, X. Liu, R. Shi, N. Zhang, R. Yi, Y. Li, G. Gao and G. Qiu, *Solid State Commun.*, 2008, **146**, 483–486.
- 34 A. Yan, X. Liu, R. Yi, R. Shi, N. Zhang and G. Qiu, *J. Phys. Chem. C*, 2008, **112**, 8558–8563.
- 35 L. J. Xu, W. Chu and L. Gan, *Chem. Eng. J.*, 2015, **263**, 435–443.
- 36 T. Li, Y. Lv, J. Su, Y. Wang, Q. Yang, Y. Zhang, J. Zhou, L. Xu, D. Sun and Y. Tang, *Adv. Sci.*, 2017, **4**, 1700226.
- 37 C. D. Pham, J. Chang, M. A. Zurbuchen and J. P. Chang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 36980–36988.
- 38 N. Dong, F. He, J. Xin, Q. Wang, Z. Lei and B. Su, *Mater. Res. Bull.*, 2016, **80**, 186–190.
- 39 N. Dong, M. Zhong, P. Fei, Z. Lei and B. Su, *J. Alloys Compd.*, 2016, **660**, 382–386.
- 40 G. P. Anipsitakis and D. D. Dionysiou, *Environ. Sci. Technol.*, 2003, **37**, 4790–4797.
- 41 T. Zhang, H. Zhu and J. P. Croué, *Environ. Sci. Technol.*, 2013, **47**, 2784–2791.
- 42 H. Liang, H. Sun, A. Patel, P. Shukla, Z. H. Zhu and S. Wang, *Appl. Catal., B*, 2012, **127**, 330–335.
- 43 Y. Lei, C.-S. Chen, J. Ai, H. Lin, Y.-H. Huang and H. Zhang, *RSC Adv.*, 2016, **6**, 866–871.
- 44 Y. Feng, J. Liu, D. Wu, Z. Zhou, Y. Deng, T. Zhang and K. Shih, *Chem. Eng. J.*, 2015, **280**, 514–524.
- 45 G. Friedman and B. Yellen, *Curr. Opin. Colloid Interface Sci.*, 2005, **10**, 158–166.
- 46 Y. Cai and X. M. Hu, *Desalination*, 2016, **391**, 16–29.
- 47 X. Li, Z. Wang, B. Zhang, A. I. Rykov, M. A. Ahmed and J. Wang, *Appl. Catal., B*, 2016, **181**, 788–799.
- 48 Y. Zhao, X. Ma, P. Xu, H. Wang, Y. Liu and A. He, *J. Hazard. Mater.*, 2018, **341**, 228–237.
- 49 X. J. Yang, X. M. Xu, J. Xu and Y. F. Han, *J. Am. Chem. Soc.*, 2013, **135**, 16058–16061.
- 50 W. Ho, Z. Zhang, W. Lin, S. Huang, X. Zhang, X. Wang and Y. Huang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 5497–5505.
- 51 X. Duan, Z. Ao, H. Sun, S. Indrawirawan, Y. Wang, J. Kang, F. Liang, Z. H. Zhu and S. Wang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 4169–4178.
- 52 X. Duan, Z. Ao, H. Sun, L. Zhou, G. Wang and S. Wang, *Chem. Commun.*, 2015, **51**, 15249–15252.
- 53 X. Duan, H. Sun, Y. Wang, J. Kang and S. Wang, *ACS Catal.*, 2015, **5**, 553–559.
- 54 X. Duan, K. O'Donnell, H. Sun, Y. Wang and S. Wang, *Small*, 2015, **11**, 3036–3044.
- 55 C. Y. Wang, X. Zhang, H. B. Qiu, G. X. Huang and H. Q. Yu, *Appl. Catal., B*, 2017, **205**, 615–623.
- 56 W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong and S. P. Chai, *Chem. Rev.*, 2016, **116**, 7159–7329.

