Spatial Confinement of a Co_3O_4 Catalyst in Hollow Metal–Organic Frameworks as a Nanoreactor for Improved Degradation of Organic Pollutants

Tao Zeng,[†] Xiaole Zhang,^{†,‡} Saihua Wang,[†] Hongyun Niu,[†] and Yaqi Cai^{*,†}

[†]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, P. R. China

[‡]College of Life Sciences, Hebei United University, Tangshan 063000, Hebei, P. R. China

S Supporting Information

ABSTRACT: We here first proposed a yolk–shell Co_3O_4 @metal–organic frameworks (MOFs) nanoreactor via a facile method to accommodate sulfate radical-based advanced oxidation processes (SR-AOPs) into its interior cavity. The mesoporous and adsorptive MOFs shells allow the rapid diffusion of reactant molecules to the encapsulated Co_3O_4 active sites, and the confined high instantaneous concentration of reactants in the local void space is anticipated to facilitate the SR-AOPs. As a proof of concept, the nanoreactor was fully characterized and applied for catalytic degradation of 4-chlorophenol (4-CP) in the presence of peroxymonosulfate (PMS). The enhancement of SR-AOPs in the nanoreactor is demonstrated by the result that degradation efficiency of 4-CP reached almost 100% within 60 min by using the yolk–shell Co_3O_4 @MOFs catalysts as compared to only 59.6% under the same conditions for bare Co_3O_4 NPs. Furthermore, the applicability of this nanoreactor used in SR-AOPs was systematically investigated in terms of effect of reaction parameters and identification of intermediates and primary radical as well as mineralization of the reaction and stability of the composite. The findings of this study elucidated a new opportunity for improved environmental remediation.

INTRODUCTION

Advanced oxidation processes (AOPs) are generally recognized as one of the innovative water treatment technologies for degradation of organic pollutants owing to the creation of highly reactive radicals, such as hydroxyl radical ($\text{OH}^\bullet$), $\text{O}_2^{\bullet-}$, $\text{OOH}^\bullet$, and sulfate radical ($\text{SO}_4^{\bullet-}$).^{1–5} Among them, $\text{SO}_4^{\bullet-}$ -based AOPs (SR-AOPs) have attracted increasing research interest as an alternative to conventional Fenton processes because of the intrinsic drawbacks of the latter.^{6,7} Furthermore, $\text{SO}_4^{\bullet-}$ has a comparable redox potential (2.5–3.1 V) to that of $\text{OH}^\bullet$ (1.9–2.7 V) and is more efficient than $\text{OH}^\bullet$ to decompose some refractory organic contaminants for its selective oxidation ability.^{8,9} For $\text{SO}_4^{\bullet-}$ production, the combination of transition metal ions with peroxymonosulfate (PMS) is highly efficient, and cobalt ions have been found to be the best activator in this system.¹⁰ While considering the disadvantages of homogeneous process associated with the precipitation of metal salts and the difficulty in catalyst recycling, researchers deflect to develop heterogeneous cobalt based catalysts. Unfortunately, most of the current heterogeneous structures are often plagued by some inherent defects when adopted for SR-AOPs. More specifically, individual Co oxides nanoparticles (NPs) usually tend to aggregate inevitably

during the operation due to the high surface energy, leading to the decrease of the catalytic activity.^{11,12} As for supported ones,¹³ the direct exposure of catalytic sites in the bulk reaction solution would undoubtedly give rise to leaching of toxic Co ions, which can induce adverse effect to environment. Even in the case of the plausible state-of-the-art methods by which Co NPs are incorporated inside the mesoporous molecule sieves,^{6,14} the possible obstruction in mass transport and reduction in available contact of catalytic sites for the reactants would also lower the catalytic activity. Consequently, for the purpose of breaking through these limitations, it is extremely desirable to design novel and well-defined Co-based nanocatalysts.

Recently, hollow structured nanomaterials with an interior cavity enclosed by porous shell have received much attention because of their intriguing properties that render them promising candidates in a variety of biomedical and catalytic applications.¹⁵ We thus conceived that encapsulating the Co

Received: October 15, 2014

Revised: January 9, 2015

Accepted: January 21, 2015

Published: January 21, 2015

oxides into a proper hollow nanostructure to form a unique yolk-shell nanoreactor, which has been rarely investigated to date, would perfectly address the above-mentioned construction obstacles. In particular, the porous shell of the hollow nanostructure can impede the aggregation of adjacent Co oxides NPs and protect the enfolded catalyst from outside harsh environment without influencing the transport of reactants and products, while its interior cavity can preserve all the exposed catalytic sites accessible to reactants and provide microenvironment to accommodate the $\text{SO}_4^{\bullet-}$ oxidation reaction. More interestingly, enveloping catalytic reactions into a specific confined space would display improved catalytic performance due to the confinement effect, which has been confirmed by several previous studies including ours.^{16–18} In this context, it is envisioned that our proposal would be more advantageous than current catalysts for SR-AOPs.

To implement this concept, choosing an appropriate hollow nanostructure to encapsulate the catalyst is crucial, and hollow mesoporous silica structures that are broadly used to accommodate guests might first come into view.¹⁹ However, despite their success in some areas, this technology still suffers from tedious post-treatment processes of the template-engaged synthetic approach and limited functionality of the amorphous silica,²⁰ which make it far from a routine task in fabricating our nanoreactor. Luckily, metal-organic frameworks (MOFs), emerging as a new class of hybrid functional materials with large surface area, favorable thermal stability, and tailorable chemistry,^{21–23} open new opportunity for the conceivment. The integration of metal ions or clusters with organic linkers endows MOFs with abundant nanosized cavities and open channels.²⁴ These lead to a highly permeable shell which can provide pathways for small molecules to access and escape the interior materials. In addition to the feasibility of template-free fabrication of the hollow structure,^{25,26} MOFs also have outstanding adsorption ability for some specific targets due to the “molecular sieving effect” and affinity interactions.^{27–29} Hereto, it is believed that constructing hollow MOFs nanostructures to envelop Co containing NPs would be an ideal way to design the as-desired nanoreactor. However, no report has been found so far in terms of this concept.

In the present study, we report a facile and simple method to prepare yolk-shell Co_3O_4 @MOFs nanocomposites with a void cavity between a catalytic active Co_3O_4 core and a uniform octahedral MOF-5 shell and first demonstrate their application in serving as a nanoreactor to accommodate SR-AOPs. At the side of the existing reports, this work is unique in that (1) arrangement of SR-AOPs into a confined microspace rather than in bulk solution would be beneficial to enhance the catalytic activity; (2) encapsulation of Co_3O_4 NPs into a definite hollow environment increases the stability while preserves their whole surface active sites; (3) such nanoscale yolk-shell reactor with novel MOFs shell can be readily synthesized by a one-pot solvothermal method without any template; (4) the organic units in MOFs shell may offer adsorptive domains for enrichment of reactants in proximity to the embedded Co_3O_4 surface and guarantee the dispersion of the materials in water solution as well. With the systematic evaluation on degradation of 4-CP in regard to the as-prepared Co_3O_4 @MOFs nanoreactor, we demonstrate such a system holds great promise in practical environmental application.

EXPERIMENTAL SECTION

Chemicals. Iron(III) acetylacetonate ($\text{Fe}(\text{acac})_3$), 4-chlorophenol (4-CP), and 1,4-benzenedicarboxylic acid (H_2BDC) were obtained from Acros Organics (Morris Plains, NJ). Poly(vinylpyrrolidone) (PVP, average M.W. 58,000), *n*-octanol, and *N,N*-dimethylformamide (DMF) were purchased from J&K Chemical Co. Ltd. (Beijing, China). $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, *tert*-butyl alcohol (TBA), and ethanol were from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Peroxymonosulfate (PMS , $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, Oxone) was supplied by Sigma-Aldrich (U.S.A.). HPLC-grade methanol was supplied by Fisher Scientific (Fair Lawn, NJ). All chemicals were used as received without any further purification. Ultrapure water was prepared in the laboratory using a Milli-Q SP reagent water system from Millipore (Milford, MA).

Preparation of Yolk-Shell Co_3O_4 @MOFs Nanocomposites. As illustrated by Scheme 1, Co_3O_4 NPs were first

Scheme 1. Synthetic Strategy of Yolk-Shell Co_3O_4 @MOFs Nanocomposites

synthesized according to the previous reports.³⁰ Next, 3.2 mL of Co_3O_4 NPs ethanol solution (3 mg mL^{-1}), 200 mg of PVP, 6.4 mL of anhydrous ethanol, and 16 mL of DMF were mixed homogeneously by ultrasound and rock treatment. Then, 60 mg of $\text{Fe}(\text{acac})_3$, 46.4 mg of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 9.6 mg of H_2BDC were added into the mixture and dispersed for 10 min. The resulting solution was subsequently transferred to a Teflon-lined stainless-steel autoclave, sealed to heat at 100 °C for 6 h, and then cooled to room temperature. The product was washed with DMF and ethanol for several times. The core-shell Co_3O_4 @MOFs nanostructures without interior void were fabricated by reducing the reaction time to 3 h in the autoclave. The hollow MOFs nanostructures were fabricated without the addition of Co_3O_4 similar to the previous study.²⁶

Catalytic Activity Test. All the experiments were conducted in a conical flask (50 mL) in the dark with a rotate speed of 300 rpm. Yolk-shell Co_3O_4 @MOFs composites (0.5 g L^{-1}) were first dispersed into 20 mL pH-adjusted solution (0.2 M of phosphate buffer, pH 7.0) containing target 4-CP (0.78 mM). The degradation reaction was initiated by adding a known concentration of peroxymonosulfate (PMS) (0.8 mM) to the mixture. Samples (0.2 mL) were taken out at given time intervals and quenched with excess pure methanol (0.2 mL) and then centrifuged for the following analysis.

Control experiments using an equivalent dosage of bare Co_3O_4 NPs, core-shell Co_3O_4 @MOFs, and hollow MOFs as catalysts were carried out under the same steps as above, and the effects of reaction parameters (including pH, PMS amount, initial concentration of 4-CP, and loading amount of catalyst) were also investigated. For the recycle tests, the nanoreactors were recovered, washed with deionized water, dried, and used in the next run with the similar experimental conditions.

Sample Analysis. Dionex ultimate 3000 HPLC (Dionex, Sunnyvale, CA) with a PDA-100 photodiode array detector and an Acclaim 120 C18 column (5 μm , 4.6×250 mm) was

Figure 1. TEM images of Co₃O₄ NPs (A) and yolk-shell Co₃O₄@MOFs (B); SEM images (C), HAADF-STEM image (D), elemental mapping (E), and EDX spectra (F) of yolk-shell Co₃O₄@MOFs. The insets in (B) are the closer TEM observations.

Figure 2. XRD patterns (A) and FTIR spectra (B) of Co₃O₄ NPs and yolk-shell Co₃O₄@MOFs; XPS wide scan survey (C) and N₂ adsorption-desorption isotherms (D) of yolk-shell Co₃O₄@MOFs, the inset in (C) shows the distribution of pore diameter.

applied to analyze the 4-CP concentration. The mobile phase was composed of acetonitrile and water (70:30, v/v) at a flow rate of 1.0 mL min⁻¹ with a column temperature of 30 °C. The detection wavelengths of 4-CP, hydroquinone, and benzoquinone were set at 280, 290, and 245 nm, respectively. The chloride ion (Cl⁻) and carboxylic acids were determined using Dionex ICS-2000 system equipped with a DS6 conductivity detector, a Dionex IonPac AS11-HC analytical column (4 × 250 nm), an IonPac AG11-HC guard column (4 × 50 mm), and a Dionex ASRS Urtra II suppressor (4 mm). The mobile phase was 1 mM KOH at a flow rate of 1.0 mL min⁻¹. TOC was measured by TOC/TN analyzer (liquic TOC II)

(Elementar Corporation, Germany) with deionized water and 0.8% HCl as mobile phase. Metal leaching was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent, CA). All the experiments were conducted in triplicate, and the average values along with one standard deviation (±SD) were provided in the figures.

Characterization. The morphologies, crystalline structure, thermal stability, and surface analysis of the synthesized materials were surveyed by transmission electronic microscopy (TEM), scan electronic microscopy (SEM), X-ray diffraction studies (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), FTIR, and N₂ adsorption/

desorption analyses. Detailed procedures are presented in the SI.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. Presynthesized Co_3O_4 NPs with nearly spherical shape and an approximate diameter of 60 nm (Figure 1a) were directly mixed with MOFs precursors in the reaction solution, where $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{acac})_3$ serve as metallic precursors, H_2BDC as organic linkers, PVP as stabilizer, and DMF–ethanol as cosolvent. With a period of hydrothermal process, hollow bimetallic MOFs formed and spontaneously grew outside the surface of Co_3O_4 NPs, thus rendering the final Co_3O_4 @MOFs products unique yolk–shell morphology (Figure 1b). In contrast with the conventional templating methods to synthesize yolk-like composites, this one with needlessness of any template greatly simplifies the preparation procedure because of the synthesis flexibility of MOFs. From a magnified TEM image, the as-prepared yolk-like NPs appear in octahedral shape with an average edge length of ~ 240 nm. This nanosized MOFs material would be more favorable to the environmental application than the usual micrometer-scale counterparts due to the higher surface area. By closer observation, the shell is composed of numerous small MOFs aggregates (the inset in Figure 1b), and the Co_3O_4 core shows a lattice fringe distance of 0.184 nm (Figure S1). A relatively rough surface of the products was revealed by the SEM images in Figure 1c, while a large interstitial void between the Co_3O_4 core and the MOFs shell can be clearly discerned from a broken particle (the inset in Figure 1c). The HAADF-STEM image (Figure 1d) further demonstrates that the Co_3O_4 @MOFs composites have a typical yolk–shell structure. The EDX analyses (Figure 1f) together with elemental mapping (Figure 1e) confirm the elemental composition of the product. The fact that Co is distributed only in the core whereas the elements of the MOFs (Zn, Fe, and O) are homogeneously distributed throughout the whole NP suggests the successful integration of the Co_3O_4 and MOFs components.

The crystallographic structures of the products were measured by X-ray diffraction (XRD) (Figure 2a). The peaks at 2θ of 19.0° , 31.4° , 36.9° , 44.8° , 59.4° , and 65.2° , corresponding to (111), (220), (311), (400), (511), and (440) reflections, match well with the characteristic peaks of Co_3O_4 . In the case of the Co_3O_4 @MOFs pattern, a new set of peaks located within 2θ of 5.0° – 19.0° that should be ascribed to the cubic phase of MOF-5 arose. At the same time, the signal intensity of the Co_3O_4 in Co_3O_4 @MOFs slightly decreased in comparison with that of pure Co_3O_4 , which likely originated from the fact that Co_3O_4 NPs were fully encapsulated by MOFs shells. A similar situation was also found in the Fourier transform infrared (FTIR) studies (Figure 2b), in which the absorptions at 575 and 660 cm^{-1} , related to Co–O groups,³¹ sharply decreased in the Co_3O_4 @MOFs spectrum than those observed in the Co_3O_4 spectrum. Meanwhile, an additional absorption band around 1580 cm^{-1} that should be assigned to either C=O stretching vibrations or aromatic framework vibration emerged, indicating the presence of the MOFs constituent. Apparently, the oxygen-containing species from MOFs help to increase the hydrophilicity and thus guarantee the dispersion of the materials in water solution. To investigate the surface chemical composition of the product, the wide scan survey X-ray photoelectron spectrum (XPS) evaluations were conducted. After the growth of MOFs shell, some new

elements including Zn 2p, Fe 2P, and N 1s exist distinctly, while the Co 2p almost vanished (Figure 2c). The binding energies at 711, 725 eV and 1021, 1044 eV are associated with Fe 2p_{3/2}, Fe 2p_{1/2} for iron(III) oxide and Zn 2p_{3/2}, Zn 2p_{1/2} for zinc(II) oxide, respectively (Figure S2).²⁶ The N 1s peak at 399.7 eV may be rooted in the PVP N-residues trapped in the MOFs shell. The comparison of the C 1s core-level XPS spectra between Co_3O_4 and Co_3O_4 @MOFs (Figure S3) provides supportive evidence for the presence of oxygen-containing groups on the materials surface. In perfect accordance with the electron microscopy results, these characterizations provide supportive evidence for the triumphant fabrication of yolk-like Co_3O_4 @MOFs NPs.

The thermal stability of the Co_3O_4 @MOFs nanocomposite was surveyed by the thermogravimetric analysis (TGA) in a nitrogen flow (Figure S4). The result shows that the yolk–shell products do not exhibit serious weight loss upon to at least 250 $^\circ\text{C}$, which may be attributed to the liberation of surface adsorbed solvent. When heated to 350 $^\circ\text{C}$, the organic ligands of MOFs decomposed. To explore the porosity, N_2 adsorption–desorption experiments were also carried out. The isotherm of the Co_3O_4 @MOFs nanocomposite (Figure 2d) displays a typical Langmuir IV behavior, which is characteristic of mesoporous materials. The existence of a discernible hysteresis loop in the isotherm indicates the macroporosity imparted by the interior cavity as well as a certain degree of mesoporosity derived from the voids between MOFs aggregates in the shell. Calculated from the desorption branch of the nitrogen isotherm with the BJH method, the pore diameter of the shell is determined to be 4.2 nm. The yolk–shell structure gave rise to a high BET surface area of 196.3 $\text{m}^2 \text{g}^{-1}$ and a total pore volume of 0.41 $\text{cm}^3 \text{g}^{-1}$, which are higher than those of bare Co_3O_4 NPs (65.9 $\text{m}^2 \text{g}^{-1}$ and 0.35 $\text{cm}^3 \text{g}^{-1}$, Figure S5). Such a unique ink-bottle-shaped pores structure is beneficial to providing sufficient surface area to facilitate chemical reactions and efficient permeation of the reactants to access the active catalytic sites.

Catalytic Activity of Co_3O_4 @MOFs Nanocomposite. In a proof of concept that the Co_3O_4 @MOFs nanocomposite can be applied as an ideal nanoreactor, degradation of 4-chlorophenol (4-CP) by activated PMS was selected as a model reaction, and various control experiments were conducted. The adsorption and degradation profiles of 4-CP against the reaction time in various situations are shown in Figure 3. Nearly no 4-CP degradation was noticed when PMS alone is present, suggesting that the production of oxidizing radicals from PMS could not occur without catalysts. A rapid decrease of the 4-CP concentration was observed once the Co_3O_4 NPs were involved, evidencing the combination of Co oxides with PMS did possess a certain degradability for 4-CP. Impressively, the catalytic degradation rate of 4-CP significantly increased in the presence of yolk–shell Co_3O_4 @MOFs catalysts and PMS, and almost 100% decomposition was achieved within 60 min, while only 59.6% decomposition was observed for bare Co_3O_4 NPs under the same conditions. Taking the equivalent dosage of Co_3O_4 into account, the different catalytic performance shown on the two nanomaterials can merely be ascribed to structural discrepancy. Without the addition of PMS, the yolk–shell Co_3O_4 @MOFs composite itself only induced 19% reduction of 4-CP even after 150 min, which is much slower than that in the presence of yolk–shell Co_3O_4 @MOFs together with PMS. According to some previous studies,^{32,33} the phenyl-containing organic linkers in

Figure 3. Removal of 4-CP under different conditions: (1) bare Co_3O_4 NPs with PMS, (2) yolk-shell $\text{Co}_3\text{O}_4@\text{MOFs}$ nanocatalyst with PMS, (3) yolk-shell $\text{Co}_3\text{O}_4@\text{MOFs}$ nanocatalyst alone, (4) hollow MOFs with PMS, (5) solid core-shell $\text{Co}_3\text{O}_4@\text{MOFs}$ nanocatalyst with PMS, (6) PMS alone. Other reaction parameters: pH = 7.0, initial 4-CP concentration = 0.78 mM, PMS = 0.8 mM, $T = 298\text{ K}$, initial nanoreactor dosage = 0.5 g L^{-1} . C_t and C_0 denote the concentration of 4-CP at reaction time t and $t = 0$, respectively. The error bars stand for the standard deviation from triplicate experiments.

the MOFs matrix could adsorb aromatic compounds through a π - π stacking interaction. Therefore, we suppose that the minor decrease of 4-CP with the yolk-shell $\text{Co}_3\text{O}_4@\text{MOFs}$ composite only might be attributed to the surface adsorption of the MOFs shell.

For a comparison, hollow MOFs nanostructures without Co_3O_4 cores and core-shell $\text{Co}_3\text{O}_4@\text{MOFs}$ nanostructures without interior void (see TEM images in Figure S6) were fabricated and used to test the catalytic activity. From Figure 3, it was seen that hollow MOFs nanostructures with PMS could only show a slight contribution to the 4-CP decrease, giving a reduction of $\sim 23\%$ after 150 min, which is close to that under yolk-shell $\text{Co}_3\text{O}_4@\text{MOFs}$ without PMS condition. This result indicates that 1) the MOFs shells are indeed responsible for the adsorption of 4-CP, and 2) the reaction merely occurred around the embedded Co_3O_4 surface rather than the metal moieties of MOFs shell in the yolk-shell nanoreactor. As for core-shell $\text{Co}_3\text{O}_4@\text{MOFs}$ nanostructures with PMS, about 51% removal of 4-CP was achieved within 150 min, which is also much lower than that of the yolk-shell structure, implying the importance of the interior cavity in the catalyst. To identify

the possible contribution of the leachate through a homogeneous reaction way, the filtrate collected from a suspension of yolk-shell $\text{Co}_3\text{O}_4@\text{MOFs}$ catalysts after being shaken for a certain time was used to catalyze the degradation of 4-CP. Almost no change in the 4-CP concentration was found, manifesting the 4-CP degradation in the yolk-shell $\text{Co}_3\text{O}_4@\text{MOFs}$ nanoreactor followed a heterogeneous catalytic reaction.

Further investigations were performed to understand the effect of reaction parameters on 4-CP degradation in the $\text{Co}_3\text{O}_4@\text{MOFs}$ nanoreactor. Figure S7a presents the degradation efficiencies of 4-CP at a varying dosage of PMS. The 4-CP removal can reach about 100% within 30, 60, and 120 min at the PMS concentration of 0.8 mM, 0.4 mM, and 0.15 mM, respectively. Further increasing the PMS concentration did not increase the degradation efficiency but resulted in a slight inhibition perhaps due to the self-quenching of $\text{SO}_4^{\bullet-}$ by excess PMS.³⁴ Meanwhile, neutral or alkaline initial pH conditions exhibit a slightly superior 4-CP removal performance than acidic conditions (Figure S7b) in this reaction process. Figure S7c shows the effect of initial 4-CP concentrations on the reaction. The removal efficiency would decrease with the increased 4-CP concentration, and 0.78 mM of 4-CP would take 60 min for $\sim 100\%$ degradation. Elimination of higher initial concentration of 4-CP seems to need more PMS, which however may cause secondary pollution because of the discharge of excess SO_4^{2-} . At the same time, we found that high $\text{Co}_3\text{O}_4@\text{MOFs}$ nanoreactor consumption would improve the 4-CP degradation significantly (seen in Figure S7d). This should be put down to the fact that increasing active sites originated from the higher catalyst loading would facilitate the generation of more radicals from PMS.

Mineralization, Identification of Primary Reactive Oxidants and Intermediates. The degree of oxidative destruction of organic pollutants is generally represented by mineralization which can be analyzed using TOC removal. Figure 4a disclosed the mineralization profiles of 4-CP with different PMS addition and reaction time in the presence of $\text{Co}_3\text{O}_4@\text{MOFs}$ nanoreactors. As observed, the mineralization clearly grew when the PMS/4-CP ratio increased from 1:2 to 1:1. A plateau or even a little decrease of the mineralization was noticed when the PMS dosage further increased, which is consistent with the tendency of 4-CP removal under different PMS loading. As the reaction time shifted from 2 to 4.5 h, the mineralization increased regardless of PMS dosage, indicating

Figure 4. (A) Mineralization of 4-CP at various PMS/4-CP molar ratios and reaction times. (B) Effect of radical scavengers on 4-CP degradation in a $\text{Co}_3\text{O}_4@\text{MOFs}$ nanoreactor. The error bars stand for the standard deviation from triplicate experiments.

the intermediates in the latter stage of reaction duration were continually decomposed in the mixture solution. The mineralization can eventually reach to 72.2% for 1:1 of the PMS/4-CP ratio, which is comparable of the results obtained in previous reports.³⁵

Three reactive oxidants including $\text{OH}^\bullet$, $\text{SO}_4^{\bullet-}$, and peroxymonosulfate radical ($\text{SO}_5^{\bullet-}$) are commonly considered as the possible radical species in a Co-PMS catalytic system.³⁶ To verify the radical type present in the yolk-like Co_3O_4 @MOFs activated PMS process, a few quenching tests were carried out by using ethanol and *tert*-butyl alcohol (TBA). Ethanol ensures the quenching of both $\text{SO}_4^{\bullet-}$ ($3.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and $\text{OH}^\bullet$ ($9.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) owing to the high reactivity toward the two radicals, whereas TBA mainly reacts with $\text{OH}^\bullet$ ($3.8\text{--}7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and is not effective for $\text{SO}_4^{\bullet-}$ ($4.0\text{--}9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).³⁷ In the interim, $\text{SO}_5^{\bullet-}$ has a low rate constant with alcohols ($\leq 10^3 \text{ M}^{-1} \text{ s}^{-1}$) and thus is relatively inert to ethanol and TBA. Figure 4b depicts the inhibition effect of the two quenchers on the 4-CP degradation in the Co_3O_4 @MOFs-PMS system. The addition of 1 M ethanol nearly entirely inhibited the degradation of 4-CP, which meant that the radicals generated in the system were mostly quenched, and the contribution of $\text{SO}_5^{\bullet-}$ on the 4-CP decomposition was ruled out. Meanwhile, 1 M of TBA has little influence on the degradation of 4-CP by the Co_3O_4 @MOFs-PMS process, implying that $\text{OH}^\bullet$ has little contribution on the 4-CP decomposition. Based on the above observations, we conclude that $\text{SO}_4^{\bullet-}$ is the dominant radical species responsible for the 4-CP degradation.

Figure 5 illustrated the main intermediate products generated during different periods of 4-CP degradation. It can be seen

Figure 5. Evolution profiles of the intermediates in 4-CP degradation: (1) hydroquinone, (2) benzoquinone, (3) formic acid, (4) chloride ion, (5) malonic acid, and (6) fumaric acid. Other reaction parameters: pH = 7.0, initial 4-CP concentration = 0.78 mM, PMS = 0.8 mM, $T = 298 \text{ K}$. The error bars stand for the standard deviation from triplicate experiments.

that chloride ions were produced quickly, and hydroquinone and benzoquinone, as the major intermediates, reached a maximum concentration at 15–30 min and were then slowly degraded within 120 min. This is in good agreement with those of previous studies that the main products formed by an $\text{SO}_4^{\bullet-}$ attack on aromatics are hydroxylation products.³⁸ Similar to the $\text{OH}^\bullet$ attack mechanism, an aromatic ring was first attacked by the likewise electrophilic $\text{SO}_4^{\bullet-}$ to form a carbon-centered radical, followed by chlorine abstraction as well as hydroxylation in solution to yield hydroquinone. Hydroquinone was subsequently dehydrogenated to generate benzoquinone under

oxidation of $\text{SO}_4^{\bullet-}$. The ring of benzoquinone was further cleaved under such an oxidation condition to form some small molecular organic acids such as fumaric acid, malonic acid, and formic acid which were identified by IC analysis and should partly assume the residue TOC.

Stability and Reusability of Catalyst. To investigate the stability, ICP-MS measurements were performed to detect the possible Co leaching in the system of either bare Co_3O_4 or yolk-shell Co_3O_4 @MOFs coupled with PMS and 4-CP (Figure 6a). It was observed that the Co leaching percent in a bare Co_3O_4 -PMS system increased dramatically in a range of 0.83–2.50% with the reaction time increasing from 2 to 6 h. On the contrary, the percentage of Co leaching in a Co_3O_4 @MOFs nanoreactor-PMS system changed gently at a lower level of 0.18–0.28% which is almost one-tenth of that in the former system. This finding verified the credible role of the MOFs shell as a barrier to alleviate the external erosion toward Co_3O_4 . The reusability, which is a crucial concern with regard to the potential application of the catalyst, was checked by recovering the yolk-like Co_3O_4 @MOFs nanoreactors from the reaction mixture and reusing them in the next run. As shown in Figure 6b, the as-prepared catalyst was still highly active with a removal efficiency of 4-CP over 99% within 150 min even after four successive cycles. Meanwhile, the TEM results revealed that the yolk-shell structure of the recovered catalyst was scarcely changed (Figure S8). Because of the good stability and reusability, the yolk-shell Co_3O_4 @MOFs nanoreactor is suitable for water treatment application.

Reaction Mechanism in the Yolk-like Co_3O_4 @MOFs Nanoreactor. The possible mechanism of superior activity and stability of the yolk-like Co_3O_4 @MOFs nanoreactor in the activation of PMS for 4-CP degradation would be ascribed to the unique structural features in several aspects (Figure 7). First, the high nanoporosity and open pore network of MOFs shell ($\sim 4.2 \text{ nm}$ pore diameter) enables fast molecule diffusion of PMS and 4-CP as well as the products in and out of the nanoreactor. Second, the organic units of MOFs shell offer specific adsorption for the enrichment of 4-CP from bulk solution through π - π interaction, leading to a high concentration of reactants in the interior of nanoreactor. Third, the cavity void permits full accessibility of PMS to Co_3O_4 catalytic sites to create plenty of $\text{SO}_4^{\bullet-}$ and confines high instantaneous concentration of $\text{SO}_4^{\bullet-}$ and 4-CP into such a local microenvironment, which provides a driving force to facilitate the oxidation degradation of 4-CP. Finally, the hollow architecture would effectively suppress the aggregation of Co_3O_4 NPs and their dissolution into a reaction mixture.

In summary, this work presents the successful fabrication of novel yolk-shell Co_3O_4 @MOFs nanocomposites through a facile and simple strategy and first demonstrates their application as a nanoreactor to accommodate SR-AOPs in the interior void space. Benefiting from the mesoporous and adsorptive MOFs shell as well as the unique cavity between the Co_3O_4 core and the shell, this nanostructure catalyst showed a higher catalytic activity and stability than bare Co_3O_4 NPs in bulk solution for the 4-CP removal in the presence of PMS. Further investigations including the effect of reaction parameters and identification of intermediates and the primary radical as well as mineralization prove that 4-CP can be effectively decomposed through $\text{SO}_4^{\bullet-}$ oxidation in the nanoreactor. The high degradation rate of 4-CP (over 99% within 150 min) was achieved after 4 consecutive cycles, implying the satisfactory reusability of the as-prepared catalyst.

Figure 6. (A) Cobalt leaching percentage of bare Co_3O_4 and Co_3O_4 @MOFs nanoreactor with different reaction times. The error bars stand for the standard deviation from triplicate experiments. (B) 4-CP removal efficiency within 150 min at each cycle.

Figure 7. Possible mechanism of 4-CP degradation in the Co_3O_4 @MOFs nanoreactor.

These results make us believe that our work may bring great extendibility to generate a multifunctional yolk-like nanostructure for the improved catalytic degradation of various environmental pollutants.

■ ASSOCIATED CONTENT

Supporting Information

Additional characterization procedures and Figures S1–S7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 86-10-6284-9182. E-mail: caiyuqi@rcees.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was jointly supported by National Scientific Instrument Research Program of China (2012YQ090229), State Environmental Protection Welfare Scientific Research Project (201409037), and the National Nature Science Foundation of China (21277152, 21277002, and 21377034).

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