Flower-Shaped C-Dots/Co$_3$O$_4$\{111\} Constructed with Dual-Reaction Centers for Enhancement of Fenton-Like Reaction Activity and Peroxymonosulfate Conversion to Sulfate Radical

Zhibin Wen 1,†, Qianqian Zhu 1,†, Jiali Zhou 1, Shudi Zhao 1, Jinnan Wang 1,*, Aimin Li 1, Lifang Chen 2 and Weilin Bian 2

Abstract: Novel flower-shaped C-dots/Co$_3$O$_4$\{111\} with dual-reaction centers were constructed to improve the Fenton-like reaction activity and peroxymonosulfate (PMS) conversion to sulfate radicals. Due to the exposure of a high surface area and Co$_3$O$_4$\{111\} facets, flower-shaped C-dots/Co$_3$O$_4$\{111\} could provide more Co(II) for PMS activation than traditional spherical Co$_3$O$_4$\{110\}. Meanwhile, PMS was preferred for adsorption on Co$_3$O$_4$\{111\} facets because of a high adsorption energy and thereby facilitated the electron transfer from Co(II) to PMS. More importantly, the Co–O–C linkage between C-dots and Co$_3$O$_4$\{111\} induced the formation of the dual-reaction center, which promoted the production of reactive organic radicals (R•). PMS could be directly reduced to SO$_4$• by R• over C-dots. On the other hand, electron transferred from R• to Co via Co–O–C linkage could accelerate the redox of Co(II)/(III), avoiding the invalid decomposition of PMS. Thus, C-dots doped on Co$_3$O$_4$\{111\} improved the PMS conversion rate to SO$_4$• over the single active site, resulting in high turnover numbers (TONs). In addition, TPR analysis indicated that the optimal content of C-dots doped on Co$_3$O$_4$\{111\} is 2.5%. More than 99% of antibiotics and dyes were degraded over C-dots/Co$_3$O$_4$\{111\} within 10 min. Even after six cycles, C-dots/Co$_3$O$_4$\{111\} still remained a high catalytic activity.

Keywords: C-dots/Co$_3$O$_4$\{111\}; dual-reaction centers; enhancement; peroxymonosulfate; conversion to sulfate radical

1. Introduction

Being attributed to higher oxidative potential (E$^0$ = 2.5–3.1 V) and longer half-life (t$_{1/2}$ = 30–40 μs), sulfate radical (SO$_4$•) could degrade organics more efficiently than OH• (E$^0$ = 2.80 V, t$_{1/2}$ = <1 μs) in neutral solutions. Generally, a Fenton-like reaction was significantly influenced by pH. In neutral/alkaline condition, transition metal ion might form precipitate, resulting in preventing the reaction. On the other hand, SO$_4$• could react with OH$^-$ to produce OH• with lower oxidative ability. To enhance the peroxymonosulfate (PMS) conversion to SO$_4$•, various transition metals (Fe, Cu, Mn, and Co) were investigated as activator [1–3]. Among them, cobalt oxides [CoO, CoO$_2$, Co(OH)$_2$, CoO$_2$, and Co$_3$O$_4$] were considered as the most promising catalysts due to high standard reduction potential (E$^0$ = +1.92 V vs. NHE) and redox of Co(III)/Co(II) [1]. During the process of a Fenton-like reaction, PMS can not only react with Co(II) as the electron acceptor but also reacts with Co(III) as the electron donor, accompanied by the

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circulation of Co(III)/Co(II) and the generation of SO$_4$$^-$$^•$ or SO$_5$$^-$$^•$ [4]. However, similar to classic Fenton reaction, the rate-limiting step [Co(III) + HSO$_5$$^-$$ \rightarrow$ Co(II) + SO$_5$$^-$$^•$ + H$^+$] and low conversion PMS to SO$_5$$^-$$^•$ seriously restrict the application of cobalt oxides as catalysts [5]. In addition, the active components of catalysts might be converted into low activity substances during the reaction process due to poor stability. For example, cobalt oxides might be corroded and dissolved during the redox process, resulting in deterioration of catalytic performance.

In general, catalysts activity and stability could be influenced by surface morphology and crystal phase. Firstly, the mass transfer between organics and catalyst active sites was affected by the catalysts morphology. Li et al. constructed Fe$_x$Co$_{3-x}$O$_4$ with porous nanocages structure, which indicated that such morphology significantly improved the catalytic activity and stability [6]. Secondly, atoms arrangement of catalyst, which led to exposure of transition metal with different chemical value, was depended on the crystal structure [7,8]. As for Co$_3$O$_4$, both Co(III) and Co(II) occupied lattice point of octahedron (110) facet, while Co(II) entirely occupied the lattice point of tetrahedron (111) facet [8,9]. More importantly, different crystal facets possessed different adsorption energies and electron transfer properties, which might directly influence the catalytic reaction. Hensen et al synthesized CeO$_2$ with different crystal planes to investigate its effect on CO oxidation, which found that the free energy barrier of Pd/CeO$_2$(100) for the CO catalytic cycle was higher than that of Pd/CeO$_2$(111) [10]. Thus, it is expected that Co$_3$O$_4$ constructed by tetrahedron(111) can not only provide more Co(II) for PMS activation, but also possess higher adsorption energies and electrons transfer properties for PMS activation.

On the other hand, although increase of Co(II) exposed can obviously improve the catalytic activity, Co(III) would be still accumulated in the system because of the rate limitation step [Co(III) + HSO$_5$$^-$$ \rightarrow$ Co(II) + SO$_5$$^-$$^•$ + H$^+$] with the reaction time. Since the oxidative potential of SO$_5$$^-$$^•$ is relatively low, the degradation rate of organics by SO$_5$$^-$$^•$ is much lower than by SO$_4$$^-$$^•$. Thus, the selective PMS conversion to SO$_4$$^-$$^•$ over cobalt oxides still remained to be improved. In general, cation–π interaction could be formed between the cations and aromatic systems, which could be applied in the classic Fenton system for improvement of transition metal redox [11]. Zubir et al. demonstrated that unpaired π electrons of GO could transfer electrons between GO and iron centers via cation–π interactions, which significantly improved the recyclability of Fe$_2$O$_4$ [12]. In addition, the active transition complex [C-H$_2$O$_2$], which was formed between covalent carbon networks and H$_2$O$_2$, can directly transfer electron from the π-system to H$_2$O$_2$ with the generation of OH• [13]. Analogous to g-C$_3$N$_4$, carbon quantum dots (C-dots) are considered as a potential carbon-based co-catalyst due to their graphene structure [14,15]. Wang et al. synthesized the SiO$_2$@C-dots/phosphotungstate catalyst with an inert SiO$_2$ core and a catalytic active shell made up of the prepared amphiphilic phosphotungstate and C-dots, which proved that C-dots were an efficient co-catalyst in the system [16]. Our previous work also demonstrated that an electron-rich Cu center and electron-deficient π-electron conjugated system could be constructed by doping of g-C$_3$N$_4$ in Cu-Al$_2$O$_3$, which provided two electron-transfer routes for OH• generation in the presence of H$_2$O$_2$ [11]. Meanwhile, addition of C-dots in the hydrothermal system could modulate the formation of crystal structure because of the large number of oxygen functional groups on the surface of C-dots, which act as “surfactants”. Thus, it is expected to simultaneously enhance the catalytic activity and selective PMS conversion to SO$_4$$^-$$^•$ by doping of C-dots into Co$_3$O$_4$(111). Notably, C-dots can improve the production of reactive organic radicals (R•) from the reaction of SO$_4$$^-$$^•$ and organics. Such reactive organic radicals play an important role in the enhancement of catalytic activity and selective PMS conversion to SO$_4$$^-$$^•$. Some of electrons can be transferred from R• to Co(III) via Co–O–C linkage for Co(III) reduction to Co(II) without PMS decomposition, and other electrons can be transferred from R• to PMS over C-dots with the generation of SO$_4$$^-$$^•$.

Based on the above research background and conception, flower-shaped C-dots/Co$_3$O$_4$ [11] with high active crystal facets are constructed for improvement of catalytic activity
and selective PMS conversion to $SO_4^{−•}$. Being attributed to [111] facets, flower-shaped C-dots/Co$_3$O$_4$[111] could not only provide large amounts of Co(II) but also possess higher adsorption energies and electrons transfer properties for PMS reduction to $SO_4^{−•}$. More importantly, doping of C-dots on Co$_3$O$_4$[111] could facilitate the production of reactive organic radicals ($R•$) which can act as the important electron donor. On one hand, Co(III) in C-dots/Co$_3$O$_4$[111] can be reduced to Co(II) by oxidation of $R•$. On the other hand, $SO_4^{−•}$ can be generated from the reaction of PMS and $R•$ over C-dots. Such synergistic effect significantly improved PMS activation and selective conversion to $SO_4^{−•}$.

2. Results and Discussion

2.1. Characterization of Catalysts

Cetrimonium Bromide (CTMAB) showed significant influence on the surface morphology of Co$_3$O$_4$ during the hydrothermal reaction process. Co$_3$O$_4$ synthesized by hydrothermal reaction without CTMAB are spherical particles with the diameter of 2 µm (Figure 1a). However, due to a decrease of the surface energy, ethanol and cobalt salts could form nano-sheets in the present of CTMAB. Thus, the product of Co$_3$O$_4$ and C-dots/Co$_3$O$_4$[111], which are synthesized in the present of CTMAB, shows a flower-shaped structure (diameter = 5 µm) with a nano-sheets thickness of 67 nm (Figure 1b,c). Notably, the flower-shaped structure increased the surface area and pore volume of catalyst, which could be confirmed by the results of the BET surface area (Table 1). The BET surface area of flower-shaped C-dots/Co$_3$O$_4$[111] was 109.11 m$^2$/g, which was much higher than that of spherical Co$_3$O$_4$[110] (35.45 m$^2$/g). A large specific surface area is beneficial to improving the catalytic activity of the catalyst.

![Figure 1](https://example.com/figure1.png)

Figure 1. SEM image of (a) spherical Co$_3$O$_4$[110], (b) flower-shaped Co$_3$O$_4$[111], and (c) flower-shaped C-dots/Co$_3$O$_4$[111]; TEM image of (d) spherical Co$_3$O$_4$[110], (e) flower-shaped Co$_3$O$_4$[111], and (f) flower-shaped C-dots/Co$_3$O$_4$[111]; (g) EDS of flower-shaped C-dots/Co$_3$O$_4$[111].

Furthermore, as shown in TEM (Figure 1d), the ‘d’ spacing of lattice fringe corresponding to (111) and (220) planes of spherical Co$_3$O$_4$ are respectively 0.464 nm and 0.284 nm, and the inter planar angles between these two planes are 90°, suggesting the [110] crystal structure of the spherical Co$_3$O$_4$ [17]. Different from spherical Co$_3$O$_4$[110], the ‘d’ spacing of lattice fringe corresponding to (220) and (442) planes of flower-shaped Co$_3$O$_4$[111] are respectively 0.286 nm and 0.167 nm (Figure 1e), and the inter planar angle between these two planes is 30°, suggesting the [111] crystal structure of flower-shaped Co$_3$O$_4$[111] [18].
Such difference between spherical Co$_3$O$_4$[110] and flower-shaped Co$_3$O$_4$[111] was due to that surfactants were preferentially adsorbed on crystal faces, which limited the directional growth of nanocrystals and stabilizing the crystal faces. Various ordered aggregates formed by self-assembly of surfactants in solution can be used as microreactors or templates, which could control the morphology of nano-materials [19]. Thus, addition of CTMAB probably played the dominant role in the formation of [111] crystal structure of Co$_3$O$_4$ during the process of hydrothermal reaction. In addition, TEM images (Figure 1f) confirm that the C-dots are successfully doped in the flower-shaped Co$_3$O$_4$[111] in which the lattice fringes spacing of 0.322 nm is in accordance with the (002) lattice planes of graphitic carbon [20]. EDS images further demonstrate that the C element is homogenously distributed on the catalyst surfaces (Figure 1g), which show that the C-dots are uniformly doped on Co$_3$O$_4$.

### Table 1. The BET specific surface area, total pore volume, and average pore diameter of catalysts prepared.

| Catalyst                      | BET Specific Surface Area (m$^2$/g) | Total Pore Volume (cm$^3$/g) | Average Pore Diameter (Å) |
|-------------------------------|-------------------------------------|------------------------------|---------------------------|
| Spherical Co$_3$O$_4$[110]    | 35.45                               | 0.045                        | 66.91                     |
| Flower-shaped Co$_3$O$_4$[111]| 83.01                               | 0.092                        | 76.25                     |
| Flower-shaped C-dots/Co$_3$O$_4$[111] | 109.11                            | 0.107                        | 68.6                      |

XRD spectra clearly describe the crystal structure of catalysts synthesized under different hydrothermal reaction conditions (Figure 2a). The diffraction peaks at 31.4°, 37.1°, 44.9°, 55.9°, 59.7°, and 65.2° were respectively ascribed to the [220], [311], [400], [442], [511], and [440] diffraction planes of Co$_3$O$_4$, which could be indexed to a pure phase of spinel Co$_3$O$_4$ (JCPDS card NO.43-1003). Since there was no impurity peaks in XRD spectra, which could confirm the excellent crystalline of flower-shaped Co$_3$O$_4$[111], spherical Co$_3$O$_4$[110], and flower-shaped C-dots/Co$_3$O$_4$[111] [21]. In general, the Co$_3$O$_4$ crystal is a typical spinel structure (Co$^{2+}$(Co$^{3+})_2$O$_2$), which consists of octahedron (CoO$_6$) and tetrahedron (CoO$_4$). Notably, Co(III) species are located in octahedral sites while Co(II) species are in tetrahedral sites (Figure 2b). Since Co(II) is the catalytic site for PMS select conversion to SO$_4$ • [22], tetrahedron structure (CoO$_4$) with more Co(II) exposed can provide more catalytic sites for PMS activation. Therefore, in perspective of atomic arrangement, accessible Co(II) with PMS is beneficial for improvement of catalytic activity. To a certain degree, it can be considered that the tetrahedron structure (CoO$_4$) shows higher catalytic activity compared with octahedron structure (CoO$_6$).

**Figure 2.** (a) XRD patterns of different catalysts, (b) schematic representation of spinel structure of Co$_3$O$_4$.

Furthermore, XPS was used to characterize the surface composition and chemical state of flower-shaped Co$_3$O$_4$[111], spherical Co$_3$O$_4$[110], and flower-shaped C-dots/Co$_3$O$_4$[111] (Figure 3 and Figure S1). The binding energy peaks near 780 and 795 eV are ascribed to orbits of Co 2p$_{1/2}$ and Co2p$_{3/2}$, respectively (Figure 3a,c,e). The orbital peak of Co
2p_{3/2} can be further separated into two peaks of Co^{3+} (779.8 eV) and Co^{2+} (781.1 eV). Then, the value of Co(II)/Co(III) on the catalysts surface can be calculated according to the peaks area of different valence state of Co (Table 2). The proportion of Co(II) on the surface of flower-shaped Co_3O_4{111} [Co(II)/Co(III) = 1.36] and C-dots/Co_3O_4{111} [Co(II)/Co(III) = 1.36] are much higher than that on spherical Co_3O_4{110} [Co(II)/Co(III) = 0.77]. Thus, compared with spherical Co_3O_4{110}, more active sites of Co(II), which plays the role of activating PMS, were exposed on the surface of flower-shaped Co_3O_4{111} and C-dots/Co_3O_4{111}. In addition, the orbital peak of O 1s can be separated into three peaks. The binding energy of 529 ± 0.2 eV was the characteristic peak of lattice oxygen (O_L) in the Co_3O_4 phase. The peak of O_V (531 ± 0.1 eV) was ascribed to the O^{2−} in oxygen-deficient regions within the matrix of Co_3O_4, and the peak of O_C (532 ± 0.2 eV) was ascribed to OH^−, chemisorbed or dissociated oxygen species (O^{2−}, O_2^−, or O^−). Notably, the value of O_C/O_L of flower-shaped C-dots/Co_3O_4{111} was much higher than those of flower-shaped Co_3O_4{111} and spherical Co_3O_4{110}, which indicated that doping C-dots into Co_3O_4 increased the oxygen functional groups on the surface of the catalyst. Since oxygen functional groups on nano-carbons can act as the catalytic sites for PMS activation to generate radicals. Since occupation of the binding sites by surface hydroxyl sites of catalyst could facilitate the oxidation reactions [22], doping of C-dots into Co_3O_4{111} could improve the catalytic performance.

![Figure 3](image-url)

**Figure 3.** XPS spectra of catalysts, Co2p of (a) spherical Co_3O_4, (c) flower-shaped Co_3O_4, (e) flower-shaped C-dots/Co_3O_4{111}; O 1s peaks of (b) spherical Co_3O_4, (d) flower-shaped Co_3O_4, (f) flower-shaped C-dots/Co_3O_4{111}.
Table 2. Element molar ratios [Co(II)/Co(III)] on the surface of different catalysts.

| Samples                         | Binding Energy (eV) | Ratios     |
|---------------------------------|---------------------|------------|
|                                 | Co(II) | Co(III) | O<sub>C</sub> | O<sub>L</sub> | Co(II)/Co(III) | O<sub>C</sub>/O<sub>L</sub> |
| Spherical Co<sub>3</sub>O<sub>4</sub>{110} | 779.8   | 781.1   | 532.1         | 529.1         | 0.77           | 0.659                   |
| Flower-shaped Co<sub>3</sub>O<sub>4</sub>{111} | 779.6   | 781    | 532           | 529           | 1.36           | 0.635                   |
| Flower-shaped C-dots/Co<sub>3</sub>O<sub>4</sub>{111} | 779.8   | 781.2  | 532.1         | 529.1         | 1.36           | 0.844                   |

FT-IR spectra can demonstrate the functional groups of spherical Co<sub>3</sub>O<sub>4</sub>{110}, flower-shaped Co<sub>3</sub>O<sub>4</sub>{111}, and flower-shaped C-dots/Co<sub>3</sub>O<sub>4</sub>{111} (Figure 4a). The characteristic peaks at 574.69 cm<sup>-1</sup> and 661.48 cm<sup>-1</sup> are assigned to the stretching vibrations of Co–O groups of Co<sub>3</sub>O<sub>4</sub>, and the peak at 3557 cm<sup>-1</sup> belongs to the free O–H stretching vibration [23]. In addition, peaks near 1633.4 cm<sup>-1</sup> of samples are related to the bending –OH vibrations of physical adsorbed water [24,25]. Furthermore, the bands in the range of 1490.73 cm<sup>-1</sup> are ascribed to the C=C aromatic stretching vibrations. The bands at 1307.52 and 1000.89 cm<sup>-1</sup> correspond to the C–O stretching absorption and COO– functional groups, respectively. According to the results of XPS and FT-IR, doping of C-dots greatly enriched the oxygen functional groups (–OH, C=O) on the Co<sub>3</sub>O<sub>4</sub> surface, which could significantly improve the catalytic performance of the catalyst.

![Figure 4.](image)

(a) The FT-IR spectrum of spherical Co<sub>3</sub>O<sub>4</sub>, flower-shaped Co<sub>3</sub>O<sub>4</sub>{111}, and flower-shaped C-dots/Co<sub>3</sub>O<sub>4</sub>{111}, (b) H<sub>2</sub>-TPR profiles of Co<sub>3</sub>O<sub>4</sub> catalysts with different conditions, (c) cyclic voltammetry (CV) curves of the as-prepared flower-shaped Co<sub>3</sub>O<sub>4</sub>{111}, and flower-shaped C-dots/Co<sub>3</sub>O<sub>4</sub>{111}, (d) EIS Nyquist plots collected at −0.3 V vs. Ag/AgCl.
The redox properties of catalysts were characterized by the H2-TPR (Figure 4b). The β peak represents the reduction of Co(II) to Co0 in Co3O4 (Equation (2)), while the α peak represents the reduction of Co(III) to Co(II) (Equation (3)). The α peak and β peak of spherical Co3O4[110] are 319 °C and 398 °C, respectively. Due to the oxygen vacancy on the surface of flower-shaped Co3O4[111] and C-dots/Co3O4[111] (Figure S3), the reduction temperature (Co3+ → Co0, Co3+ → Co2+) decreased obviously. The surface oxygen vacancy can promote the reduction of the catalyst, which leads to the reduction of the flower-shaped Co3O4[111] and C-dots/Co3O4[111] at the lower temperature. In addition, the α peak intensity of flower-shaped Co3O4[111] and C-dots/Co3O4[111] are much lower than that of spherical Co3O4[110]. The area ratio of α peak to β peak of spherical Co3O4[110] is 0.31 by calculation, while that of flower-shaped Co3O4[111] and C-dots/Co3O4[111] is only 0.27, which confirmed that there are more CoO contents in flower-shaped Co3O4[111] and C-dots/Co3O4[111] crystal compared with spherical Co3O4[110]. In addition, TPR results of flower-shaped C-dots/Co3O4[111] with different C-dots amounts are provided to explore the optimal doping of C-dots for PMS activation (Figure S2). The temperature of Co3+ reduction to Co2+ decreases gradually as the C-dots content increase from 0.5% to 2.5%, which indicates that doping of C-dots can improve the reducibility of Co3O4[111]. However, the temperature of Co3+ reduction to Co2+ increases as the C-dots content increased from 2.5% to 3.5%, suggesting that excessive doping of C-dots weaken the reduction ability of Co3O4. Similar results are also observed in TPR results of Co2+ reduction to Co0. Such adverse effect can be explained by that excess C-dots could cover the surface of the catalyst, resulting in the inhibition of the Co3O4 reduction by H2. Thus, C-dots (2.5%)/Co3O4[111] were selected for further studies.

Cyclic voltammetry (CV) was used to test the charge transfer at the interfacial region of Co3O4/PMS in a three-electrode system (Figure 4c). Ag/AgCl was used as reference electrode, platinum was used as pair electrodes, and glassy carbon was used as working electrode. The mixture of 0.1 M Na2SO4 and 0.3 mM PMS was used as electrolyte. The CV curves of flower-shaped Co3O4[111] and flower-shaped C-dots/Co3O4[111] showed distinct reduction peaks beginning at a low potential of −0.25 V (Figure 4c). These reduction peaks indicated that the surface C-dots served as the active sites for the PMS activation. Compared with flower-shaped Co3O4[111], flower-shaped C-dots/Co3O4[111] have a higher current density in the cathode, suggesting that C-dots can transfer electrons to PMS. In addition, compared with flower-shaped Co3O4[111], flower-shaped C-dots/Co3O4[111] show the smaller semicircle within a higher frequency region in the EIS Nyquist plots (Figure 4d). Due to the similar graphene structure of C-dots, the Dirac Point effect improved the electron transfer of C-dots. Thus, C-dots doped on flower-shaped Co3O4[111] could accelerate the redox cycle of Co(II)/Co(III).

\[
\begin{align*}
3\text{CoO} + 3\text{H}_2 & \rightarrow 3\text{Co} + 3\text{H}_2\text{O}, \\
\text{Co}_3\text{O}_4 + \text{H}_2 & \rightarrow 3\text{CoO} + \text{H}_2\text{O}.
\end{align*}
\]

2.2. Catalytic Activity and Stability

The degradation rate of OTC and ENR by PMS over flower-shaped C-dots/Co3O4[111] are much higher than that over other catalysts (Figure 5a,c). More than 99.3% OTC was degraded in 5 min (PMS = 0.075 mM), while more than 99.7% ENR was degraded in 10 min over the flower-shaped C-dots(2.0 wt%)/Co3O4[111] (PMS = 0.3 mM). The degradation kinetics by PMS over various catalysts can be well described by pseudo-first-order kinetic model (\(−\ln C/C_0 = kt\)), where ‘C0’ is the initial concentration of OTC, ‘C’ is the concentration of reactant at time ‘t’, and ‘k’ is the rate constant. The rate constants followed the order of flower-shaped C-dots/Co3O4[111] > flower-shaped Co3O4[111] > spherical Co3O4[110] (Table S1). Notably, the rate constant of flower-shaped C-dots/Co3O4[111] is four times higher than spherical Co3O4[110] and flower-shaped Co3O4[111] (Figure 5b,d). Accordingly, the addition of C-dots could obviously improve the catalytic activity of Co3O4. The optimal content of C-dots doped in flower-shaped Co3O4[111] was 2%. 

\[\text{Co}_3\text{O}_4 + \text{H}_2 \rightarrow 3\text{CoO} + \text{H}_2\text{O} \]
The influences of catalyst dosage and oxidant concentration on the catalytic degradation of ENR were tested. The degradation rate of ENR increases from 56.4% to 99.4% within 10 min while the dosage of flower-shaped C-dots/Co$_3$O$_4${111} increases from 0.01 to 0.05 g·L$^{-1}$ (Figure S3a). This was because an increase of the catalysts dosage could supply more active sites for catalytic generation of radicals, which promoted the antibiotics degradation. Similar to the catalyst dosage, the increase of PMS concentration can also improve the degradation of ENR (Figure S3b). As the PMS concentration increased from 0.05 to 0.3 mM, the removal rate of ENR increased from 74.2% to 99.8% within 10 min. Since the generation rate of the radicals was related to the catalyst dosage, further increase of PMS concentration from 0.3 to 0.7 mM could not obviously improve the removal rate of ENR anymore. Therefore, the optimal concentration of PMS for ENR degradation was 0.3 mM.

Since high temperature is beneficial to PMS activation and generation of radicals, the removal rate of ENR obviously increases as the temperature increases from 25 °C to 55 °C (Figure S3c). The degradation kinetic constants also followed the order of $K_{25^\circ C}$ (2.837 min$^{-1}$) > $K_{45^\circ C}$ (1.355 min$^{-1}$) > $K_{55^\circ C}$ (0.913 min$^{-1}$) > $K_{25^\circ C}$ (0.469 min$^{-1}$). More than 99% of ENR could be degraded at 25 °C within 10 min. In consideration of energy consumption, the room temperature (25 °C) was selected for subsequent catalytic degradation experiments. Furthermore, due to changing the surface charge of catalyst, solution pH also influenced the degradation process obviously. The degradation rate of ENR increases as the initial solution pH increases from 3.0 to 6.0 (Figure S3d). Only 50% of ENR was removed at pH 3.0 within 20 min while ENR was almost completely degraded at pH 6.0. This is

Figure 5. Degradation of (a) Oxytetracycline (OTC) and (c) Enrofloxacin (ENR) in the presence of flower-shaped C-dots/Co$_3$O$_4${111} and PMS (pH = 7.00 with 0.075 mM/0.3 mM peroxymonosulfate (PMS), 0.05 g/L catalyst dosage, and 10 ppm OTC/ENR (200 mL)); pseudo-first-order kinetic model fits the degradation kinetic curves of (b) OTC and (d) ENR.
because that Co leached from flower-shaped C-dots/Co$_3$O$_4$[111] in acid conditions was unfavorable to PMS activation. Notably, the concentrations of Co leached from catalysts in solution could meet the limit of Environmental Quality Standards for Surface Water in China (1.0 mg/L) (Figure S4). However, the degradation rate of ENR decreases as pH increases from 6.0 to 9.0, which indicated that alkaline conditions made adverse effect to catalytic degradation. This was because the large amount of OH$^-$ reacted with SO$_4^{2-}$ to generate OH•, resulting in lower oxidation ability in neutral/basic conditions.

In order to evaluate the reusability of flower-shaped C-dots/Co$_3$O$_4$[111], OTC (10 mg/L), and ENR(10 mg/L) solutions are used to further test the catalytic degradation stability of C-dots/Co$_3$O$_4$[111] in the present work (Figure 6a,b). After six cycling runs, the degradation rate of OTC was still more than 90% within 2 min, and even 100% within 5 min (Figure 6a). Furthermore, the degradation kinetics did not decrease after the sixth cycle runs, showing a perfect catalytic stability of flower-shaped C-dots/Co$_3$O$_4$[111]. Similar to catalytic degradation of OTC, flower-shaped C-dots/Co$_3$O$_4$[111] also show high catalytic degradation rate of ENR, Rh B, and MB even after six cycles (Figure 6b–d), which also confirm the excellent stability of flower-shaped C-dots/Co$_3$O$_4$[111] for PMS activation.

In addition, the surface state of catalyst after six cycling runs is characterized by XPS spectra (Figure 6e). In this work, we propose that Co–O–C bonds conjugated in flower-shaped C-dots/Co$_3$O$_4$[111] facilitate electron transfer and corrulate well with the transformation from R to R•. Such synergistic interaction between C-dots and Co$_3$O$_4$[111] could accelerate the Co(III)$\rightarrow$Co(II) redox cycles. The bridge role played by C-dots could transfer electrons to Co(III) for its quick reduction as organic pollutants are oxidized [12]. XPS spectra of catalysts before and after reaction confirmed this inference. The value of Co(II)/Co(III) of flower-shaped C-dots/Co$_3$O$_4$[111] did not decreased after catalytic reaction (Figure 6f), which indicated that Co(II) was not oxidized to Co(III). This synergistic effect can not only effectively maintain the number of active sites of catalysts, but also reduce the ineffective decomposition of PMS. As for flower-shaped Co$_3$O$_4$[111], the value of Co(II)/Co(III) decreased from 1.36 to 1.16 obviously after cycled uses (Figure 6f), indicating that some Co(II) of flower-shaped Co$_3$O$_4$[111] was oxidized to Co(III). Previous studies have already demonstrated that Co(II) play important role in PMS activation for generation of sulfate radicals. Thus, compared with flower-shaped Co$_3$O$_4$[111], flower-shaped C-dots/Co$_3$O$_4$[111] showed higher catalytic activity and selective peroxymonosulfate (PMS) conversion to sulfate radicals.

### 2.3. Density Functional Theory (DFT) Calculation

In general, adsorption of PMS on catalysts was the premise of activation process. According to the density functional theory (DFT), the adsorption energy of PMS on [110] and [111] facets of Co$_3$O$_4$ are calculated by using the Materials Studio 7.0 CASTEP program (Figure S5). The convergence criteria were as follows: the maximal force on the atoms was 0.03 eV Å$^{-1}$, the stress on the atomic nuclei was less than 0.05 GPa, the maximal atomic displacement was 0.001 Å, and the maximal energy change per atom was 1.0 e$^{-5}$ eV. The adsorption energy of PMS ($E_{ads}$) on Co$_3$O$_4$ can be calculated by the equation of $E_{ads} = E_{PMS+Cat} - E_{abs} - E_{Cat}$, where $E_{PMS+Cat}$, $E_{abs}$, and $E_{Cat}$ refer to the energy of the optimized adsorption system, PMS and Co$_3$O$_4$, respectively. To obtain accurate results, we optimized the atomic coordinates by minimizing the total energy and atomic forces. The optimum adsorption energy of PMS on [110] and [111] facets are $-1.12$ eV and $-5.97$ eV, respectively, suggesting that PMS are preferred to be adsorbed on Co$_3$O$_4$[111] facet than on Co$_3$O$_4$[110] facet. Moreover, the total charge of PMS adsorbed on [111] facet ($-0.32$ e) was higher that on [110] facet ($-0.16$ e), which also indicated that PMS can obtain more electrons from Co$_3$O$_4$[111] for activation. Thus, Co$_3$O$_4$[111] can exhibit higher catalytic activity and selective peroxymonosulfate (PMS) conversion to sulfate radical.
2.3. Density Functional Theory (DFT) Calculation

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![Figure 6](image-url)

**Figure 6.** Cyclic performance of flower-shaped C-dots/Co$_3$O$_4$[111] for degradation of (a) OTC, (b) ENR, (c) Rh B, and (d) Methyl orange (MO) (pH = 7.00, PMS: 0.075/0.3 mM, C-dots/Co$_3$O$_4$[111]: 0.05 g/L, pollutant concentration:10 ppm (200 mL)); the (e) Co 2p XPS spectra of different catalysts before and after 6 cycling degradation of ENR. (f) Co$^{2+}$/Co$^{3+}$ ratio based on XPS analysis.

2.4. The Possible Degradation Pathway of OTC and ENR

Generally, the unsaturated bonds of organic pollutants are easy to be broken in catalytic oxidation process. Based on the Frontier Orbital Theory, the highest occupied molecular orbital (HOMO) acts as the electron donor because of its weak binding force to electrons, while lowest unoccupied molecular orbital (LUMO) acts as electrons acceptor because of its strong binding force to electrons. In the present work, we calculated the bond energy of OTC and ENR by using Gaussian program, which indicates that the overlap of electronic clouds in LUMO and HOMO obviously influence the separation of e$^-$ and h$^+$ (Figure S6). The large density of the electron cloud in OTC is mainly in the area of 1C, 9C, 14C, 24N. In the case of ENR, the electronic cloud mainly distributed in 3C, 6C, 19C,
20C. The active sites of pollutants were greatly contributed by the frontier orbitals, and unsaturated bonds strongly influenced the activity of antibiotic molecules. Thus, bonds in these positions of ENR and OTC are broken preferentially. In addition, the electron cloud density of OTC is much greater than that of ENR, which caused a higher degradation rate of OTC compared with ENR.

Furthermore, the intermediates of OTC and ENR degradation are identified by LC-MS/TOF, and iron spectra at different retention time (RT) are presented in ESI Scan (Figures S7 and S8). As for OTC degradation intermediates, the original iron at m/z = 461.1 ([M + H]+) could be identified as C22H34N2O8. Furthermore, from the mass spectra, some other peaks appeared as the degradation of OTC, which suggested that there were other intermediate products produced. These main products ions at m/z = 460.2 ([M + H]+), m/z = 434.2 ([M + H]+), m/z = 447.2 ([M + H]+), m/z = 432.2 ([M + H]+), m/z = 218.2 ([M + H]+) might be identified as C22H34N2O8, C22H32NO8, C22H27N2O8, C22H26NO8, C19H23NO5, C12H7NO2, and C9H6O4, respectively. In addition, all these substances were thoroughly decomposed into CO2, H2O, and other gaseous components. Similarly, iron spectra at different retention time (RT) of ENR degradation are presented in ESI Scan (Figure S8). The original iron at m/z = 360.2 ([M + H]+) can be identified as C19H22FN3O3. These main product ions at m/z = 344.3 ([M + H]+), m/z = 332.2 ([M + H]+), m/z = 361.1 ([M + H]+), m/z = 242.3 ([M + H]+), m/z = 174.2 ([M + H]+), m/z = 202.2 ([M + H]+), and m/z = 102.1 ([M + H]+) might be identified as C19H23N2O3, C17H18FN3O3, C17H12FN3O3, C13H10N2O3, C7H13N2O3, C10H5N2O3, C10H5N2O3, and C7H6O2; m/z = 302.2 ([M + H]+) might be identified as C16H19N3O3 or C16H22N3O2; and m/z = 192.2 ([M + H]+) might be identified as C12H24F3N2O2 or C10H11N2O3 [30–33]. Finally, these substances were decomposed into CO2, H2O, and other gaseous components. TOC removal over different catalyst is shown in Figure S9, which indicates that more than 60% organics are mineralized over flower-shaped C-dots/Co3O4[111]. Based on the above results, the possible catalytic degradation pathways of OTC and ENR are proposed (Figure 7).

2.5. Proposed Catalytic Mechanism

Generally, sulfate radicals (SO4−•) and hydroxyl radicals (OH•) are considered as the most important radicals for degradation of organic pollutants in the PMS activation system [34–36]. To identify which radical played the dominant role for the ENR degradation, classic quenching tests were carried out in which ethanol (EtOH) and tert-Butanol (TBA) were used as radical scavenger. In different quenching conditions, the reaction rate constants of sulfate radical and hydroxyl radical are shown in Table 3 [37,38]. As shown in Figure 8a, about 100% of ENR is degraded in 15 min in the absence of scavenger, while the degradation of ENR obviously decreased as the TBA was added in. Notably, compared with TBA, EtOH showed stronger inhibition to catalytic degradation of ENR. Thus, both hydroxyl radical and sulfate radical played the important role in catalytic degradation process.

To further elucidate the catalytic mechanism, DMPO-trapped EPR signals were detected in different aqueous dispersions of the corresponding samples with the addition of PMS (Figure 8). In the absence of catalysts, signals were not observed in the system of DMPO/PMS/ENR dispersion and the blank experiment (Figure S10). As flower-shaped C-dots/Co3O4[111] were added, characteristic signals of DMPO-OH and DMPO-SO4 were still not observed. However, unexpected characteristic signals which were ascribed to the oxidation products of DMPO (DMPOX) with the intensity ratios of 1.2:1:2:1:2:1:2 were captured (Figure S10). Since the dosage of oxidant (PMS) was more than pollutants (ENR), the excessive PMS would generate active substance/radicals (OH•, SO4−•, H2O2) which could oxidize DMPO to DMPOX [34,39]. As the PMS dosage decreased to 1.6 g/L, the characteristic peaks of DMPO-OH adduct (with hyperfine splitting constants of αH = 14.6 G) and DMPO-SO4 adducts (with hyperfine splitting constants of αH = 12.7 G, αH = 10.3 G, αβH = 2.1 G, αγH = 1.1 G) are observed, revealing the simultaneous presence
of OH• and SO₄²⁻•. The characteristic peaks of DMPO-SO₄²⁻• and DMPO-OH• were observed in the dispersions of catalysts with their intensities following the order of flower-shape C-dots/Co₃O₄{111} > flower-shaped Co₃O₄{111} > spherical Co₃O₄{110}, which indicated that doping C-dots on Co₃O₄{111} could effectively improve the generation of sulfate radicals.
In addition, in spherical Co₃O₄[110] and flower-shaped Co₃O₄[111] aqueous suspensions, PMS was not only reduced to SO₄•⁻ (Equation (7)) but also oxidized to large amounts of SO₅•⁻ (Equation (9)) due to the decomposition of PMS following the classic Fenton reaction mechanism. Thus, with the oxidation from Co(II) to Co(III), the value of Co(II)/Co(III) [spherical Co₃O₄[110], flower-shape Co₃O₄[111]] decreased from 1.36 to 1.16 obviously after cycled uses (Figure 6f). Meanwhile, the accumulated Co(III) was reduced by PMS with the generation of SO₅•⁻ in dispersions of flower-shaped Co₃O₄[111] and spherical Co₃O₄[110], resulting in a low selective PMS conversion to sulfate radicals. Different from spherical Co₃O₄[110] and flower-shaped Co₃O₄[111] aqueous suspensions, PMS was mainly reduced to SO₄•⁻ and OH• by the Co(II) and C-dots in the aqueous

Figure 7. The possible degradation pathway for (a) OTC, (b) ENR.
suspension of flower-shaped C-dots/Co3O4[111]. Although some Co(II) was oxidized to Co(III) by PMS with the generation of SO4•− and OH• (Equations (6) and (7)), R• could transfer the electron to Co (III) for its quick reduction via Co–O–C linkage, resulting in a stable value of Co(II)/Co(III) [flower-shaped C-dots/Co3O4[111]] before and after catalytic reaction (Figure 6f). Thus, such different mechanism of PMS activation over Co3O4 and flower-shaped Co3O4[111] led to higher selective PMS conversion to SO4•− over flower-shaped C-dots/Co3O4[111].

Table 3. The reaction rate constants of ethanol (EtOH) and tert-Butanol (TBA) with hydroxyl radical and sulfate radical.

| Radical Probo | Reaction Rate Constant (M−1 S−1) |
|---------------|----------------------------------|
| Ethanol (EtOH)| (1.6–7.7) × 10⁷                  |
| Tert-Butanol (TBA) | (4–9.1) × 10⁷          |

Figure 8. (a) Degradation of ENR in the system of PMS and flower-shaped C-dots/Co3O4[111] in the presence of TBA or EtOH; (b) EPR spectra in various conditions. Center field: 34,800 G; microwave frequency: 9.849 GHz; modulation frequency: 100 kHz; and power: 20.17 mW. ■ DMPO-OH; ● DMPO-SO4.

In order to further illustrate the co-catalyst effect of C-dots on Co3O4[111], PMS activation rate per second on a single active site was calculated. In classic Fenton reaction system, the concentration of OH• in the aqueous dispersion with H2O2 could be directly measured by using the terephthalic acid (TPA) probe method. Accordingly, the turnover frequencies (TOF) of Fenton catalyst could be obtained from the conversion number of H2O2 into OH• per second on a single active site [40]. However, TOF cannot be calculated in PMS activation system because it is difficult to accurately quantify the SO4•−. Thus, the turnover numbers (TONs) are selected to evaluate the catalytic efficiency for PMS activation (Equation (3)) [41].

\[
\text{TONs} = \frac{n \text{ (converted reactants)}}{n \text{ (catalyst active sites)}}.
\]  

The number of active sites of catalysts can be calculated by the following method [42]:

\[
\frac{\text{catalyst surface area}}{\text{unit cell area}} \times \frac{\text{Co}^{2+}}{\text{Co}^{3+}}.
\]

(4)

The specific surface area and Co2+/Co3+ of the catalyst can be obtained by BET and XPS spectra, respectively. Moreover, the unit cell area can be calculated by the length of Co3O4 cell [42]. Then, the PMS concentration was obtained by low-concentration iodide methods (ESI). As expected, C-dots/Co3O4[111] show higher TONs than Co3O4[111] (Figure S11). Such improvement can be explained as follows: Besides of PMS reduction to SO4•− by Co(II), graphene structure of C-dots could facilitate the production of R• (R•,
the product of $SO_4^- \cdot/OH\cdot$ attacking to organics) (Equation (10)). Such reactive organic radicals promote the PMS conversion to $SO_4^- \cdot$ (Equation (11)). Electrons were not only transferred from $R\cdot$ to Co(III) via the Co–O–C linkage for Co(III) reduction to Co(II), but also transferred from $R\cdot$ to PMS over C-dots with the generation of $SO_4^- \cdot$ (Equation (12)). Thus, the PMS conversion rate is obviously increased after C-dots doped on $Co_3O_4$[111].

Based on the above results, the possible catalytic mechanism of flower-shape C-dots/$Co_3O_4$[111] is proposed (Figure 9). Both $Co_3O_4$ crystal structure and doped C-dots played an important role in PMS activation. On the one hand, flower-shaped C-dots/$Co_3O_4$[111] exposed more Co(II) for PMS activation with generation of $SO_4^- \cdot$. On the other hand, graphene structure of C-dots facilitated the production of reactive organic radicals ($R\cdot$) (Equation (10)). Some of electrons are transferred from $R\cdot$ to Co(III) via the Co–O–C linkage with the reduction of Co(III) to Co(II) (Equation (11)), which decrease the ‘invalid decomposition’ of PMS (Equation (9)). Other electrons are transferred from $R\cdot$ to PMS over C-dots with the generation of $SO_4^- \cdot$ (Equation (12)) ($R*$ is the intermediate product from the reaction of $R\cdot$ and Co(III)/$HSO_4^-\cdot$). Thus, there were threeelectron transfer routes in the catalytic process: the first route was from Co(II) to PMS with the generation of $SO_4^- \cdot$, the second route was from $R\cdot$ to Co(III) via the Co–O–C linkage with the quick reduction of Co(III) to Co(II), and the third route was from $R\cdot$ to PMS via C-dots with the generation of $SO_4^- \cdot$. Consequently, high catalytic activity and selective PMS conversion to $SO_4^- \cdot$ was achieved.

\[
Co(II) + HSO_5^- \rightarrow Co(III) + SO_4^{2-} + OH\cdot, \quad (5)
\]
\[
Co(II) + HSO_5^- \rightarrow Co(III) + SO_4^- \cdot + OH^-\cdot, \quad (6)
\]
\[
OH\cdot + SO_4^{2-} / HSO_4^- \leftrightarrow SO_4^- \cdot / HSO_4\cdot + OH^-\cdot, \quad (7)
\]
\[
Co(III) + HSO_5^- \rightarrow Co(II) + SO_5^- \cdot + H^+, \quad (8)
\]
\[
R + SO_4^- \cdot / OH\cdot \rightarrow R\cdot + SO_4^{2-} / H_2O, \quad (9)
\]
\[
R\cdot + Co(III)-O-C-dots \rightarrow R^* + Co(II)-O-C-dots, \quad (10)
\]
\[
OH\cdot / SO_4^- \cdot + OTC/ENR \rightarrow SO_4^{2-} \rightarrow CO_2 + H_2O. \quad (12)
\]

Figure 9. The possible catalytic mechanisms in the suspension of PMS and flower-shaped C-dots/$Co_3O_4$[111].
3. Materials and Methods

3.1. Chemicals

All chemicals were analytical grade and used without further purification. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and Oxone (KHSO$_5$·0.5KHSO$_4$·0.5K$_2$SO$_4$, ≥95% purity) were purchased from Shanghai Macklin Biochemical Co. Ltd (Shanghai, China). Oxytetracycline (OTC, ≥99%), Enrofloxacin (ENR, ≥99%), Rhodamine B (Rh B, ≥99%), and Methyl orange (MO, ≥99%) were purchased from the Aladdin Industrial Corporation. (Shanghai, China). Acetonitrile (99.9% purity) was supplied from the Aladdin Chemistry Co. Ltd. (Shanghai, China). Acetonitrile (99.9% purity) for LC-MS was supplied from the Aladdin Chemistry Co. Ltd. (Shanghai, China). Tetrabutylammonium bromide (TBAb, ≥99.0%) was obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China). Other reagents including methanol (99.5%), ethanol (99.7%), acetic acid, tert-Butanol (TBA, ≥99.0%), Cobalt acetate Co(CH$_3$COO)$_2$·4H$_2$O, and Cetrimonium Bromide (CTMAB, ≥99.0%) were purchased from Nanjing Chemical Reagent Co. LTD (Nanjing, China).

3.2. Synthesis of Catalysts

C-dots: The synthesis method of C-dots is presented in a previous article [43]. Two graphite rods were inserted in a beaker containing 400 mL ultrapure water as two electrodes and the DC voltage of 30 V were attached at both ends of the electrode under continuous stirring. Five days later, the graphite rods were corroded and the water in the beaker turned black. Then, the large particles in the solution were filtered out with a filter paper. The solution was centrifuged with high speed centrifuge at 15,000 rpm for 30 min to remove the small particles. Finally, the solution was evaporated at 60 °C, and C-dots was obtained.

Flower-shaped C-dots/Co$_3$O$_4$(111): Synthesis processes of catalysts are shown as following method in Figure S12. A total of 1.192 g Co(CH$_3$COO)$_2$·4H$_2$O was dissolved in 60 mL ethanol containing a certain amount of C-dots. Then, CTMAB (Co(CH$_3$COO)$_2$·4H$_2$O:CTMAB = 2:1) was added into the above solution, and the mixture was stirred at 120 rpm for 15 min. The mixture was transferred to a Teflon-lined stainless steel autoclave and then heated in a high temperature oven at 170 °C for 48 h. The solid product was dried at 80 °C for 12 h to obtain C-dots/Co$_3$O$_4$(111). The synthesis process of flower-shaped Co$_3$O$_4$(111) was similar to C-dots/Co$_3$O$_4$(111), except that C-dots were not added into the hydrothermal reaction system. As for spherical Co$_3$O$_4$, C-dots and CTMAB are not added.

3.3. Characterization of Catalysts

The surface morphology of the material is characterized by field emission scanning electron microscopy (FESEM, S-3400NII, Hitachi, Tokyo, Japan). Microstructure and diffraction patterns were characterized by transmission electron microscopy (TEM, JEM-200CX, JEOL, Tokyo, Japan). Furthermore, the specific surface area and pore structure of catalysts were measured by Micromeritics Instrument (Nova 3000, Quantachrome).

The crystal structure of catalysts was characterized by the X-ray diffraction (XRD, Cu-Kα radiation, λ = 1.540562 Å, X’TRA, ARL, Switzerland). The XRD patterns were tested in the range of 30–70° (2θ). The binding energies of Co of the catalyst were measured by X-ray photoelectron spectroscopy (PHI 5000 Versa Probe, ULVAC-PHI, Chigasaki, Japan). In addition, the Fourier Transform Infrared Spectrometer (FT-IR, NEXUS870, NICOLET, Wilmington, NC, USA) was used to analyze the chemical structural functional groups.

To analyze the redox properties of Co in catalyst composites, the H$_2$-TPR experiments were conducted on the chemisorption analyzer (2920, AutoChem II, Micromeritics). The samples were heated to 400 °C in the Ar atmosphere for 60 min. After cooling down to 50 °C, the samples were heated to 900 °C with temperature ramp of 10 °C min$^{-1}$ in 10% H$_2$/Ar. Electrochemical impedance test was carried out by using CHI 760D electrochemical workstation (Austin, TX, USA).

Electrochemical measurements were conducted by an electrochemical workstation (CHI660D Instruments) with a standard three-electrode system. A total of 0.01 g catalyst was ultrasonic dispersed in 1 mL chitosan solution (0.05 M), then the dispersed droplets were placed on the glass electrode and dried in a vacuum oven before use.
DMPO-trapped EPR signals were detected in different aqueous dispersions of the corresponding samples with and without the addition of PMS. A detailed information for the recorded EPR signals is provided in the Figure S10.

3.4. Catalytic Performance

Four aromatic pollutants (OTC, ENR, MB, and Rh B) were selected to evaluate the catalysts activity. Preliminary experiments for ENR degradation indicated that the optimal doses of the catalyst and PMS were 0.05 g/L and 12.5 mM, respectively (Figure 6). Thus, these two doses were used in all catalytic degradation experiments unless otherwise specified. Typically, 200 mL aqueous solutions with certain pollutant and 0.01 g catalyst were placed in 250 mL beaker flasks. To ensure the adsorption–desorption equilibrium, the suspensions were magnetically stirred for 30 min before the catalytic reaction. Then, 12.5 mM PMS was added in the suspensions with magnetic stirring (120 rpm). At given time intervals, 2 mL aliquots were sampled and followed by adding methanol into the sample to quench the radicals for termination of the catalytic reaction, and subsequently filtrated through a Millipore filter (pore size 0.45 µm) prior to the analysis. In addition, to test the catalytic stability, the catalyst was recovered by filtration, washed with deionized water, dried, and reused in the following cycle. The degradation rate of pollutants is calculated. Concentrations of OTC and ENR were measured using Agilent 1200 HPLC (Agilent Technologies, Palo Alto, CA, USA) equipped with a quaternary pump and a UV detector. Chromatographic analysis was performed by a reversed-phase C-18 column (4.6 × 150 mm, 5 µm particle diameter), and the specific liquid conditions are listed in Table S2. The degradation intermediates of OTC and ENR were detected by HPLC–TOFMS in positive polarity. Rh B and MB concentrations in solutions were analyzed by the UV–1800 UV–vis spectrometer (Shimadzu, Japan).

4. Conclusions

Novel flower-shaped C-dots/Co3O4{111} were constructed for the improvement of the catalytic activity and selective peroxymonosulfate (PMS) conversion to sulfate radicals. Being attributed to the exposure of {111} facets, C-dots/Co3O4{111} could provide plenty of Co(II) for PMS activation. In addition, the Co3O4{111} facet not only possessed high adsorption energy of PMS on catalyst, but also facilitated the electron transfer from Co(II) to PMS. On the other hand, the graphene structure of C-dots facilitated the production of reactive organic radicals (R•), which provided the electrons for Co(III) and PMS reduction. Thus, C-dots doped on Co3O4{111} could obviously enhance the TONs. The catalytic degradation tests indicated that antibiotics and dyes could be efficiently degraded over flower-shaped C-dots/Co3O4{111}. Even after six cycling runs, flower-shaped C-dots/Co3O4{111} still remained a high catalytic activity. Additionally, according to degradation intermediates identified by LC-MS/TOF and electron cloud density calculated by Gaussian program calculation, the possible degradation pathways of OTC/ENR were proposed. EPR spectra and radical capture experiments further demonstrated that both OH• and SO4•− played a dominant role in catalytic degradation processes. Thus, the present work provided a simple and efficient way for PMS activation, which could be applied in the treatment of wastewater.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4344/11/1/135/s1, Figure S1. Co2p peaks of (a) flower-shape C-dots/Co3O4[111] before reaction, (b) flower-shape C-dots/Co3O4[111] after reaction (c) flower-shape Co3O4[111] before reaction, (d) flower-shape Co3O4[111] after reaction. Figure S2. TPR results of flower-like Co3O4 doped with different carbon quantum dots. Figure S3. Influence of different conditions on ENR degradation over flower-shape C-dots/Co3O4[111]: (a) catalyst dosage (pH = 7.00, 0.3 mM PMS, 25 °C), (b) PMS dosage (pH = 7.00, 0.05 g/L catalyst dosage, 25 °C), (c) temperature (pH = 7.00, 0.3 mM PMS, 0.05 g/L catalyst dosage), (d) pH (0.3 mM PMS, 0.05 g/L catalyst dosage, 25 °C). Figure S4. Co leaching during different pH conditions in flower-shape C-dots/Co3O4[111]/PMS/ENR system.
Figure S5. Density functional theory (DFT) calculations of PMS on different crystalline planes of Co3O4. Figure S6. Frontier electron densities of OTC and ENR calculated by Gaussian. Figure S7. Iron spectra at different retention time (RT) of OTC catalysis sample. Figure S8. Iron spectra at different retention time (RT) of ENR catalysis sample. Figure S9. TOC removal under different reaction conditions. Figure S10. EPR spectra in various conditions. Center field: 34,800 G; microwave frequency: 9.849 GHz; modulation frequency: 100 kHz; and power: 20.17 mW. Figure S11. The turnover numbers (TONs) of different catalysts prepared (Firstly, 10 mM potassium iodide (KI) solution was prepared to dilute the PMS sample 50 times. Then the solution was shaken for 5 minutes and detected with UV–vis spectrometer at λ = 352 nm). Figure S12. Schematic of synthesize process of flower-shape C-dots/Co3O4. Table S1. The pseudo-first-order kinetic equations, rate constants (K) and regression coefficients (R²) of degradation of OTC/ENR over different catalysts. Table S2. Operating conditions for HPLC about OTC and ENR.

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