



Degradation of organic pollutants by peroxymonosulfate activated by MnO₂ with different crystalline structures: Catalytic performances and mechanisms

Zhi-Gang Zhou^{a,1}, Hong-Mei Du^{a,1}, Zhenhua Dai^b, Yi Mu^a, Lin-Lin Tong^c, Qiu-Ju Xing^a,
Shan-Shan Liu^a, Zhimin Ao^{b,*}, Jian-Ping Zou^{a,*}

^a Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, PR China

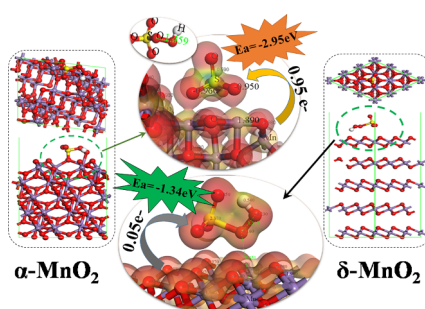
^b Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, Institute of Environmental Health and Pollution Control, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 51006, PR China

^c School of Metallurgy, Northeastern University, Shenyang 110819, PR China

HIGHLIGHTS

- A novel α -MnO₂ with featured morphology was synthesized by phase transitions from δ -MnO₂.
- The two kinds of MnO₂ show different catalytic activity for the 4-NP degradation in the presence of PMS.
- Mechanisms were proposed to explain the different catalytic performance of the two types of MnO₂.

GRAPHICAL ABSTRACT



ARTICLE INFO

Dedicated to Prof. Jin-Shun Huang on the occasion of his 80th birthday.

Keywords:

Advanced oxidation processes
Manganese dioxide
Organic pollutants
Sulfate radical
Hydroxide radical

ABSTRACT

In this study, a novel α -MnO₂ (OMS-2) material with long and uniform nanofibers was synthesized by morphological and phase transitions from δ -MnO₂ (OL-1) under a hydrothermal reaction. We systematically investigated the catalytic performances of OMS-2 and OL-1 for the activation of PMS (peroxymonosulfate) to degrade 4-nitrophenol (4-NP) in water. According to the results from Brunauer Emmett Teller (BET), thermo gravimetric analyzer (TGA), H₂-temperature programmed reduction (H₂-TPR), cyclic voltammetry, X-ray photoelectron spectroscopy (XPS), and density-functional theory (DFT) calculation, OMS-2 has a larger BET area, more active sites, better adsorption ability, a faster electron transfer rate, and more multiple valence states of Mn than OL-1. These results also well illustrate OMS-2 has much better catalytic performance than OL-1. The results of the electron paramagnetic resonance (EPR) and the radical quantification experiments confirmed that sulfate radicals (SO₄^{•-}) and hydroxyl radicals (•OH) were the main oxidants and OMS-2 has better radical generation capability than OL-1. The LC-MS results indicated that there were two routes for the degradation of 4-NP and the degradation mechanism of 4-NP in the OMS-2/PMS system was similar to that in the OL-1/PMS system. Finally, we proposed the PMS activation mechanism, the formation mechanism of radicals, and the degradation mechanism of 4-NP based on the two different kinds of MnO₂ with different morphologies.

* Corresponding authors.

E-mail addresses: zhimin.ao@gdut.edu.cn (Z. Ao), zjp_112@126.com (J.-P. Zou).

¹ The two authors have equal contribution to the paper.

1. Introduction

With the rapid development of urbanization and industrialization, organic contaminants, discharged from industrial refineries have become an urgent environmental issue. For example, 4-nitrophenol (4-NP) is toxic, non-biodegradable and highly persistent in the environment, so it has been considered to be priority toxic pollutant by U.S. Environmental Protection Agency (EPA) [1,2]. Advanced oxidation processes (AOPs) have been considered as effective technologies to degrade organic compounds in aqueous media because they can generate highly reactive species, such as $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radicals, that quickly oxidize a broad range of organic pollutants [3,4,5]. Recently, sulfate radicals have received increasing interest in both research and applications for the remediation of organic pollutants in groundwater and wastewater, because $\text{SO}_4^{\cdot-}$ is more powerful, selective and effective for the degradation of persistent organic pollutants than $\cdot\text{OH}$ [6,7]. Furthermore, peroxymonosulfate (PMS) and peroxydisulfate (PDS), as the origin of $\text{SO}_4^{\cdot-}$, are relatively stable, easily stored and transported, environmental friendly, and cost effective [8,9]. In general, $\text{SO}_4^{\cdot-}$ can be produced from PMS or PDS activated by alkaline [10,11], nanocarbons [12], UV [13], heat [14], microwave [15], electrosorption [16], and transition metal ions or oxides [17,18]. Many studies have demonstrated that metal oxides or supported metal oxides are good and effective heterogeneous catalysts for activating PMS or PDS to generate sulfate radicals due to easily recycle these catalysts [19,20,21]. Many researchers reported that Co-based materials are effective as PMS activators but that they have the drawback of dissolution of highly toxic cobalt ions during the degradation of organic pollutants [22,23,24,25]. One appealing alternative transition metal is Mn because Mn is eco-friendly and abundant in soils, and it has various forms with a various oxidation states, such as MnO_2 , Mn_2O_3 and Mn_3O_4 .

To date, Mn-based catalysts for the activation of PMS, especially manganese oxides, have been extensively reported, including α -, β - and γ - MnO_2 [26], Mn_2O_3 [27], and MnFe_2O_4 [6]. For example, Wang et al. reported that α -, β -, and γ - MnO_2 show different catalytic abilities for phenol degradation in the activation of PMS because the three kinds of MnO_2 could have different oxygen liabilities and MnO_6 edges, which are important in the activation of oxone for sulfate radical production [26]. Wang et al. investigated the effect of the different morphologies of Mn_2O_3 (cubic, octahedral and truncated octahedral- Mn_2O_3) and one-dimensional α - MnO_2 (nanorods, nanotubes and nanowires) on PMS activation during the degradation of organic pollutants [27,28]. The results showed that an active surface facet or metal stable facet is crucial to the generation of $\text{SO}_4^{\cdot-}$ radicals for Mn_2O_3 and one-dimensional α - MnO_2 with different morphologies. Ren et al. found that the different catalytic performances of MFe_2O_4 ($\text{M} = \text{Co}, \text{Cu}, \text{Mn}$, and Zn) for PMS activation are mainly attributed to the different reducibility of MFe_2O_4 [6].

Based on the previous reports, we found that different researchers have different explanations for the mechanism of PMS activation by manganese oxides, especially MnO_2 with different crystalline forms. Thus, further investigation is needed to determine: (i) why different crystalline phases of MnO_2 show different catalytic performance for PMS activation; (ii) how to activate PMS to produce $\text{SO}_4^{\cdot-}$ or $\cdot\text{OH}$ radicals by MnO_2 with different crystalline phases; and (iii) how $\text{SO}_4^{\cdot-}$ or $\cdot\text{OH}$ radicals degrade organic pollutants.

In the present work, we synthesized a novel α - MnO_2 material (hereafter named as OMS-2) with long and uniform nanofibers via morphological and phase transitions from δ - MnO_2 (hereafter named as OL-1) nanoparticles using a hydrothermal method in the presence of graphene oxide (GO). In addition, we systematically investigated the PMS activation mechanism by the as-prepared OMS-2 and OL-1 to explain the fundamental reasons for the different catalytic properties of the two different MnO_2 phases for the activation of PMS and to determine the formation mechanism of different radicals from PMS activation and p-nitrophenol degradation pathways using more advanced

measurements, such as EPR, XPS, LC-MS, Raman, H_2 -TPR, and cyclic voltammetry.

2. Experimental section

2.1. Syntheses

The chemicals used for the preparation were all analytical grade reagents and were used without further purification. The detailed information of the chemicals is shown in the [Supporting Information \(Text S1\)](#).

2.1.1. Synthesis of OL-1 nanoparticles

OL-1 nanoparticles were prepared by the reported method in the literature [29,30,31]. Typically, the mixed solution of ethanol (20 mL), water (20 mL) and KOH (16.8 g) was added into a beaker. After stirring for 5 min, solution A was obtained. Then, 4.74 g KMnO_4 was dissolved into 250 mL beaker with 50 mL deionized water, stirred adequately to get solution B. Next, solution A was slowly added into the solution B to turn into uniform mixture and then gray precipitation was formed after 2 h. Finally, the obtained precipitation was washed several times with purified water, and dried in a vacuum-drying oven at 80 °C to obtain OL-1.

2.1.2. Synthesis of OMS-2 nanofibers

OMS-2 nanofibers were synthesized through hydrothermal reaction. Firstly, 0.25 g OL-1 and 88 mL deionized water were mixed together by stirring for 5 min. Then, 10 mL graphene oxide was added into the above solution and stirred for 5 min. The obtained solution was transferred into 120 mL Teflon reactor, and kept for 24 h at 200 °C. The obtained solid was filtered by vacuum filtration and washed for several times. Finally, the product of OMS-2 was dried at 60 °C overnight.

2.2. Characterizations

The crystalline phases of the samples were investigated by X-ray diffraction (Bruker D8 ADVANCE) using graphite monochromatized $\text{Cu-K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. The XRD data for indexing and the cell-parameter calculations were collected in a scanning mode with a scanning speed of $2^\circ/\text{min}$ in the 2θ range of 10 to 70° . Ultraviolet-visible (UV-vis) diffuse reflection spectra were measured using a UV-vis U-3900H spectrophotometer. The morphologies of the samples were investigated by scanning electron microscopy (SEM, FEI, Holland), transmission electron microscopy (JEM-2010HR) and high-resolution TEM (HRTEM) images. Brunauer-Emmett-Teller (BET) measurements were performed on an ASAP 2020 (accelerated surface area and porosimetry system 2020) at 77 K using dinitrogen. Zeta-potential analysis was conducted on a Malvern Zetasizer NanoZS 90 instrument. A ContrAA 700 (AAS, Analytik Jena, Germany) high-resolution continuum source atomic absorption spectrometer was used for the identification of the Mn ions released in the solution after catalytic reaction, and the wavelength was set at 279.48 nm. X-ray photoelectron spectroscopy (XPS) was obtained using a VG 250 Escalab spectrometer equipped with an Al anode ($\text{Al-K}\alpha = 1486.7 \text{ eV}$) as an X-ray source. Raman spectra were investigated by InVia-Reflex (Renishaw, England). Electron paramagnetic resonance (EPR) spectroscopy graphs were obtained from a Bruker X-band A200 (Bruker, Germany). Hydrogen temperature-programmed reduction (H_2 -TPR) experiments were performed on a Micromeritics Autochem II 2920. Cyclic voltammetry was performed using a Chenhua CHI630D (China) with a standard three electrode system. The detailed descriptions of the H_2 -TPR, EPR, and CV experiments are available in the [Supporting Information \(Text S2\)](#).

2.3. DFT theoretical calculation

Density functional theory (DFT) calculation was employed to simulate the activation of PMS on MnO_2 surfaces. All the DFT

calculations are carried out by using CASTEP module in Material Studio software package [32]. The electronic structure was calculated using the Generalized Gradient Approximation (GGA) of Perdew, Burke and Ernzerhof with Hubbard U corrections (PBE + U) with U value of 0 [33]. The PBE + U exchange–correlation functional has been demonstrated to give a good description of defect properties in other oxides including CeO_2 and TiO_2 . $2 \times 3 \alpha\text{-MnO}_2$ (211) and $2 \times 2 \delta\text{-MnO}_2$ (006) surface super cells with a vacuum width of $24 \text{ \AA}$ are chosen in the simulation based on experimental lattice parameters [34,35]. $\alpha\text{-MnO}_2$ (211) surface is terminated by 4 and 5 coordinated Mn atoms, while $\delta\text{-MnO}_2$ (006) surface is terminated by fully coordinated O atoms [36]. The k-point is set to $4 \times 4 \times 4$ when optimizing structures and top two layers of atoms are allowed to relax. An energy cut off of 570 eV is used. For PMS adsorption on MnO_2 surfaces, adsorption energy is determined via the following equation: $E_{\text{ad}} = E_{\text{PMS}/\text{MnO}_2} - (E_{\text{PMS}} + E_{\text{MnO}_2})$. The $E_{\text{PMS}/\text{MnO}_2}$, E_{PMS} , and E_{MnO_2} are total energies of the PMS/ MnO_2 system, the isolate PMS molecule and MnO_2 surface in the same slab, respectively. To investigate the minimum energy pathway for PMS molecule activation on MnO_2 surfaces, linear synchronous transit/quadratic synchronous transit (LST/QST) tools in CASTEP module are used, which have been well validated to determine the structure of the transition state and the minimum energy reaction pathway [37].

2.4. Experimental procedures of 4-NP degradation

All experiments were carried out in 500 mL glass beaker at room temperature ($25 \pm 1^\circ \text{C}$). Firstly, 0.0250 g solid 4-NP was dissolved into a 1 L volumetric flask. Then, 0.4 g/L catalyst was dispersed into 25 ppm 4-NP in the 500 mL glass beakers with constant magnetic stirring for 10 min . 3 mL solution was withdrawn as the initial solution. Finally, 4 g/L PMS ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$, $47\% \text{ KHSO}_5$ basis) was added into the glass beakers to begin reaction. Magnetic stirring was applied during the reaction at a rotary speed of 550 rpm at room temperature ($25 \pm 1^\circ \text{C}$). The solution was sampled after pre-determined time intervals by plastic syringe, and then it was filtrated by a cellulose acetate membrane of $0.45 \mu\text{m}$ pore size for analysis using UV–Vis spectroscopy (3900H, HITACHI, Japan) at $\lambda = 317 \text{ nm}$. For recycle tests of catalysts, the used solid material was obtained by vacuum filtration and washed with ultrapure water for several times after each run. And then the washed catalyst was dried in an oven at 80°C for 12 h . The total organic carbon (TOC) was measured by a Shimadzu TOC (TOC-L CSH CN200). The intermediates were detected by LC-MS (Thermo, Finnigan, LCQ-Deca xp) equipped with an electrospray ionization (ESI) source and high performance liquid chromatography (HPLC, SHIMADZU, Japan) with a UV detector at λ of 254 nm . The column of HPLC was an XB-C18 with a mobile phase of $0.3\% \text{ CH}_3\text{COOH}$ and $100\% \text{ acetonitrile}$ with flow rate of $0.5:0.5 \text{ mL/min}$. To evaluate the contribution of these radicals to the degradation, four sets of quenching experiments were performed by adding into a certain amount of ethanol, *tert*-butanol, sodium azide, and benzoquinone (BQ) as radical quenching reagents, respectively. To ensure the reliability of the experimental results, the catalytic experiments are repeated three times, and the final concentration of 4-NP shown in the figures is the mean value of triplicate results.

2.5. Quantification of sulfate radicals and hydroxyl radicals

In the OMS-2/PMS and OL-1/PMS systems, nitrobenzene (NB) and benzoic acid (BA) were used simultaneously as probe compounds to indicate the variations in the formation rates of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ with different reaction times, respectively. All the experiments were carried out in a 1 L glass beaker with constant magnetic stirring in a $25 \pm 1^\circ \text{C}$ water bath kettle. The concentration of NB was analyzed using a SHIMADZU (Japan) HPLC with a UV detector at λ of 263 nm and 227 nm . The column was an XB-C18 with a mobile phase of $60\% \text{ CH}_3\text{OH}$ and

$40\% \text{ ultrapure water}$, and the pH was changed to 3.0 by phosphoric acid.

3. Results and discussion

3.1. Materials characterizations

$\alpha\text{-MnO}_2$ is normally prepared via a hydrothermal, reflux or other chemical method, using permanganates as reactants. For the first time, we synthesized the novel $\alpha\text{-MnO}_2$ nanofibers (OMS-2) via phase transition from $\delta\text{-MnO}_2$ nanoparticles using a hydrothermal reaction with the addition of GO. GO could be oxidized to carbon dioxide during the reaction process, which provides a certain pressure and pH required for the phase transition reaction. pH value of the solution is about 9.83 before reaction, whereas the pH value is about 8.09 after reaction. The result confirm the role of GO in the reaction process. The XRD patterns of the as-prepared OMS-2 and OL-1 are shown in Fig. 1. OMS-2 shows broad peaks at 2θ of 12.7° , 18.0° , 25.6° , 28.7° , 37.5° , 42.1° , 49.8° , 56.1° and 60.1° , which can be well indexed to (110) , (200) , (220) , (310) , (211) , (301) , (411) , (600) and (521) planes of $\alpha\text{-MnO}_2$, respectively (JCPDS No. 29-1020) [7]. The diffraction peaks of OMS-2 are sharp and intense, indicating their good crystalline nature [38]. For OL-1, peaks at 12.2° , 24.6° , 36.8° , and 66.3° are also observed, corresponding to the crystal planes of the layered birnessite-type MnO_2 ($\delta\text{-MnO}_2$) of (003) , (006) , (101) and (113) , respectively (JCPDS No. 52-0556) [39]. Different from the good crystalline of OMS-2, the OL-1 shows amorphous feature [40]. And there are no any impurities peaks observed in OMS-2, which confirms the high purity of the product. For OL-1, the signal-to-noise ratio is low due to its amorphous feature. What is more, there is nearly no change for the OMS-2 after catalytic reaction, which indicates the good stability of OMS-2. By contrast, there is a little change in OL-1 after catalytic reaction because of its slightly structural instability. Noteworthily, the peaks of GO or reduced graphene oxides (rGO) were not found in the XRD patterns of OMS-2. As a comparison, when GO was not added in the reaction, OMS-2 cannot be prepared but only mixed compounds of $\alpha\text{-MnO}_2$ nanoparticles and little amount of $\delta\text{-MnO}_2$ nanoparticles are obtained (Fig. S1 in SI). GO could act as a structure-directing agent during the synthesis of OMS-2 as described in the literature [41].

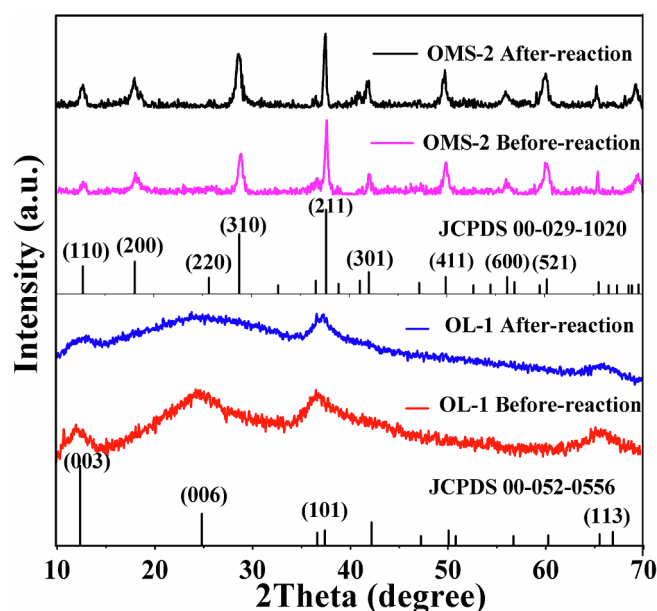


Fig. 1. XRD patterns of the OMS-2 and OL-1 before and after 80 min catalytic reaction.

The morphology of the as-prepared OMS-2 and OL-1 are shown in Fig. 2. As shown in Fig. S2a and 2b, the OMS-2 shows very long (about 5 μm), uniform and compact nanofiber morphology with the diameter of ~ 10 nm, while the OL-1 shows nanoparticles with diameters of 100–350 nm (Fig. S2c and S2d in SI). Fig. 2c clearly shows the lattice fringe with a lattice spacing of 0.298 nm between adjacent planes, which corresponds to the distance between the (3 1 0) planes of OMS-2, demonstrating that OMS-2 exhibits high-quality single-crystalline feature. And the OL-1 sample shows no ordered lattice planes, which confirms its nearly amorphous structure (Fig. 2f). After 80 min catalytic reaction, the morphology of the OL-1 became a little smaller than that before reaction, which could be due to the drastically catalytic reaction, whereas the OMS-2 nearly became unchanged (Fig. S2 in SI). And there is no GO or rGO found in the TEM or HRTEM of OMS-2. In addition, the BET specific surface area of OL-1 (35.1 m^2/g) was smaller than that of OMS-2 (43.4 m^2/g) (Table S1 in SI). The larger BET value of OMS-2 than OL-1 can be explained that OMS-2 shows tunnel structure with many pores but OL-1 shows layered structure. And the larger BET value of OMS-2 for PMS activation than that of OL-1.

To verify the absence of GO or rGO in the as-synthesized OMS-2, we analyzed Raman spectra of OMS-2 and OL-1. The Raman spectra of OMS-2 and OL-1 confirm the presence of $\alpha\text{-MnO}_2$ and $\delta\text{-MnO}_2$ bands and the absence of GO and rGO in OMS-2 (Fig. S3 in SI). Combined with the above XRD and TEM results, we can conclude that the as-synthesized OMS-2 consists of pure $\alpha\text{-MnO}_2$ nanofibers. Therefore, GO should act as a structure-directing and morphology-controlling agent during the synthesis of OMS-2, similar to that reported in the literature [42].

3.2. Activities of the catalysts.

Fig. 3a describes the degradation of 4-NP in the PMS solution alone and in the PMS solution coupled with the as-prepared OMS-2 and OL-1. 4-NP directly oxidized by OMS-2 and OL-1 is approximately 10.95% and 8.82% after 80 min without addition of PMS, respectively, which is similar to the reports in the literatures [43,44,45]. As shown in Fig. S4 in SI, the point of zero charge (pH_{pzc}) of OL-1 and OMS-2 is 2.69 and 5.38, respectively, while the pH_{pzc} of 4-NP is 2.83. And the pH of 4-NP solution is 2.23 during the catalytic reaction, indicating that there are

no electrostatic interactions between 4-NP and the catalysts (OMS-2 and OL-1). Meanwhile, results of high performance liquid chromatography (HPLC) shown in Fig. S5 show that new small peak appeared in both OMS-2 system OL-1 system without addition of PMS, indicating that the direct oxidation of 4-NP by OMS-2 and OL-1 are involved in the process of 4-NP degradation. The HPLC results also confirm the degradation of 4-NP is mainly attributed to the direct oxidation by OMS-2 and OL-1 but not the adsorption of 4-NP on catalysts when PMS was not added. And 4-NP cannot be decomposed in PMS solution alone. As a comparison, more than 97% 4-NP was degraded within 40 min in OMS-2/PMS system, while only 31.11% 4-NP was removed within 80 min in OL-1/PMS system (Figs. 3a and S6 in SI). The total organic carbon (TOC) result (Fig. S7 in SI) also show that 4-NP can be nearly completely degraded to CO_2 and water in the OMS-2/PMS system after 80-min reaction. The above results suggest that the manganese catalysts were essential for activating PMS and OMS-2 shows much higher catalytic performance than OL-1. The stability of OMS-2 during catalytic reactions for 4-NP degradation was further examined by recycling experiments (Fig. S8 in SI). No significant change in the catalytic activity was observed after four cycles, indicating that the OMS-2 was very stable during catalysis reaction.

On the basis of the 4-NP degradation rate in the OMS-2/system and OL-1/system, a general pseudo first order kinetics for 4-NP degradation was applied by the below equation:

$$\ln\left(\frac{C}{C_0}\right) = -k_{\text{obs}}t$$

where C is 4-NP concentration at time (t) and C_0 is the 4-NP concentration at initial time (t_0). k_{obs} is the first order reaction rate constant of 4-NP removal.

As shown in Fig. S9, the degradation process was well-fitted by first-order kinetic model with a regression coefficient of 0.998 and 0.988 for OMS-2 and OL-1, respectively. The apparent rate constant of 4-NP degradation obtained by OMS-2/PMS and OL-1/PMS was evaluated to be 0.086 and 0.004 min^{-1} , respectively. The K (0.086 min^{-1}) of the OMS-2 shows 21.5 times as that of OL-1 (0.004 min^{-1}). The pseudo constants obtained were normalized by specific surface area per volume under catalyst loading of 0.4 $\text{g}\cdot\text{L}^{-1}$. After normalization, the constant of the OMS-2 (0.0050 $\text{L}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$) is 17.39 times as that of OL-1

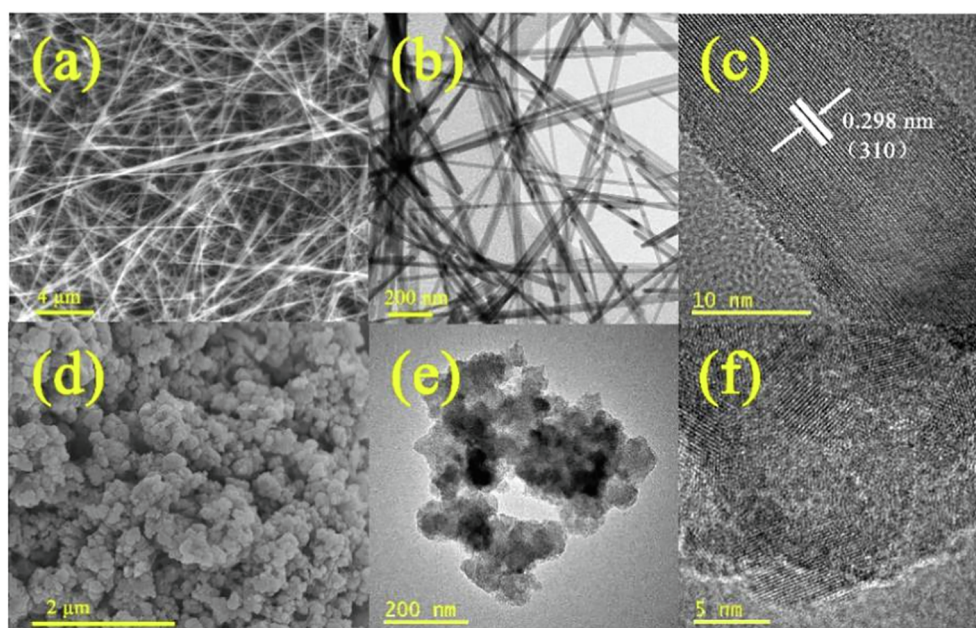


Fig. 2. SEM images of the as-prepared OMS-2 (a) and OL-1 (d), respectively. TEM images of OMS-2 (b) and OL-1 (e), respectively. HRTEM images of OMS-2 (c) and OL-1 (f), respectively.

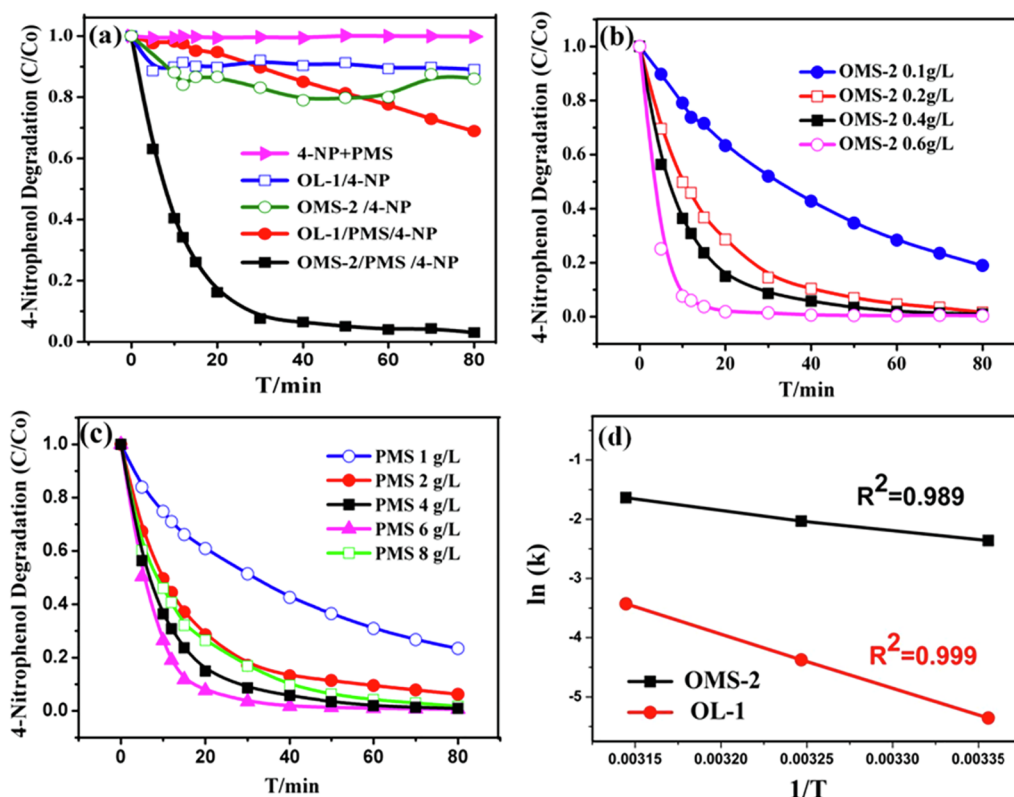
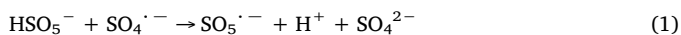


Fig. 3. 4-NP degradation in the different PMS oxidation systems (a); Effects of OMS-2 dosage (b), PMS concentration (c) on 4-NP degradation in the OMS-2/PMS catalytic system; Linear line based on $1/T$ at varying $\ln(k)$ (d). Reaction conditions: $[4\text{-nitrophenol}]_0 = 25 \text{ mg/L}$, catalyst loading = 0.4 g/L , PMS concentration = 4.0 g/L , temperature: 25°C (a); PMS concentration = 4 g/L , $T = 25^\circ\text{C}$ (b); catalyst loading = 0.4 g/L , $T = 25^\circ\text{C}$ (c); PMS concentration = 4 g/L , catalyst loading = 0.4 g/L (d).

($0.0003 \text{ L}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$), indicating the active sites on the OMS-2 surface are more reactive than that on the OL-1 [42].

3.3. Effects of the catalyst loading, PMS loading, reaction temperature.

To investigate the effect of the OMS-2 dosage and PMS concentration on the degradation of 4-NP, different catalyst dosages and PMS concentrations were used. As shown in Fig. 3b, with the increase of OMS-2 dosage, 4-NP degradation was greatly enhanced, suggesting that the increase in the catalyst dosage provides more catalytic sites for PMS activation. The reaction data could be fitted by a first-order kinetic model. The rate constants increased from 0.022 min^{-1} to 0.140 min^{-1} with an increasing catalyst dose. Considering the cost, the optimal OMS-2 dosage is 0.4 g/L . For the PMS concentration, 4-NP degradation increases with an increase in the concentration of PMS but it becomes worse when the concentration is larger than 6 g/L (Fig. 3c). The PMS concentration is known to be directly related to the number of radicals generated (i.e., $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$), leading to 4-NP degradation. Thus, when the PMS concentration is above 6 g/L , scavenging of $\text{SO}_4^{\cdot-}$ radicals would occur as expressed by the following Eqs. (1)–(3) [23,24]:



According to some research reports, $\text{SO}_5^{\cdot-}$ is less reactive than $\text{SO}_4^{\cdot-}$ [46,47]. Hence an increased concentration of PMS would result in a decrease of the degradation efficiency of 4-NP, indicating the existence of an optimum oxidant concentration in the oxidation process. The optimal concentration of PMS is 4 g/L .

Fig. 3d shows that a general trend in the 4-NP degradation rate with the OMS-2/PMS and OL-1/PMS systems increase with the increase of temperature. The correlation between the rate constant and reaction temperature was fitted well by the Arrhenius equation. Activation energy (E_a) and prefactor (A) could calculate from following equation:

$$\ln(k) = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T} \right)$$

where K is rate constant of a chemical reaction; T is the temperature in kelvin; E_a is the activation energy; A is the prefactor; R is the universal gas constant.

According to the above equation, the rate constant (K) of chemical reaction in the OMS-2/PMS system are 0.094 min^{-1} , 0.131 min^{-1} , 0.195 min^{-1} at 25 , 35 , 45°C , respectively, indicating the PMS activation by the OMS-2 is the endothermic process. In addition, one linear line based on $1/T$ at varying $\ln(k)$ indicates high regression coefficients of 0.989 and 0.999 for the OMS-2 and OL-1 systems, respectively. And the K of chemical reaction in the OL-1/PMS system are 0.005 min^{-1} , 0.013 min^{-1} , 0.032 min^{-1} at 25 , 35 , 45°C , respectively, showing the PMS activation by OL-1 is the endothermic process as well. Accordingly, the activation energy (E_a) of the OMS-2 was calculated to be 28.53 kJ/mol , which is much smaller than the E_a (75.91 kJ/mol) of OL-1 and that of the reported $\alpha\text{-MnO}_2$ (50.3 kJ/mol) in the literature [20]. The results confirm that OMS-2 possesses much better catalytic performance for PMS activation and then leads to much better degradation efficiency of 4-NP than OL-1.

3.4. DFT calculations

To understand the mechanism of the crystalline structure-dependent reactivity of MnO_2 on PMS activation, we carefully investigated the process of PMS adsorption over $\alpha\text{-MnO}_2$ nanofibers (OMS-2) and $\delta\text{-MnO}_2$ (OL-1) by DFT calculation. As evidenced by XRD characterization, (2 1 1) and (0 0 6) are the main facets for $\alpha\text{-MnO}_2$ (OMS-2) and $\delta\text{-MnO}_2$ (OL-1), respectively. The $\alpha\text{-MnO}_2$ crystalline phase has the space-group symmetry $I4/m$ (87) with a body-centered tetragonal lattice, [37,48], and the relaxed (2 1 1) facet shows long nanofiber morphology. And $\delta\text{-MnO}_2$ crystal has the space-group symmetry $P6_3/mmc$ (1 9 4) with a hexagonal lattice and the relaxed (0 0 6) facet shows layered morphology. For PMS adsorption, all possible adsorption sites and orientation of PMS were considered. Fig. S10 shows the relaxed

atomic structures of a PMS molecule adsorption on $\alpha\text{-MnO}_2$ (2 1 1) (panel a) and $\delta\text{-MnO}_2$ (0 0 6) surfaces (panel b), respectively. For adsorption on the (2 1 1) of $\alpha\text{-MnO}_2$ surface, it shows that the PMS is lying on the $\alpha\text{-MnO}_2$ (2 1 1) surface with the S, O atoms on the SO_4 side bonding with O and Mn atoms on the surface. The two bond lengths are 2.122 and 1.566 Å, respectively. For the adsorption of PMS on the $\delta\text{-MnO}_2$ (0 0 6) surface, the PMS molecule lies down and no chemical bond is observed. Table S2 provides the adsorption energy of PMS (E_{ads}) on the two different surfaces, charge transfer Q between PMS and surface, and the bond length $l_{\text{O}-\text{O}}$ between the OH group and SO_4 group. As shown in Table S2, the adsorption on $\alpha\text{-MnO}_2$ (2 1 1) surface is strong with E_{ad} being -2.95 eV, while the value of E_{ad} is just -1.34 eV for $\delta\text{-MnO}_2$ (0 0 6) surface. This is also consistent with the formation of covalent bonds between PMS and $\alpha\text{-MnO}_2$ (2 1 1) surface as shown in Fig. S10a. Comparing the two surfaces, the adsorption of PMS on $\alpha\text{-MnO}_2$ (2 1 1) is stronger, and it has longer $l_{\text{O}-\text{O}}$, resulting in that PMS receives more electrons. Therefore, the PMS on the $\alpha\text{-MnO}_2$ (2 1 1) is more active and expected to be easier to generate $\text{SO}_4^{\cdot-}$ radicals. The energy profile for the PMS decomposition mechanism is

shown in Fig. S11. Normally, it is considered that reaction can spontaneously happen at room temperature when the reaction energy barrier is lower than 0.9 eV [49]. The activation energy barrier (0.4 eV) of PMS on $\alpha\text{-MnO}_2$ (2 1 1) surface is very low and PMS molecules are easy to be activated at ambient conditions. As for $\delta\text{-MnO}_2$ (0 0 6), the adsorption energy and $l_{\text{O}-\text{O}}$ show that PMS decomposition is not easy to happen, so the activation route is not calculated here. Thus, it could be concluded that the PMS molecules can be easily activated by OMS-2 (the (2 1 1) of $\alpha\text{-MnO}_2$) and generating $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radicals, while it is comparatively difficult for the case of OL-1 (the (0 0 6) of $\delta\text{-MnO}_2$) surface at ambient condition.

3.5. Identification of radicals

EPR spectra technology was then employed to investigate the radicals generated in OMS-2/PMS and OL-1/PMS systems, and DMPO was used as the spin-trapping agent. As shown in Fig. 4a, the $\text{DMPO}\cdot\text{SO}_4^{\cdot-}$ signal was observed in the OMS-2/PMS and OL-1/PMS systems. The obvious $\text{DMPO}\cdot\text{OH}$ signal was also detected as $\cdot\text{OH}$ can be generated

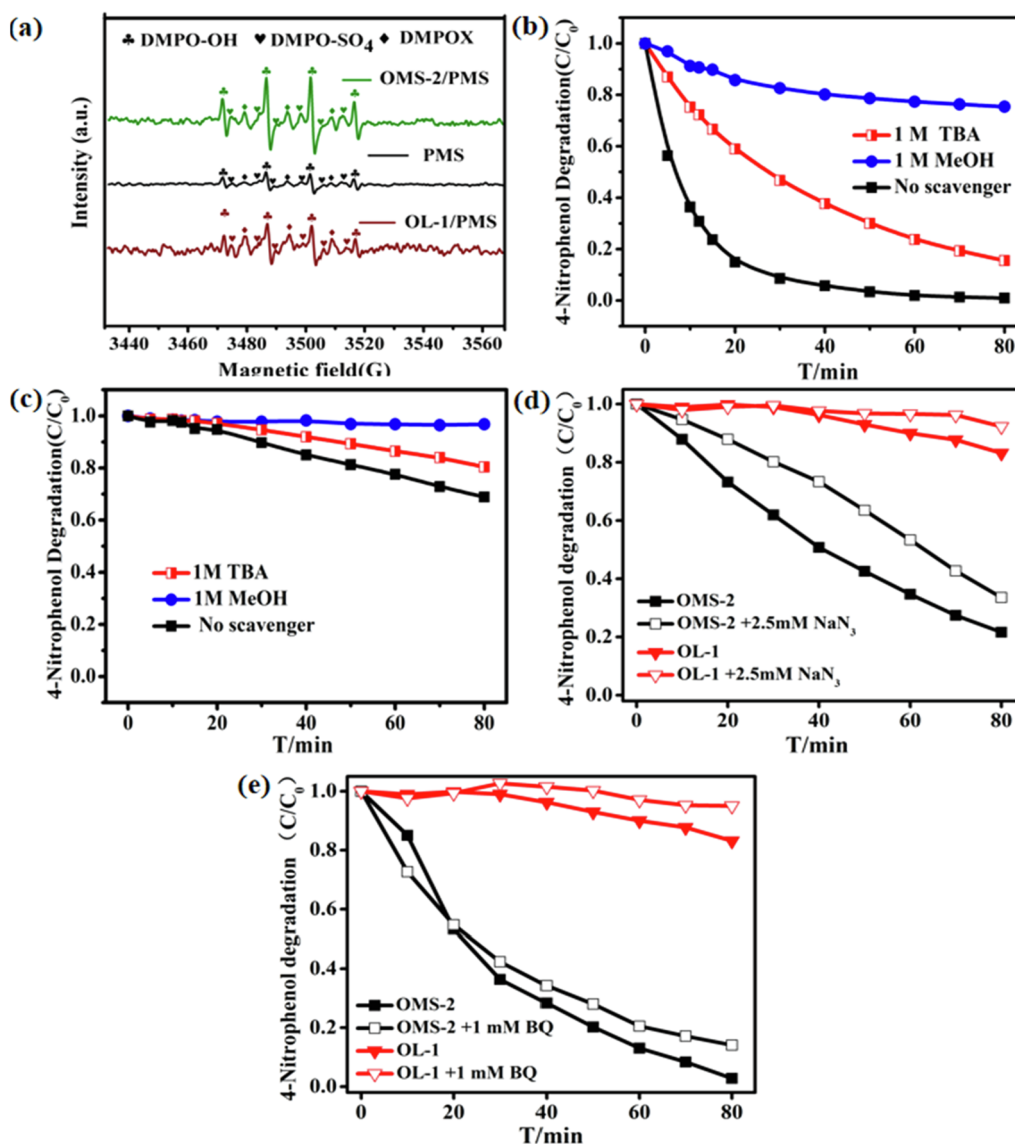


Fig. 4. (a) EPR spectra of various catalytic processes (reaction conditions: [catalyst] = 0.04 g/L, [PMS] = 4.0 g/L, [DMPO] = 35.16 mM, pH = 2.23, T = 25 °C). Catalytic degradation of 4-NP in the OMS-2/PMS system (b) and in the OL-1/PMS system (c) with the addition of the scavenger MeOH or TBA (reaction conditions: [4-NP] = 25 mg/L, [catalyst] = 0.40 g/L, [PMS] = 4.0 g/L, T = 25 °C). Catalytic degradation of 4-NP in the OMS-2/PMS system and in the OL-1/PMS system with the addition of Na_3N (d) or BQ (e) (reaction conditions: [4-NP] = 25 mg/L, [catalyst] = 0.40 g/L, [PMS] = 4.0 g/L, T = 25 °C).

by the reaction between Mn(II or III) and PMS or the reaction between $\text{SO}_4^{\cdot-}$ and H_2O [50]. While, no DMPO- $\text{SO}_4^{\cdot-}$ and DMPO- $\cdot\text{OH}$ signals were observed in the PMS system alone. The results confirmed that $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radicals are generated in the OMS-2/PMS and OL-1/PMS systems. The intensities of the DMPO- $\cdot\text{OH}$ and DMPO- $\text{SO}_4^{\cdot-}$ signals in the OMS-2/PMS system are much higher than those in the OL-1/PMS system, suggesting that the amount of active $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radicals are much larger in the OMS-2/PMS system than in the OL-1/PMS system, resulting in more efficient degradation of 4-NP in the OMS-2/PMS system than in the OL-1/PMS system [51]. And the above results are agreement to the DFT analysis.

In order to estimate the relative contribution of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radicals to the NB degradation, the radical trapping experiments were subsequently conducted in the OMS-2/PMS and OL-1/PMS systems after the addition of different scavengers. TBA was used as the radical scavenger for $\cdot\text{OH}$ but not for $\text{SO}_4^{\cdot-}$ radicals because of its much higher reactivity with $\cdot\text{OH}$ ($k_{\text{HO}} = 3.8\text{--}7.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) than with $\text{SO}_4^{\cdot-}$ ($k_{\text{SO}_4^{\cdot-}} = 4\text{--}9.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) [52]. MeOH is typically used to scavenge both $\cdot\text{OH}$ ($k_{\text{HO}} = 1.2\text{--}2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and $\text{SO}_4^{\cdot-}$ ($k_{\text{SO}_4^{\cdot-}} = 1.6\text{--}7.8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) due to its high reactivity [22,53]. As shown in Fig. 4b, when MeOH was added to the OMS-2/PMS system, the degradation rate of 4-NP decreased from 97.0% to 24.6%, while the degradation rate of 4-NP declined from 97.0% to 84.4% after the addition of TBA. For the OL-1/PMS system, the removal rate of 4-NP decreased from 31.11% to 3.20% with the addition of MeOH, whereas the removal rate of 4-NP decreased from 31.11% to 19.60% when TBA was added (Fig. 4c). In addition, in order to verify whether non-radicals other than $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ also play a role in the degradation of 4NP, such as singlet oxygen ($^1\text{O}_2$) and superoxide radical anion ($\text{O}_2^{\cdot-}$) that have been reported [54]. The radical scavengers of sodium azide (NaN_3 , 2.5 mM) and Benzoquinone (BQ, 1 mM) were used to probe $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$, respectively. As shown in Fig. 4(d) and (e), the addition of 2.5 mM NaN_3 or 1 mM BQ show a little impact on 4-NP degradation, suggesting that both $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$ have a little contribution for the

degradation of 4-NP, which is similar to the previous reports in the literatures [54]. The above results reveal that $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ act as the main reactive species, while $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$ just have a little effect on the degradation of 4-NP. And $\text{SO}_4^{\cdot-}$ take much more important role than $\cdot\text{OH}$ in the process of the catalytic degradation of 4-NP in the OMS-2/PMS system and the OL-1/PMS system.

3.6. Analyses of TGA, CV, H_2 -TPR and XPS

To further understand the difference in the catalytic performance of OMS-2 and OL-1, TGA analysis, CV, and H_2 -TPR were then used to probe morphology, electron transfer activity and surface phase of OMS-2 and OL-1, respectively. The TGA curves of OMS-2 and OL-1 are displayed in Fig. 5a, which shows different weight loss and differential thermal analysis profiles. For OMS-2, the distinct weight loss that occurred at 360 °C could be attributed to the dehydration of the OMS-2 surface [55]. When the temperature is between 400 and 647 °C, the peak can be assigned to the consumption of surface-absorbed oxygen and the reduction of MnO_2 to Mn_2O_3 . The peak in the range of 647 and 800 °C corresponds to the transformation of Mn_2O_3 into Mn_3O_4 [28]. For OL-1, there is one distinct peak between 400 and 600 °C that represents the consumption of surface-absorbed oxygen and the reduction of MnO_2 to Mn_2O_3 . The processes of dehydration, oxygen potential loss and manganite transformation all appeared in OMS-2 and OL-1 but OMS-2 possesses two transformations in the Mn state, while OL-1 only shows one Mn state transformation. The results indicate that OMS-2 possessed more multiple valence states of Mn than OL-1.

Fig. 5b shows a continuous CV curve for three scans. The oxidation peak and reduction peak of OMS-2 were located at 0.399 V (vs. SCE) and 0.208 V (vs. SCE), respectively. The oxidation peak and reduction peak of OL-1 were located at 0.379 V (vs. SCE) and 0.229 V (vs. SCE), respectively. The oxidation peak of OMS-2 was higher than that of OL-1, and the reduction peak of OMS-2 was lower than that of OL-1, leading to a wider redox potential of 0.191 V (vs. SCE) for OMS-2 than

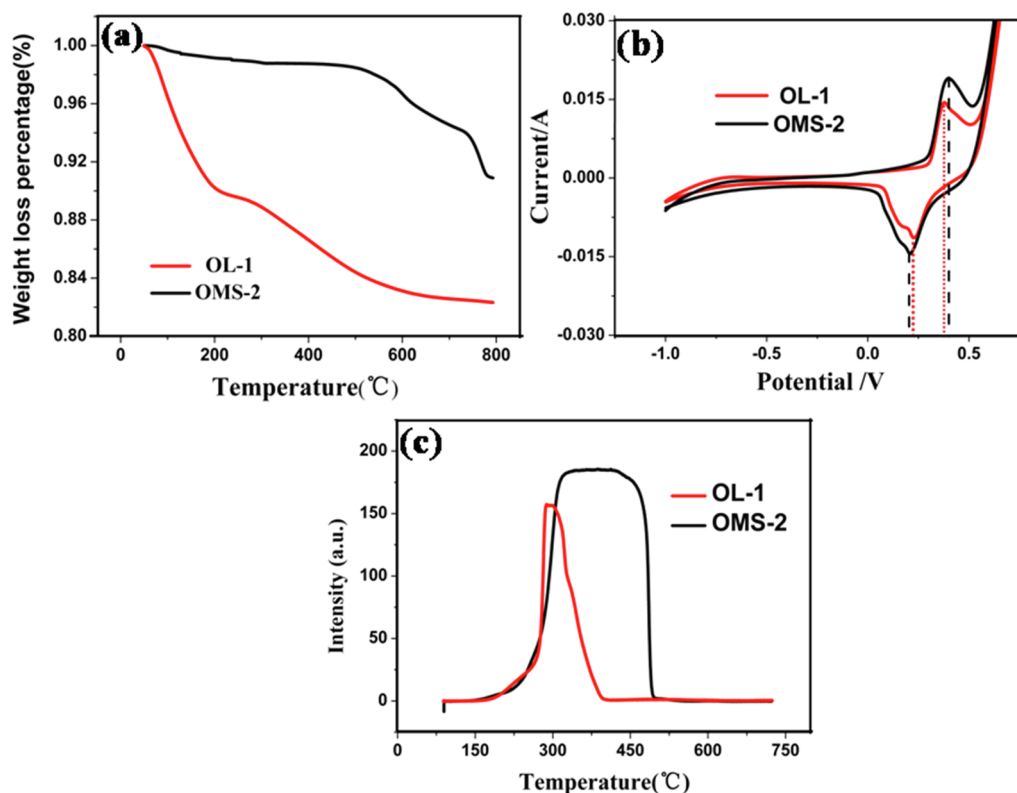


Fig. 5. TGA profiles (a), cyclic voltammetry (b) and H_2 -TPR (c) of OMS-2 and OL-1. The redox potentials of OMS-2 and OL-1 were evaluated by cyclic voltammetry (CV).

that of OL-1 (0.150 V (vs. SCE)). The capacity of the reduction potential could be related to the chemical activity and the capacity of electrons' transfer of the metal ions in the process of reduction and oxidation [6]. The results indicate a faster electron transfer rate in OMS-2 than in OL-1, which results in much better catalytic performance of OMS-2 as compared to OL-1 [56].

Fig. 5c shows the temperature-programmed reduction diagrams of OMS-2 and OL-1. The peak area of OMS-2 is much larger than that of OL-1, indicating that the H_2 consumption of OMS-2 was considerably higher than that of OL-1. In addition, the peaks of OMS-2 at 328 and 425 °C correspond to the reduction of MnO_2 to MnO with Mn_2O_3 and Mn_3O_4 as intermediates, while the peak of OL-1 at 296 °C is attributed to the consumption of semi-stable surface-absorbed oxygen [57]. The results indicate that OMS-2 has a much larger number of active sites than OL-1, which could be an important reason for OMS-2 showing a better catalytic activity for the activation of PMS than OL-1.

In order to further investigate the PMS activation on OL-1/PMS and OMS-2/PMS surfaces, High-resolution X-ray photoelectron spectroscopy (HRXPS) was used to monitor the chemical state changes of Mn species on OL-1/PMS surface before and after the catalytic reaction. Before the catalytic process, three peaks at 641.76, 642.34 and 643.31 eV are ascribed to Mn(II), Mn(III) and Mn(IV) in OMS-2, respectively (Fig. 6a). The relative contributions to the overall Mn intensity are 18.36%, 26.15% and 55.49% for the Mn(II), Mn(III) and Mn(IV), respectively. After an 80-min catalytic reaction, their relative contributions to the overall Mn intensity were 12.61%, 25.77% and 61.62%, respectively. The results indicate that the transformation of the valence states of Mn (III)/Mn(II) and Mn(IV)/Mn(III) occurred on the surface of OMS-2 during the process of PMS activation, which is similar to the results indicating that PMS was activated by MFe_2O_4 ($M = Co, Cu, Mn$, and Zn) reported in the literature [6,58]. For OL-1, only two peaks at 642.08 and 642.98 eV are attributed to Mn(III) and Mn(IV), respectively. The relative contributions of Mn(III) and Mn(IV) to the overall Mn intensity changed from 41.62% and 58.38% to 35.48% and 64.52%, respectively, after the 80-min catalytic reaction (Fig. 6b). The results demonstrate that there are only Mn^{3+} and Mn^{4+} in OL-1, which is consistent with the case reported in the literature [59,60]. Different from the OMS-2/PMS system, only one transformation of the Mn(III)/Mn(IV) valence states exists on the OL-1 surface during the process of PMS activation.

The O 1s spectra of OMS-2 includes two individual peaks located at 529.87 and 531.76 eV (Fig. 6c), which are assigned to the surface lattice oxygen of metal oxides (O^{2-} , denoted as O_{latt}) and adsorbed oxygen or surface hydroxyl species (denoted as O_{ads}), respectively. After the 80-min catalytic reaction, the relative content of O_{latt} and O_{ads} to the overall O intensity transformed from 66.05% and 33.95% to 76.52% and 23.48% in OMS-2, respectively. The decrease in the concentration of O_{ads} could be transformed to surface lattice oxygen to improve the mutual contact between pollutants and catalyst and then promote the PMS activation. For OL-1, the relative contents of O_{latt} and O_{ads} transformed from 58.37% and 41.63% to 60.30% and 39.70%, respectively, indicating that both O_{latt} and O_{ads} are involved in the catalytic reaction (Fig. 6d).

To investigate whether manganese oxides with a single Mn valence state have catalytic performance for PMS activation, some control experiments were done. As shown in Fig. S13a in the Supporting Information, 4-NP can hardly be degraded in the presence of the commercial MnO_2 , and only 19.60% 4-NP was degraded in the commercial MnO_2 /PMS system, much worse than those in the OMS-2/PMS and OL-1/PMS systems, which indicates that the commercial MnO_2 has a much inferior reactivity for PMS activation than OMS-2 and OL-1. In addition, the XPS spectra of the commercial MnO_2 was unchanged after the 80-min catalytic reaction (Fig. S13b in SI), indicating that there is only Mn^{4+} in the commercial MnO_2 and that the valence state of Mn did not change during the catalytic process (detailed information is available in Text S3 in SI). Therefore, the above results indicate that the multiple Mn valence states in the manganese oxides are a key factor for the efficient activation of PMS that leads to the removal of 4-NP.

3.7. The mechanism of PMS activation by OMS-2 and OL-1

According to the above results, the mechanism of PMS activation by OMS-2 and OL-1 is proposed in Scheme 1. DFT calculation suggested that PMS on the α - MnO_2 (2 1 1) is more active and expected to be easier to get $SO_4^{\cdot -}$ radicals than on δ - MnO_2 (0 0 6) facets, resulting in that OMS-2 shows much higher catalytic performance than OL-1. In addition, the metal ions (Mn^{2+} and/or Mn^{3+}) on the surfaces of OMS-2 and OL-1 could act as active sites for reduction of PMS to generate $SO_4^{\cdot -}$ and $\cdot OH$ radicals. First, HSO_5^- was adsorbed on the surface of OMS-2 and OL-1. Then, Mn^{2+} and Mn^{3+} in OMS-2 serve as active sites to

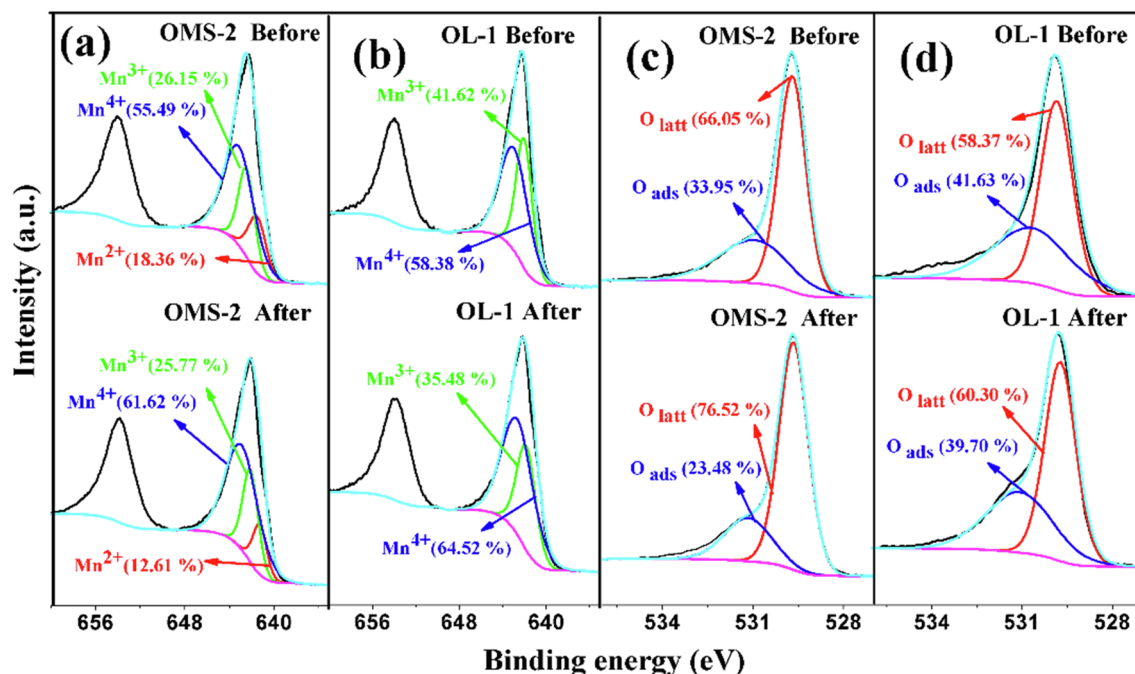
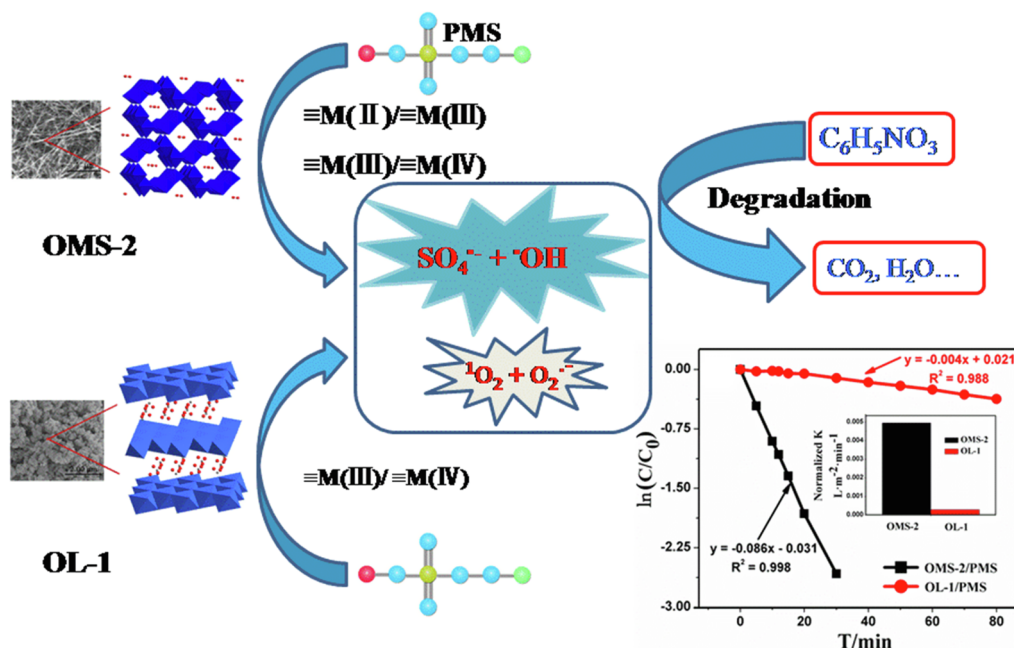
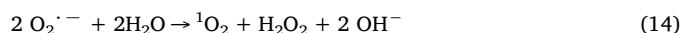
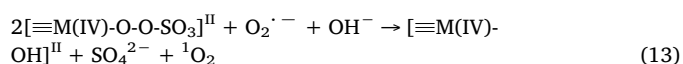
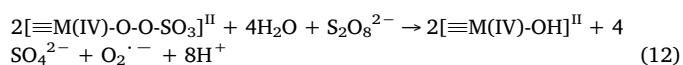
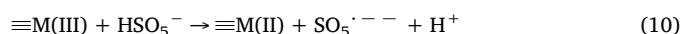
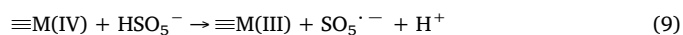
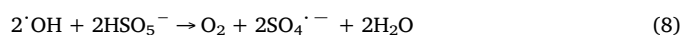
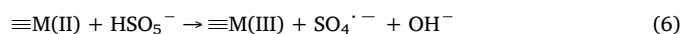
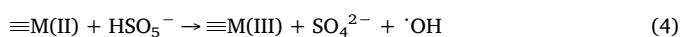


Fig. 6. XPS spectra of Mn 2p and O 1s for OMS-2 and OL-1 before and after the oxidation process.



Scheme 1. The mechanism diagram of PMS activation by OMS-2 and OL-1.

provide redox electrons for the reduction of PMS, and the oxidation of Mn(II)/Mn(III) and Mn(III)/Mn(IV) occurred accordingly (Eqs. (4)–(7)) [22,39]. Additionally, the Mn^{3+} on OL-1 surface serve as active sites to transfer redox electrons during the oxidation of Mn(III)/Mn(IV) (Eqs. (5) and (7)). Accordingly, to maintain charge balance on the OMS-2 and OL-1 surfaces, a small amount of adsorbed oxygen is reduced to O^{2-} by the donated electrons generated in Eqs. (4)–(7) [6]. Finally, the reduction reactions on the surface of OMS-2 (Eqs. (9)–(10)) and OL-1 (Eq. (9)) resulted in the recovery of the original state of the catalyst as well as the further generation of $\text{SO}_5^{\cdot-}$. In addition, small amount of $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$ were produced during the reaction according to quenching experiment results. The $^1\text{O}_2$ generation could be resulted from the direct oxidation or recombination of $\text{O}_2^{\cdot-}$ over manganese dioxide [54,61,62]. Therefore, a superoxide-based reaction pathway toward $^1\text{O}_2$ evolution on OMS-2 or OL-1 was proposed as displayed in Eqs. (11)–(14). A metastable manganese intermediate ($\text{Mn}^{\text{IV}}\text{-O-O-SO}_3$) was first formed at the surface of OMS-2 or OL-1, and then $\text{O}_2^{\cdot-}$ was generated by reacting with $\text{S}_2\text{O}_8^{2-}$ along with the breakage of $\text{Mn}^{\text{IV}}\text{-O}$. Afterward, $^1\text{O}_2$ was generated from a direct oxidation of $\text{O}_2^{\cdot-}$ by Mn^{IV} , which is thermodynamically favored ($E_0(\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}) = 0.95 \text{ eV}$ and $E_0(\text{O}_2^{\cdot-}/^1\text{O}_2) = -0.34 \text{ eV}$) or a recombination of two superoxide radicals [54]. The above results suggest that the crystalline structure of MnO_2 and transformations of Mn(II)/Mn(III), Mn(III)/Mn(IV) and $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ on the MnO_2 surface were the main factors involved in determining the high catalytic performance of MnO_2 for the activation of PMS. Then, the $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$ formed from the chain reaction will react with 4-NP, leading to the degradation and mineralization of 4-NP. We employed liquid chromatography-mass spectrometry (LC-MS) to detect the intermediates to figure out degradation pathway of 4NP. The degradation intermediates, including p-benzoquinone, hydroquinone, p-dihydroxybenzenes, 1, 2, 3-tribenzoquinone and some low molecular organic acids (such as malonic acid, pyruvic acid and oxalic acid), were detected during the reaction (Figs. S14 and S15 in SI). The detailed information and mass spectra of these intermediates were provided in the supporting information. On the basis of these intermediates, we proposed a possible degradation pathway of 4NP (Fig. S16 in SI).



4. Conclusions

This study reported that PMS was activated by two different crystallites of MnO_2 with featured morphologies and explained why the two kinds of MnO_2 shows markedly different catalytic performances for the degradation of 4-NP in the presence of PMS for the first time. The experimental results show that 4-NP can be quickly and thoroughly degraded in the OMS-2/PMS system but only 31.11% 4-NP was degraded in the OL-1/PMS system after an 80-min reaction. Analyses of TGA, CV, H_2 -TPR, and XPS indicate that OMS-2 possesses more active sites, a faster electron transfer rate and more multiple valence states of Mn than OL-1, leading to much better catalytic performance for OMS-2 than OL-1. The results of the EPR and radical quantification demonstrate that $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ are the main active radicals for 4-NP degradation in the OMS-2/PMS system and OL-1/PMS system, and the formation rate of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ in OMS-2/PMS is much faster than that in the OL-1/PMS system. DFT calculation also confirms that the adsorption of PMS on OMS-2 is stronger than that on OL-1, and the PMS on OMS-2 is easier to be activated to get $\cdot\text{SO}_4^{\cdot-}$ radicals than the PMS on OL-1. Based on

the above results, we put forward the mechanism of PMS activation and the formation mechanism of radicals over OMS-2 and OL-1, which explains the difference in the catalytic performance of OMS-2 and OL-1. This study has important implications for the potential application of AOPs based on sulfate radicals in water treatment.

Acknowledgements

We gratefully acknowledge the financial support of National Key R&D Program of China (2018YFC1902002), the NSF of China (51878325, 51868050, 51622806, 51378246, 51720105001, 21607029, and 21777033), the NSF of Jiangxi Province (20162BCB22017, 20165BCB18008, 20171ACB20017, and 20171BAB206049), Science and Technology Program of Guangdong Province (2017B020216003), and Science and Technology Program of Guangzhou City (201707010359).

Appendix A. Supplementary data

Electronic Supplementary Information (ESI) available: XRD of OMS-2 and OL-1 before and after the reaction; SEM and TEM images of OMS-2 and OL-1 before and after the reaction; BET of OMS-2 and OL-1; physical parameters for OMS-2 and OL-1 obtained from N₂ sorption measurements; recycling performance of OMS-2; degradation of 4-NP by PMS under different dosages of Cl[−]; Raman spectra of OMS-2 and OL-1; zeta-potential measurements of OMS-2 and OL-1; UV-vis spectra of OMS-2 and OL-1; XPS spectra of OMS-2 and OL-1 before and after the reaction; plot of ln(C/C₀) versus reaction time; 4-NP degradation in the various catalytic systems; XPS spectra of Mn 2p and Mn 3s before and after the reaction in the commercial MnO₂; mass spectra of 4-NP degradation in the OMS-2/PMS and OL-1/PMS systems; 4-NP degradation pathway in the OMS-2/PMS and OL-1/PMS systems

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2019.05.170>.

References

- [1] F.C. Xie, Y. Xu, K.Y. Xia, C.X. Jia, C.P. Zhang, Alternate pulses of ultrasound and electricity enhanced electrochemical process for p-nitrophenol degradation, *Ultrason. Sonochem.* 28 (2016) 199–206.
- [2] A.L. Zhang, N.N. Wang, J.T. Zhou, P. Jiang, G.F. Liu, Heterogeneous Fenton-like catalytic removal of p-nitrophenol in water using acid-activated fly ash, *J. Hazard. Mater.* 201 (2012) 68–73.
- [3] E. Saputra, S. Muhammad, H. Sun, A. Patel, P. Shukla, Z.H. Zhu, S. Wang, α -MnO₂ activation of peroxymonosulfate for catalytic phenol degradation in aqueous solutions, *Catal. Commun.* 26 (2012) 144–148.
- [4] F. Ghanbari, M. Moradi, Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants, *Rev. Chem. Eng. J.* 310 (2017) 41–62.
- [5] X.L. Zhang, M.B. Feng, L.S. Wang, R.J. Qu, Z.Y. Wang, Catalytic degradation of 2-phenylbenzimidazole-5-sulfonic acid by peroxymonosulfate activated with nitrogen and sulfur co-doped CNTs-COOH loaded CuFe₂O₄, *Chem. Eng. J.* 307 (2017) 95–104.
- [6] Y. Ren, L. Lin, J. Ma, J. Yang, J. Feng, Z. Fan, Sulfate radicals induced from peroxymonosulfate by magnetic ferrosulfate MF₂O₄ (M = Co, Cu, Mn, and Zn) as heterogeneous catalysts in the water, *Appl. Catal. B: Environ.* 165 (2015) 572–578.
- [7] Y. Wang, X. Zhao, D. Cao, Y. Wang, Y. Zhu, Peroxymonosulfate enhanced visible light photocatalytic degradation bisphenol A by single-atom dispersed Ag mesoporous g-C₃N₄ hybrid, *Appl. Catal. B: Environ.* 211 (2017) 79–88.
- [8] P.R. Shukla, S. Wang, H. Sun, H.M. Ang, M. Tadé, Activated carbon supported cobalt catalysts for advanced oxidation of organic contaminants in aqueous solution, *Appl. Catal. B: Environ.* 100 (2010) 529–534.
- [9] X. Ao, W. Liu, Degradation of sulfamethoxazole by medium pressure UV and oxidants: peroxymonosulfate, persulfate, and hydrogen peroxide, *Chem. Eng. J.* 313 (2017) 629–637.
- [10] O.S. Furman, A.L. Teel, R.J. Watts, Mechanism of base activation of persulfate, *Environ. Sci. Technol.* 44 (2010) 6423–6428.
- [11] X. Duan, Z. Ao, H. Zhang, M. Saunders, H. Sun, Z. Shao, S. Wang, Nanodiamonds in sp²/sp³ configuration for radical to nonradical oxidation: core-shell layer dependence, *Appl. Catal. B: Environ.* 222 (2018) 176–181.
- [12] X. Duan, H. Sun, Z. Shao, S. Wang, Nonradical reactions in environmental remediation processes: uncertainty and challenges, *Appl. Catal. B: Environ.* 224 (2018) 973–982.
- [13] H. Zeng, S. Liu, B. Chai, D. Cao, Y. Wang, X. Zhao, Enhanced photoelectrocatalytic decomplexation of Cu-EDTA and Cu recovery by persulfate activated by UV and cathodic reduction, *Environ. Sci. Technol.* 50 (2016) 6459–6465.
- [14] C. Zhu, F. Zhu, C. Liu, N. Chen, D. Zhou, G. Fang, J. Gao, Reductive hexachloroethane degradation by S₂O₈^{2−} with thermal activation of persulfate under anaerobic conditions, *Environ. Sci. Technol.* 52 (2018) 8548–8557.
- [15] C. Qi, X. Liu, C. Lin, H. Zhang, X. Li, J. Ma, Activation of peroxymonosulfate by microwave irradiation for degradation of organic contaminants, *Chem. Eng. J.* 315 (2017) 201–209.
- [16] C. Nie, Z. Ao, X. Duan, C. Wang, S. Wang, T. An, Degradation of aniline by electrochemical activation of peroxydisulfate at MWCNT cathode: the proofed concept of nonradical oxidation process, *Chemosphere* 206 (2018) 432–437.
- [17] L. Ling, Z. Li, J. Fang, C. Shang, Controlling bromate formation in the Co(II)/peroxymonosulfate process by ammonia, chlorine-ammonia and ammonia-chlorine pretreatment strategies, *Water Res.* 139 (2018) 220–226.
- [18] Y. Lei, C.S. Chen, Y.J. Tu, Y.H. Huang, Hui. Zhang, Heterogeneous degradation of organic pollutants by persulfate activated by CuO-Fe₃O₄: mechanism, stability, effects of pH and bicarbonate ions, *Environ. Sci. Technol.* 49 (2015) 6838–6845.
- [19] H. Liu, T.A. Bruton, W. Li, J.V. Buren, C. Prasse, F.M. Doyle, D.L. Sedlak, Oxidation of benzene by persulfate in the presence of Fe(III)- and Mn(IV)-containing oxides: stoichiometric efficiency and transformation products, *Environ. Sci. Technol.* 50 (2016) 890–898.
- [20] J.-P. Zou, Y. Chen, S.-S. Liu, Q.-J. Xing, X.-B. Luo, W.-L. Dai, J. Luo, J. Crittenden, Electrochemical oxidation and advanced oxidation processes using a 3D hexagonal Co₃O₄ array anode for 4-nitrophenol decomposition coupled with simultaneous CO₂ conversion to liquid fuels via a flowerlike CuO cathode, *Water Res.* 150 (2019) 330–339.
- [21] X. Cheng, H. Liang, A. Ding, X. Tang, B. Liu, X. Zhu, Z. Gan, D. Wu, G. Li, Ferrous iron/peroxymonosulfate oxidation as a pretreatment for ceramic ultrafiltration membrane: Control of natural organic matter fouling and degradation of atrazine, *Water Res.* 113 (2017) 32–36.
- [22] Y. Wang, S. Indrawirawan, X. Duan, H. Sun, H.M. Ang, M.O. Tadé, S. Wang, New insights into heterogeneous generation and evolution processes of sulfate radicals for phenol degradation over one-dimensional α -MnO₂ nanostructures, *Chem. Eng. J.* 266 (2015) 12–20.
- [23] X.M. Lin, Y.W. Ma, J.Q. Wan, Y. Wang, LiCOPO₄ (LCP) as an effective peroxymonosulfate activator for degradation of diethyl phthalate in aqueous solution without controlling pH: efficiency, stability and mechanism, *Chem. Eng. J.* 315 (2017) 304–314.
- [24] C. Gong, F. Chen, Q. Yang, K. Luo, F.B. Yao, S.N. Wang, X.L. Wang, J.W. Wu, X.M. Li, D.B. Wang, G.M. Zeng, Heterogeneous activation of peroxymonosulfate by Fe-Co layered double hydroxide for efficient catalytic degradation of Rhodamine B, *Chem. Eng. J.* 321 (2017) 222–232.
- [25] N. Jaafarzadeh, F. Ghanbari, M. Ahmadi, Efficient degradation of 2,4-dichlorophenoxyacetic acid by peroxymonosulfate/magnetic copper ferrite nanoparticles/ozone: a novel combination of advanced oxidation processes, *Chem. Eng. J.* 320 (2017) 436–447.
- [26] E. Saputra, S. Muhammad, H. Sun, H.M. Ang, M.O. Tade, S. Wang, Different crystallographic one-dimensional MnO₂ nanomaterials and their superior performance in catalytic phenol degradation, *Environ. Sci. Technol.* 47 (2013) 5882–5887.
- [27] E. Saputra, S. Muhammad, H. Sun, H.M. Ang, M.O. Tadé, S. Wang, Shape-controlled activation of peroxymonosulfate by single crystal α -Mn₂O₃ for catalytic phenol degradation in aqueous solution, *Appl. Catal. B: Environ.* 154–155 (2014) 246–251.
- [28] W.C. Peng, S.B. Wang, X.Y. Li, Shape-controlled synthesis of one-dimensional α -MnO₂ nanocrystals for organic detection and pollutant degradation, *Sep. Purif. Technol.* 163 (2016) 15–22.
- [29] W. Xiao, D. Wang, X.W. Lou, Shape-controlled synthesis of MnO₂ nanostructures with enhanced electrocatalytic activity for oxygen reduction, *J. Phys. Chem. C* 114 (2009) 1430–1434.
- [30] Y. Cheng, S. Dou, M. Saunders, J. Zhang, J. Pan, S. Wang, S.P. Jiang, A class of transition metal-oxide@MnOx core-shell structured oxygen electrocatalysts for reversible O₂ reduction and evolution reactions, *J. Mater. Chem. A* 4 (2016) 13881–13889.
- [31] S.J. Bao, B.L. He, Y.Y. Liang, W.J. Zhou, H.L. Li, Synthesis and electrochemical characterization of amorphous MnO₂ for electrochemical capacitor, *Mater. Sci. Eng., A* 397 (2005) 305–309.
- [32] S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.I. Probert, K. Refson, M.C. Payne, First principles methods using CASTEP, *Z. Kristallogr* 220 (2005) 567–570.
- [33] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, K. Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, *Phys. Rev. Lett.* 100 (2008) 136406–1364010.
- [34] M. Nolan, S.C. Parker, G.W. Watson, The electronic structure of oxygen vacancy defects at the low index surfaces of ceria, *Surf. Sci.* 595 (2005) 223–232.
- [35] B.J. Morgan, G.W. Watson, A Density Functional Theory plus U study of oxygen vacancy formation at the (110), (100), (101), and (001) surfaces of rutile TiO₂, *J. Phys. Chem. C* 113 (2009) 7322.
- [36] D.A. Tompsett, S. Parker, M.S. Islam, Surface properties of α -MnO₂: relevance to catalytic and supercapacitor behaviour, *J. Mater. Chem. A* 2 (2014) 15509–15518.
- [37] T.A. Halgren, W.N. Lipscomb, LST method as implemented in the SPARTAN program, *Chem. Phys. Lett.* 49 (1977) 225–232.
- [38] J.-P. Zou, H.-L. Liu, J. Luo, Q.-J. Xing, H.-M. Du, X.-H. Jiang, X.-B. Luo, S.-L. Luo, S.L. Suib, Three-dimensional reduced graphene oxide coupled with Mn₃O₄ for highly efficient removal of Sb(III) and Sb(V) from water, *ACS Appl. Mater. Interfaces* 8 (2016) 18140–18149.
- [39] Y. Wang, H. Sun, H.M. Ang, M.O. Tadé, S. Wang, Facile synthesis of hierarchically structured magnetic MnO₂/ZnFe₂O₄ hybrid materials and their performance in

- heterogeneous activation of peroxymonosulfate, *ACS Appl. Mater. Interfaces* 6 (2014) 19914–19923.
- [40] M.W. Kanan, D.G. Nocera, In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co^{2+} , *ChemInform* 39 (2008) 1072–1075.
- [41] J.-P. Zou, J. Ma, Q. Huang, S.-L. Luo, J. Yu, X.-B. Luo, W.-L. Dai, J. Sun, G.C. Guo, C.T. Au, Graphene oxide as structure-directing and morphology-controlling agent for the syntheses of heterostructured graphene- $\text{Bi}_2\text{MoO}_6/\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$ composites with high photocatalytic activity, *Appl. Catal. B: Environ.* 156 (2014) 447–455.
- [42] X. Zou, X. Huang, A. Goswami, R. Silva, B.R. Sathe, E. Mikmeková, T. Asefa, Cobalt-embedded nitrogen-rich carbon nanotubes efficiently catalyze hydrogen evolution reaction at all pH values, *Angew. Chem. Int. Ed.* 53 (2014) 4372–4376.
- [43] A.T. Stone, Reductive dissolution of manganese(III/IV) oxides by substituted phenols, *Environ. Sci. Technol.* 21 (1987) 979–988.
- [44] L.H. Shonali, R.G. Luthy, Oxidation of aniline and other primary aromatic amines by manganese dioxide, *Environ. Sci. Technol.* 24 (1990) 363–373.
- [45] H.C. Zhang, C.H. Huang, Oxidative transformation of triclosan and chlorophene by manganese oxides, *Environ. Sci. Technol.* 37 (2003) 2421–2430.
- [46] Y.H. Guan, J. Ma, X.C. Li, J.Y. Fang, L.W. Chen, Influence of pH on the formation of sulfate and hydroxyl radicals in the UV/peroxymonosulfate system, *Environ. Sci. Technol.* 45 (2011) 9308–9314.
- [47] T. Zhang, Y. Chen, T. Leiknes, Oxidation of refractory benzothiazoles with PMS/ CuFe_2O_4 : kinetics and transformation intermediates, *Environ. Sci. Technol.* 50 (2016) 5864–5873.
- [48] Y. Noda, K. Ohnobe, S. Nakamura, Momentum-dependent band spin splitting in semiconducting MnO_2 : a density functional calculation, *Phys. Chem. Chem. Phys.* 18 (2016) 13294–13303.
- [49] Q.G. Jing, Z. Ao, M.S. Li, Z. Wen, Density functional theory calculations on the CO catalytic oxidation on Al-embedded graphene, *RSC. Adv.* 4 (2014) 20290–20296.
- [50] Y. Feng, D. Wu, Y. Deng, T. Zhang, K. Shih, Sulfate radical-mediated degradation of sulfadiazine by CuFeO_2 rhombohedral crystal-catalyzed peroxymonosulfate: synergistic effects and mechanisms, *Environ. Sci. Technol.* 50 (2016) 3119–3127.
- [51] M.B. Feng, R.J. Qu, X.L. Zhang, P. Sun, Y.X. Sui, L.S. Wang, Z.Y. Wang, Degradation of flumequine in aqueous solution by persulfate activated with common methods and polyhydroquinone-coated magnetite/multi-walled carbon nanotubes catalysts, *Water Res.* 85 (2015) 1–10.
- [52] L. Luo, D. Wu, D. Dai, Z. Yang, L. Chen, Q. Liu, J. He, Y. Yao, Synergistic effects of persistent free radicals and visible radiation on peroxymonosulfate activation by ferric citrate for the decomposition of organic contaminants, *Appl. Catal. B: Environ.* 205 (2017) 404–411.
- [53] Y.J. Yao, H. Chen, C. Lian, F.Y. Wei, D.W. Zhang, G.D. Wu, B.J. Chen, S.B. Wang, Fe Co, Ni nanocrystals encapsulated in nitrogen-doped carbon nanotubes as Fenton-like catalysts for organic pollutant removal, *J. Hazard. Mater.* 314 (2016) 129–139.
- [54] S.S. Zhu, X.J. Li, J. Kang, X.G. Duan, S.B. Wang, Persulfate activation on crystallographic manganese oxides: mechanism of singlet oxygen evolution for nonradical selective degradation of aqueous contaminants, *Environ. Sci. Technol.* 53 (2018) 307–315.
- [55] S.D. Zhang, N. Munichandraiah, Effect of crystallographic structure of MnO_2 on its electrochemical capacitance properties, *J. Phys. Chem. C* 112 (2008) 4406–4417.
- [56] A.L. Lv, C. Hu, Y.N. Nie, J.H. Qu, Catalytic ozonation of toxic pollutants over magnetic cobalt and manganese co-doped $\gamma\text{-Fe}_2\text{O}_3$, *Appl. Catal. B: Environ.* 100 (1–2) (2010) 62–67.
- [57] J. Jia, P. Zhang, L. Chen, The effect of morphology of $\alpha\text{-MnO}_2$ on catalytic decomposition of gaseous ozone, *Catal. Sci. Technol.* 6 (2016) 5841–5847.
- [58] Y. Yao, Y. Cai, G. Wu, F. Wei, X. Li, H. Chen, S. Wang, Sulfate radicals induced from peroxymonosulfate by cobalt manganese oxides ($\text{Co}_{(x)}\text{Mn}_{(3-x)}\text{O}_4$) for Fenton-Like reaction in water, *J. Hazard. Mater.* 296 (2015) 128–135.
- [59] S. Fritsch, A. Navrotsky, Thermodynamic properties of manganese oxides, *J. Am. Chem. Soc.* 79 (2010) 1761–1768.
- [60] S. Ching, D.J. Petrovay, M.L. Jorgensen, S.L. Suib, Sol–gel synthesis of layered birnessite-type manganese oxides, *Inorg. Chem.* 36 (1997) 883–890.
- [61] O. Furman, D.F. Laine, A. Blumenfeld, A.L. Teel, K. Shimizu, I.F. Cheng, R.J. Watts, Enhanced reactivity of superoxide in water-solid matrices, *Environ. Sci. Technol.* 43 (2009) 1528–1533.
- [62] R.J. Watts, J. Sarasa, F.J. Loge, A.L. Teel, Oxidative and reductive pathways in manganese-catalyzed Fenton's reactions, *J. Environ. Eng.* 131 (2005) 158–164.