ZIF-67 Derived Co Nanoparticles Embedded N-Doped Mesoporous Carbon Nanocages as an Active Heterogeneous Fenton Catalyst for the Degradation of Tetracycline

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Abstract

Herein, the novel application of ZIF-67 derived HCo@NC as a highly active and stable catalyst for Fenton treatment of organic wastewater is discussed. The carbonization of the Cobalt based Zeolitic Imidazolate Framework-67 (ZIF-67) yielded of HCo@NC~700 nm shows a hollow structure inheriting the rhombic dodecahedron shape of the precursor ZIF-67. XPS analysis reveals the coexistence of Co^{2+} and Co^0 . The treatment of Tetracycline (TC) in HCo@NC catalyzed Fenton system indicates that hydroxyl radicals generated to oxidize TC to decompose, and the optimal condition is determined to be $0.71 \text{ mmol}\cdot\text{L}^{-1} \text{ H}_2\text{O}_2$ and $0.03 \text{ g}\cdot\text{L}^{-1}$ HCo@NC at pH 3 for the treatment of $15 \text{ mg}\cdot\text{L}^{-1}$ TC. H_2O_2 is catalyzed by HCo@NC to decompose to hydroxyl radicals for the degradation of TC, and the reaction mechanism is proposed.

Keywords: HCo@NC; Fenton; Antibiotic wastewater; catalysis; degradation mechanism

1. Introduction

There is no doubt that, the Fenton process is one of the most concerned technologies to deal with waters polluted by toxic, refractory organic pollutants, for its great effectiveness, as well as simplicity and low cost (Zhang et al., 2020). For its toxicity to people's health and its damage to biological diversity, antibiotic wastewater need to be treated urgently. Fenton process characterized by the generation of hydroxyl radicals ($\cdot\text{OH}$), which is a strong oxidant with a potential of 1.90-2.80 eV under neutral to acidic conditions, is the most attractive technology tracking water pollution (Wang et al. 2020a; Zhou et al. 2020). The scientific fundamental of Fenton process is quite well known. But the wide application of traditional Fenton consist of ferrous ion and hydrogen peroxide is limited by its narrow pH window and the generation of iron sludge. The complex of industrial waste waters also gives a discount of the efficiency of Fenton process. In order to make the maximum utilization of Fenton, modifications are made, mainly in two ways. On the one hand, extra energies including light and electricity are reported to be introduced in to assist Fenton reactions, the introduction of these energies improved the efficiencies of the degradation of pollutants, but also raise the cost of the reaction. On the other hand, efforts are committed to develop new solid catalysts. High catalytic potential and stability are considered essential for a good catalyst, and large surface area is considered important.

Co-content materials were reported many times to be of good photocatalytic potential, but the catalytic property of Co-content materials as a Fenton-like catalyst

on the decomposition of H_2O_2 has rarely been reported. And usually, these materials are not uniform, and particle size is reported an important factor influencing the catalytic activity. Template-sacrifice method is considered eminent in preparing uniform catalysts (Wang et al. 2020b; Hou et al. 2020; Zhao et al. 2020). To obtain nanomaterials with specific morphology, large surface area and hollow structure, templates such as Metal Organic Frameworks (MOFs) were occupied (Liu et al. 2014; Han et al. 2018). As a series of porous MOFs, Zeolitic imidazolate framework (ZIF) are reported as templates or precursors for the fabrication of 3D hollow nanomaterials many times. ZIF as a series of porous crystalline material are reported to transform to three dimensional hollow nano-materials (Jiang et al. 2013). Porous N-doped carbon nanocages derived from MOFs (Chaikittisilp et al. 2014; Salunkhe et al. 2016; Zhang et al. 2017; Han et al. 2017) commonly obtained from the process of calcination in inert atmosphere or in air. ZIF-67 consists of cobalt ion and organic metal framework is chosen as precursor to prepare the hollow Co-modified N-doped porous carbon nanpcages in this study.

In this work, ZIF-67 was prepared using solution method as reported (Wang et al. 2020c) and occupied as precursor for the synthesis of the hollow Co-modified N-doped porous carbon nanocages (HCo@NC). The large BET surface area and hollow structure provided it a large amount of active site for adsorption and catalysis, and catalytic reactions may be promoted by adsorption (Zhu et al. 2020; Wu et al. 2020; Duan et al. 2020). The HCo@NC obtained performed excellent in the degradatation of Tetracycline (TC), and batch experiments were carried out to explore

the influence of factors on the catalytic behavior in Fenton-like system, including pH, temperature, dosage of adsorbent and initial concentration of pollutant. The reactive oxygen species (ROS) play the dominated role in the AOPs are further elucidated by scavenger experiments and electron paramagnetic resonance (EPR) analysis. Finally, a possible reaction mechanism of the HCo@NC/H₂O₂ Fenton-like system was proposed based on the experimental results and data analysis.

2. Experimental section

2.1 Chemicals and Materials

Polyvinyl pyrrolidone (PVP), CoCl₂·6H₂O, 2-methylimidazole, methanol, ethanol, H₂SO₄, NaOH, Tetracycline, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), KI and NaN₃ were purchased from Aladdin, and used directly without purification.

2.2 Synthesis of ZIF-67

The preparation process of ZIF-67 was expounded systematically in Scheme 1, it was prepared according to previous report (Jiang et al. 2013). Synthesis of ZIF-67: 1.00 g polyvinyl pyrrolidone (PVP) and 1.04 g CoCl₂·6H₂O were uniformly dissolved in 80 mL methanol. After then, 80 mL methanol solution of 5.26 g 2-methylimidazole was ultrasonic added to the above solution for 5 min. Afterwards, the mixture was stirred at room temperature for 1 h and aged for 24 h. Finally, The solution obtained by centrifugation and washing was dried at 80°C for 12 h.

Scheme 1

2.3 Fabrication of HCo@NC

HCo@NC was obtained by directly carbonizing the precursor ZIF-67 in Ar

atmosphere. ZIF-67 was firstly heated at the rate of $2^{\circ}\text{C}\cdot\text{min}^{-1}$ and kept at 350°C for 120 min, and then heated at the rate of $5^{\circ}\text{C}\cdot\text{min}^{-1}$ and kept at the pyrolysis temperature of 700°C for 120 min.

2.4 Characterizations

The crystal structure of precursors and the component of derivatives are analyzed by X-ray diffraction (XRD) (BRUKER D8, Cu $K\alpha$ at 40 kV and 40 mA). The morphology and structure are characterized by scanning electron microscope (SEM) (Quanta 400F) and transmission electron microscope (TEM) (JEM-2010), and the test acceleration voltage was 200 kV. The element composition is investigated by X-ray photoelectron spectroscopy (XPS) (PHI Quantera II ESCA System with Al $K\alpha$ radiation at 1486.8V). Thermogravimetric analysis and differential thermal analysis (TGA/DSC, TGA/DSC1, Mettler Toledo) were simultaneously recorded. Conditions were flow rate of $50\text{ cm}^3\cdot\text{min}^{-1}$, heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ and argon atmosphere.

2.5 Catalytic experiments

To evaluate the catalytic performance of HCo@NC, TC was chosen as the target pollutant. All the degradation experiments were conducted in deionized water except radical quenching experiments. In a typical experiment, 200 mL of TC solution ($20\text{ mg}\cdot\text{L}^{-1}$) was added into a 500 mL of barker with 400 rpm stirring, and then 8 mg of catalyst was added into the above solution for 10 min to reach the absorption equilibrium. NaOH and H_2SO_4 solution were used to adjust the initial pH of system. Fenton reaction was initiated as H_2O_2 added, and samples were taken out for analyzing at predetermined time intervals.

The quenching agent experiments were conducted by adding different ratio of KI and NaN_3 in the degradation system. Reactive oxygen species, played the dominant role, was further confirmed by electron paramagnetic resonance (EPR) experiments and DMPO and methanol were used as trapping agents were carried out.

2.6 Electrochemistry tests

The mixture of 90 wt% HCo@NC and 10 wt% PVDF was coated onto Ni foam, and the cyclic voltammograms (CV) was recorded using CHI660E at a scan rate of $0.05 \text{ mV}\cdot\text{s}^{-1}$, and the frequency of the electrochemical impedance spectroscopy (EIS) was from 100 kHz to 10 mHz.

3. Results and discussion

3.1 Characterization

Figure 1a presents X-ray diffraction (XRD) pattern of HCo@NC , and the embedded is the XRD pattern of ZIF-67. As shown in Figure 1a, the inset is the XRD pattern of ZIF-67, the diffractions of ZIF-67 match well with the simulated pattern (Wang et al. 2018), demonstrates that the precursor synthesized are phase-pure. The diffraction peaks of the derivate at $2\theta=51.88^\circ$ and 60.62° (JCPDS No. 15-0806) indicating the formation of HCo-NC (Salunkhe et al. 2015). The morphology of ZIF-67 seems like a box in dodecahedron shape with a diameter around 700 nm as shown in TEM and SEM images (Fig.1b-c). The derivate HCo@NC inherits the dodecahedron shape of ZIF-67 (Fig. 1d-e), but with a hollow structure (Fig. 1d). Fig. 1f-i show the SEM image and elements mapping of the derivate, it is found that the distribution of Co and C (Fig. 1g-i) are in the same size and area of the image of

HCo@NC, indicating that Co, and C atoms are homogeneously distribute on HCo@NC.

Figure 1

The content of Co in the obtained material is measured with thermogravimetric analysis (TGA) (Fig. 2). The weight loss from 215°C to 373°C (32.67%) is due to the pyrolysis of N-dopped carbon. The exothermic peak in the heat flow curve at the corresponding region verified the combustion of N-dopped carbon. The residual 67.34% weight is the contribution of cobalt.

Figure 2

XPS analysis is carried out to investigate surface compositions and the oxidation states of Co. The XPS spectra of fresh HCo@NC and HCo@NC after Fenton reaction are showed in Fig. 3. In the XPS survey spectrum of fresh HCo@NC, a set of peaks corresponding to C 1s, N 1s, O 1s, and Co 2p (Fig. 3a) are shown. In the high-resolution XPS spectra (Fig. 3b) of Co, Co 2p_{3/2} and Co 2p_{1/2} bands could be deconvoluted into three peaks corresponding to Co (0), Co (2+), and the shake-up (satellites) peak at 780.3, 781.3, 784.6 eV and 794.7, 796.5, 804.4eV, respectively. The appearance of Co (2+) might be resulted from the superficial cobalt oxide, for Co is susceptible to air (Li et al. 2016a; Li et al. 2016b). The surface composition of Co(2+)/Co(0) is calculated to be 0.553, according to peaks areas (Table 1). A peak at 796.5 eV ascribed to the Co 2p_{1/2} of the Co³⁺ ions appeared (Fig. 3c) (Wang et al. 2020d; Liu et al. 2020), and the surface composition of Co(2+)/Co(3+) and Co(2+)/Co(0) are calculated to be 7.128 and 0.607, respectively (Table 1). The

increased proportion of Co(2+) and the generation of Co(3+) maybe ascribed to their catalysis behavior on the generation of hydroxyl radicals.

Figure 3

Table 1

3.2 Catalytic mechanism

An excellent catalyst is reported to be of good reversible redox character (Ai et al. 2008), which is usually analyzed using cyclic voltammetry tests, and the electron diffusion on the surface of catalyst is determine using AC impedance tests (Wang et al. 2013). The results are shown in Fig. 4(a) and Fig. 4(b). CV curve in Fig. 4(a) depicts the redox behavior of HCo@NC. Two pair of redox peaks could be observed (Fig. 4(b)) in the potential range for HCo@NC showing that the material is of good reversible redox character, and two electrons may transfer during the catalytic reaction (Ai et al. 2008), which may be due to the reversible transformation between Co^{2+} and Co^0 . From the EIS spectra shown in Fig. 4(b), the internal resistance of HCo@NC is determined to be 0.53 Ω , and the diffusion resistance calculated to be 0.48 Ω . Electrons are easy to diffuse during the catalytic process.

Figure 4

The catalytic performance of HCo@NC is evaluated by comparing the removal efficiencies of pollutants in different reaction systems (Fig. 5a) and the corresponding reaction rates are calculated (Fig. 5b). TC is selected as target organic pollutant for its toxicity and commonly seen. As shown in Fig. 5a, H_2O_2 is too weak to oxidize TC to decompose (Wang et al. 2020e; Wang et al. 2021) ($1.291 \times 10^{-4} \text{ min}^{-1}$). The removal

efficiency of 43.04% at 180 min in the presence of HCo@NC maybe caused by its hollow structure, and some TC molecules are adsorbed onto HCo@NC ($5.67 \times 10^{-3} \text{ min}^{-1}$). 99.15% removal of TC can be obtained with the presence of HCo@NC+H₂O₂, this may be due to the adsorption of HCo@NC and some generation of active radicals with strong oxidation potential. Active radicals generated in HCo@NC/H₂O₂ system made TC removed in a faster rate (0.033 min^{-1} , Fig. 5b).

To further ascertain the primary active radicals for the degradation of TC, the quenching experiments are carried out. Hydroxyl radicals ($\cdot\text{OH}$), superoxide anion radicals ($\text{O}_2^{\cdot-}$) are reported exist in Fenton-like process (Nie et al. 2020; Sun et al. 2020; Zhong et al. 2020). In this HCo@NC/H₂O₂ Fenton-like system, the two active radicals mentioned above are detected, and KI is utilized to scavenge $\cdot\text{OH}$ on the catalyst surface, and NaN₃ is used as scavenger for oxygen and $\cdot\text{OH}$ in solution. As shown in Fig. 5c, 99.15% discoloration of TC can be obtained without any scavenger. When NaN₃ is added to the HCo@NC/H₂O₂ system, the discoloration efficiency of TC decreased from 93.3% to 85.5% at 180 min as the dosage of NaN₃ increased from 0.03 mM to 0.08 mM. As expected, the degradation efficiency of TC decrease from 99.15% to 53.2% with 0.03 mM KI added and the efficiency even decreased to 12.1% as the dosage of KI further increased to 0.08 mM. This phenomenon indicated that $\cdot\text{OH}$ radicals play a dominant role in HCo@NC/H₂O₂ system, and ESR with DMPO is acquired to clarify the active radicals involved (Fig. 5d). No obvious $\text{O}_2^{\cdot-}$ signals can be detected. However, four sharp signal peaks with the intensity ratio of 1:2:2:1 can be observed. The results indicated that, $\cdot\text{OH}$ played the main role in the

degradation of TC in HCo@NC catalyzed Fenton-like system.

Figure 5

According to the characterization and tests mentioned above, the possible degradation mechanism is put forward as follows (eqs 1–3) and proposed in Fig.

6. $\cdot\text{OH}$ generated with the catalysis of HCo@NC for the degradation of TC.

Figure 6

3.3 Influence factors

To investigate the optimal degradation condition, the Fenton-like system catalyzed by HCo@NC is evaluated under different initial pH, various dosages of catalyst and H_2O_2 , and the results were presented in Fig. 7. As shown in Fig. 7(a), the degradation of TC increase as the initial solution pH increased from 2.02 to 2.98. The most removal efficiency appeared at pH 2.98, and 97.8% removal is achieved. As pH further increased from 2.98 to 7.95, the removal efficiency reduced to 69.5% (especially sharply from 85.6% to 69.5% as pH increased from 7.02 to 7.95). Acidic conditions favor the production of reactive radicals, and hydroxyl radicals show higher oxidation potential (2.80 eV) under acidic conditions than under neutral condition (1.90 eV) (Duan et al. 2020; Qu et al. 2020). Hydroxyl radicals generated may be scavenged by H^+ under strong acidic conditions, whereas the combination of OH^- with active catalytic components (Fe^{2+} and Fe^{3+}) may inhibit the catalytic

potential on radical production (Kuang et al. 2013; Xu et al. 2012). As shown in Fig. 7b, 69.7% removal of TC is obtained with no catalyst present. Almost 100% removal of MB is obtained with catalyst added in our study. As the dosage of HCo@NC increased from 17.7 mg·L⁻¹ to 66.3 mg·L⁻¹, the degradation rate of TC increase, and then decrease as the dosage of HCo@NC further increased to 100 mg·L⁻¹. In Fig. 7c, as the dosage of H₂O₂ increased from 0.137 to 0.548 mmol·L⁻¹, the degradation efficiency of TC increase from 42.1% to 98.0%, and decrease to 96.7% as the dosage of H₂O₂ further increased to 0.070 mmol·L⁻¹. This phenomenon is ascribed to the capture of hydroxyl radicals by H₂O₂. Reaction temperature is also considered significant parameter influencing a catalytic oxidation process. The effect of reaction temperature on the discoloration of TC at pH 3 is tested ([H₂O₂] = 0.71 mmol L⁻¹, [TC] = 15 mg L⁻¹, catalyst dosage = 0.03 g L⁻¹ and initial pH = 3;) and the result is depicted in Fig. 7d. Higher reaction temperature obviously avail the catalytic oxidation process. The reason maybe that H₂O₂ decomposes at a faster rate to generate more ·OH and more energy is provided to overcome reaction activated energy at higher temperature (Wang et al. 2014a; Wang et al. 2014b). Experimental plot data in the range of 0–30 min are fitted to a pseudo-second-order equation, and the coefficients R² and k_a are also listed in Table 2. Rate constants k_a are 6.66×10⁻³, 7.11×10⁻³, and 49.35×10⁻³ min⁻¹ in correlation with reaction temperatures at 10, 20, and 30°C. This phenomenon indicate that the reaction of TC degradation catalyzed by HCo@NC is favored at higher temperature and the reaction is endothermic.

Figure 7

Table 2

Kinetic studies of the degradation of TC are studied to quantitatively characterize the removal of target pollutant under different conditions. It helps us to clarify the relationship between influence factors and degradation of target pollutant and make the activated reaction energy (E_a) clear. E_a can be calculated from the Arrhennius equation as listed in Eq(4):

$$k_a = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

The linear form of the equation is

$$\ln(k_a) = \ln(A) - \frac{E_a}{RT} \quad (5)$$

Are k_a the rate constant, A the preexponential factor, E_a the reaction activation energy (J/mol), R the gas constant (8.314 J/mol K), and T the absolute temperature (K). Using the data listed in Table 2, $\ln(k_a)$ versus $1/T$ are plotted in Figure 8, and E_a can be obtained from the slope of the linear fitted to the plots. The E_a value obtained in the case of the Fenton-like process catalyzed by HCo@NC was 73.05 kJ/mol.

Figure 8

4. Conclusions

A template method to prepare the nanomaterial HCo@NC with hollow structure as catalyst for the treatment of antibiotic wastewater has been put forward for the first time. HCo@NC as-prepared showed good catalytic behavior in the Fenton-like system, and $\cdot\text{OH}$ generated on the surface of HCo@NC played the main role in the degradation of TC. 98% degradation of TC can be obtained with the presence of 66.3

mg·L⁻¹ HCo@NC and 0.548 mmol·L⁻¹ H₂O₂. The *E_a* value obtained in the case of the Fenton-like process catalyzed by HCo@NC was 73.05 kJ/mol. In all, HCo@NC is a promising catalyst in Fenton-like process.

Credit Author Statement

Qian Wang: Supervision, Topic suggestion, Planning, Experimentation, Results analysis, Writing - main manuscript; **Huairu He:** Co-supervision, Project administration, Review & editing; **Xiaofei Wang:** Co-supervision, Project administration, Review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Scheme captions

434 **Scheme 1** Synthetic procedure of HCo@NC

435

Figure captions

Figure 1 (a) XRD pattern of HCo@NC (the inset is the XRD pattern of ZIF-67); (b) TEM and (c) SEM images of ZIF-67; (d) TEM and (e) SEM images of HCo@NC; (f) SEM image and elemental mapping results of HCo@NC; (g) elemental mapping images of C and Co of the HCo@NC.

Figure 2 The thermogravimetric analysis (TGA) curves of HCo@NC

Figure 3 (a) Survey XPS spectra of HCo@NC; (b) Co 2p spectrum of HCo@NC

Figure 4 (a) CV curve of HCo@NC at 0.05 mV s⁻¹; (b) EIS spectra of HCo@NC

Figure 5 (a) The removal efficiency of TC and (b) the rate constants under different conditions (Reaction condition: [H₂O₂] = 0.71 mmol L⁻¹, [TC] = 15 mg L⁻¹, catalyst dosage = 0.03 g L⁻¹ and initial pH = 3); (c) the effects of different scavengers; (d) EPR spectra of H₂O₂ activation on HCo@NC.

Figure 6 Possible mechanism of Fenton-like system catalyzed by HCo@NC

Figure 7 Effects of (a) initial solution pH; (b) dosages of catalyst; (c) dosages of H₂O₂; (d) temperature on degradation of TC.

Figure 8 Plot of ln(*k*_a) versus 1/*T* for the estimation of the reaction activated energy

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Table captions

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Table 1 Fitted parameters from XPS analysis of the HCo@NC

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Table 2 Pseudo-second-order rate constants under different reaction temperatures

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Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

492

Table 1

Materials	Co ²⁺ /Co ³⁺	Co ²⁺ /Co ⁰
Fresh	-	0.553
HCo@NC		
HCo@NC after Fenton reaction	7.128	0.607

493

494

Table 2

Condition	K _a , min ⁻¹	R ²
10°C (283 K)	0.00666	0.915
20°C (293 K)	0.00711	0.892
30°C (303 K)	0.04935	0.903

495

Figures

Figure 1

(a) XRD pattern of HCo@NC (the inset is the XRD pattern of ZIF-67); (b) TEM and (c) SEM images of ZIF-67; (d) TEM and (e) SEM images of HCo@NC; (f) SEM image and elemental mapping results of HCo@NC; (g) elemental mapping images of C and Co of the HCo@NC.

Figure 2

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Figure 6

Possible mechanism of Fenton-like system catalyzed by HCo@NC

Figure 7

Effects of (a) initial solution pH; (b) dosages of catalyst; (c) dosages of H₂O₂; (d) temperature on degradation of TC.

Figure 8

Plot of $\ln(k_a)$ versus $1/T$ for the estimation of the reaction activated energy

Supplementary Files

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