The MIL-88A-Derived Fe₃O₄-Carbon Hierarchical Nanocomposites for Electrochemical Sensing

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Metal or metal oxides/carbon nanocomposites with hierarchical superstructures have become one of the most promising functional materials in sensor, catalysis, energy conversion, etc. In this work, novel hierarchical Fe₃O₄/carbon superstructures have been fabricated based on metal-organic frameworks (MOFs)-derived method. Three kinds of Fe-MOFs (MIL-88A) with different morphologies were prepared beforehand as templates, and then pyrolyzed to fabricate the corresponding novel hierarchical Fe₃O₄/carbon superstructures. The systematic studies on the thermal decomposition process of the three kinds of MIL-88A and the effect of template morphology on the products were carried out in detail. Scanning electron microscopy, transmission electron microscopy, X-ray powder diffraction, X-ray photoelectron spectroscopy and thermal analysis were employed to investigate the hierarchical Fe₃O₄/carbon superstructures. Based on these resulted hierarchical Fe₃O₄/carbon superstructures, a novel and sensitive nonenzymatic N-acetyl cysteine sensor was developed. The porous and hierarchical superstructures and large surface area of the as-formed Fe₃O₄/carbon superstructures eventually contributed to the good electrocatalytic activity of the prepared sensor towards the oxidation of N-acetyl cysteine. The proposed preparation method of the hierarchical Fe₃O₄/carbon superstructures is simple, efficient, cheap and easy to mass production. It might open up a new way for hierarchical superstructures preparation.

Fe₃O₄ has attracted tremendous attention for its novel magnetic and catalytic properties. However, its poor conductivity, easy aggregation and uselessness in strong acidic solution exclude it as promising materials in many fields such as electrochemistry and biology. To overcome these drawbacks, other agents (e.g., liposome, micelle, polymer, silica) with compensatory properties was introduced into Fe₃O₄. Among them, carbon was the typical material used to promote Fe₃O₄’s conductivity and stability. For example, Fe₃O₄ embedded into porous carbon nanosheets or nanotube was benefit from the conductivity of carbon and used as a durable high-rate lithium ion battery anode material. At the same time, the carbon matrix might effectively inhibit the aggregation of Fe₃O₄. The Fe₃O₄@carbon nanocomposites after further modification with strong oxidizing agents might be biocompatible and applied as drug delivery. Recently, one-step hydrothermal synthesis of Fe₃O₄@carbon nanocomposites has been reported with great performance in biomedicine.

Generally, there are two strategies to synthesize Fe₃O₄@carbon nanocomposites. The first method is wet chemistry, that is, Fe₃O₄@carbon is synthesized by mixing Fe₃O₄ nanoparticles or their precursors with a carbon source (e.g., glucose, dopamine, ethylene glycol, citric acid, oleic acid, EDTA, etc.) followed by a carbonization process. For this strategy, a strong dependence on reaction conditions was required,
thus aggregation and chemical wastes were inevitably occurred. Furthermore, most products had compact and smooth exteriors, limiting the effective utilization of inner surface. The second method is dry method such as magnetron sputtering. With this method, the resulted Fe\(_3\)O\(_4\)@carbon always showed low dimensionality\(^2\). In fact, the property of materials can be enhanced by tailoring their shapes, sizes and compositions\(^11\). Much effort has been devoted to design the morphology of materials for further promoting their performance\(^12,13\). Recently three-dimensional (3D) architecture was employed as a template to afford both high porosity and good conductivity\(^14,15\). For example, Pt-based bimetallic flower-like or dendritic-like NPs showed great potential as catalysts for reducing the Pt consumption, providing a high surface area, and facilitating enhanced performance in the catalytic applications\(^16–20\).

Recently, metal-organic framework (MOF), a new class of hybrid functional materials has attracted extensive attention for their diverse structures, topologies and compositions. The MOFs-template method has been adopted to form metal/metal oxide micro/nanostructures with various controlled shapes including microplates, nanowires, nanorods, nanoparticles, nanosheets, hollow and coralloid nanostructures via controlling reaction temperature, reaction time, precursors, etc\(^21–25\). Generally, metal ions with a reduction potential of \(-0.27\) volts or higher present in MOFs form metal NPs during thermolysis in N\(_2\), whereas metal ions with a reduction potential lower than \(-0.27\) volts form metal oxide NPs during thermolysis in N\(_2\). MIL-88A as an important kind of MOFs was synthesized by linking Fe(III) to the oxygen atoms of fumaric acid regularly\(^26\). The ordered structure effectively prevented the aggregation of Fe\(_3\)O\(_4\) nanoparticles and the unsaturated organic linker not only acted as reducing agent but also could be further transformed into porous carbon when MIL-88A was decomposed to Fe\(_3\)O\(_4\)\(^27\). Recently, Hee Jung Lee et al. synthesized magnetic particle-embedded porous carbon composites from MIL-88A under relatively high temperature\(^28\). Differing from their work, the present work focused on the transformation process of MIL-88A when it was calcinated from 200 °C to 500 °C. Furthermore, the relationship between the structure of precursors and morphologies of products was also presented in this work. We found that, calcinated at low temperatures, the MIL-88A could convert to 3D hierarchical Fe\(_3\)O\(_4\)/carbon superstructures with controllable particle size and shape and performed good electrical conductivity due to the carbon matrix enhanced the electrochemical property of the nanocomposites (Fig. 1). Although remarkably significant progress has been obtained in shape-controlled synthesis of MOFs so far, MOF-derived Fe\(_3\)O\(_4\)@carbon with different particle sizes and morphologies have not been reported yet.

**Results and Discussion**

Porous carbon coated Fe\(_3\)O\(_4\) was synthesized based on the solid-template method. The hierarchical Fe\(_3\)O\(_4\)/carbon superstructures with different morphologies can be achieved by pyrolysis of MIL-88A with different morphologies as depicted in Figure 1. The MIL-88A with different morphologies were successfully synthesized by changing the solvent and the concentration of FeCl\(_3\)-6H\(_2\)O. Fig. 2a–c showed scanning electron microscopy (SEM) images of MIL-88A crystals prepared under different conditions. The rod shaped small size particle with an average diameter of 500 nm was shown in Fig. 2a. The spindle-like
particles with an average diameter of 1 μm and the diamond-shaped large size precursor with diameter of 5 μm were presented in Fig. 2b and c, respectively. The particle size is crucially determined by the nucleation rate. In general, fast nucleation gives a large number of nuclei, and shortens the crystal growth stage, leading to small-sized particles. In contrast, slow nucleation gives a smaller number of nuclei, and elongates the growth stage, leading to large-sized particles29. Considering the solvation effect, the stronger solvation of Fe^{3+} ions in N,N-dimethyl formamide (DMF, μ = 3.86D) solution drastically slowed down the generation speed of MIL-88A crystals, leading to large-sized MIL-88A crystals. In water (μ = 1.85D), the nucleation quickly proceeded to generate small-sized nanoparticles with high yield. For middle-sized MIL-88A, FeCl₃·6H₂O concentration was decreased to 2.4 mmol and two reactants of FeCl₃·6H₂O and fumaric acid were mixed beforehand. The first mixture made Fe^{3+} reacted directly with fumaric acid as soon as DMF was added. Therefore, the middle-sized particle appeared due to mild crystallization speed. As comparison, the product synthesized by dissolving 2.4 mmol FeCl₃·6H₂O and fumaric acid in 10 ml ultra–pure water separately was also studied and the diameter was found to be 10 μm.

X-Ray powder diffraction (XRD) measurements (Fig. 2d) were performed to examine the crystal structure of the resulted three kinds of MIL-88A samples with different morphologies (r-MIL-88A, s-MIL-88A and d-MIL-88A). All these X-ray diffraction patterns of prepared samples were consistent with the well-known MIL-88A crystal structure30. The different shapes were determined by the growth rates along different directions. In this case, the (100), (101), (002) crystallographic facets developed apparently and other diffraction peaks at 2θ = 11°, 12°, 14.5° of s-MIL-88A and d-MIL-88 were stronger than that of r-MIL-88A. Compared with r-MIL-88A, the right shift was observed at the diffractions of (100), (101), (002) crystallographic facets of s-MIL-88A and d-MIL-88. The shift might be due to the solvent absorption and swelling effect.

For the present work, the MOF-template method was used to prepare Fe₃O₄-carbon hierarchical nanocomposites. The progress could be followed by thermo-gravimetric analysis (TGA) curve as shown in Fig. S1 (Supporting Information). The first main mass loss stage was due to the volatilization of the solvent (H₂O or DMF) accompanied by slight degradation of fumaric acid. The further degradation from 200°C to 300°C was consistent with the breakdown of fumaric acid in a similar range (200–250°C). Another degradation from 300°C to 500°C was observed and the XRD characterization indicated that the conversion from Fe₂O₃ to Fe₃O₄ occurred at this stage (discussed in the following). The conversion could be attributed to the incomplete calcined products as evidenced by thermal stability27. The phase corresponding to the Fe₃O₄@C nanocomposites was stabilized at 500°C. After 500°C, the MIL-88A was totally decomposed thus no more mass loss was observed. The carbon generated during the calcination which has been proven in XPS full-spectra of Fe₃O₄@C₄₀₀ (Fig. S2, Supporting Information) could act as a buffer to prevent aggregation of metal oxides24.

The XRD patterns of FeOₓ@C₂₀₀, FeOₓ@C₃₀₀ and FeOₓ@C₄₀₀ (Here, X was used to represent the iron oxide due to the uncertain of the proportion of iron and oxygen) were also shown in Fig. S3 (Supporting Information).
Information). The diffraction peaks of FeO$_x$@C$_{200}$ at $\theta = 24^\circ$, $32^\circ$, $35^\circ$, $41^\circ$, $49^\circ$, $54^\circ$, $62^\circ$, and $64^\circ$ in all XRD patterns matched well with crystal planes of pure solid $\alpha$-Fe$_2$O$_3$ (Hematite, JCPDS card no. 06–0502, curve a). Both the characteristics diffraction peaks of Fe$_2$O$_3$ and Fe$_3$O$_4$ were simultaneously observed on the XRD patterns of FeO$_x$@C$_{200}$. During the thermal decomposition, the relatively high temperature induced the conversion of Fe$_2$O$_3$ into Fe$_3$O$_4$. The XRD patterns of FeO$_x$@C$_{200}$ as shown in pattern c, the characteristic diffraction peaks at $30^\circ$, $36^\circ$, $43^\circ$, $54^\circ$, $57^\circ$, and $63^\circ$ were indexed as the diffractions of the (220), (311), (400), (422), (511), and (440) crystalline planes of Fe$_3$O$_4$ according to the standard spectrum of magnetite (JCPDS card no. 19–629).

SEM and transmission electron microscopy (TEM) were both employed to reveal the morphology change of the three kinds of samples at different pyrolysis temperatures at $N_2$. In the first temperature gradient, MIL-88A was heated at 200 °C for 30 min, the rod-shape of r-MIL-88A was kept and the formation of Fe$_2$O$_3$ was indicated by XRD while the edge disappeared (Fig. 3a). In the second stage (300 °C), iron oxide was formed on the near-surface and there were spherical FeO$_x$ particles decorating the incomplete calcined precursors (Fig. 3b). The long holding time induced the conversion of hematite into magnetite incompletely due to organic residues acting as reducing agents$^{27}$. The further studies confirmed that the total heating time of over 40 min was required to complete such decomposition and the conversion of hematite into magnetite was evidenced by XRD pattern and X-ray photoelectron spectroscopy (XPS) spectra (discussed in the following). Growth of iron metal crystal was induced by increasing the calcined temperature to 400 °C (Fig. 3c). Further increasing the annealing temperature to 500 °C and holding this temperature for 30 min caused the enlarged iron oxide particles as a result of crystal aggregation (Fig. 3d). TEM images (Fig. 3e,f) for rod-shape materials calcined at 400 °C gave further evidence of the composite structure showing FeO$_x$ coated with porous carbon. It could be established from Fig. 3e,f that the FeO$_x$ nanoparticles with average diameter of 100 nm were encapsulated individually by a thin carbon boundary and such particles were dispersed in a porous carbon matrix. When the thermal treatment was performed at 400 °C for 30 min in $N_2$ atmosphere with a heating rate of 5 °C/min, the products had shapes of parent precursors and improved Fe$_3$O$_4$ content. The XRD (Fig. 3g) revealed that the diffraction peaks of Fe$_2$O$_3$ became more intense and sharper in the FeO$_x$@C$_{400}$, again providing evidence of the growth of Fe$_3$O$_4$ crystallites and the structural evolution at elevated temperature.

The XPS spectroscopy was employed to identify the composition of the products synthesized at 400 °C. The binding energy values of 710.8 eV and 724.6 eV were ascribed to Fe 2p$_{3/2}$ and 2p$_{1/2}$, respectively (Fig. S4A, Supporting Information). The analysis data of XPS of Fe 2p$_{3/2}$ spectra (Fig. S4A, Supporting Information) indicated the conversion rate from Fe$_2$O$_3$ to Fe$_3$O$_4$ was as high as 91.1 w% for r-MIL-88A.

For s-MIL-88A, the volatilization of solvent in the first stage led the smooth surface to be rough (Fig. 4a) and the burrs of product at 300 °C converted into bulk (Fig. 4b). No obvious change was found when the temperature was increased from 300 °C to 400 °C (Fig. 4c). The TGA curve of s-MIL-88A in this range was more moderate than that of r-MIL-88A (Fig. S1, Supporting Information). When the temperature surpassed 400 °C, the decomposition of the precursors was very quickly thus the iron oxide was aggregated significantly (Fig. 4d). As shown by the TEM image given in Fig. 4e,f, the size of FeO$_x$ crystals was less than 50 nm and dispersed uniformly in dendritic carbon matrix. Different from other MO$_x$@C (MO$_x$: metal oxides) derived from MOFs, the s-MIL-88A transformed to dendritic shape rather than a smooth and compact surface, which could increase the specific surface area and utilization rate of the MO$_x$. The XRD (Fig. 4g) and XPS (Fig. 4h) spectroscopy were employed to identify the composition of the products prepared at 400 °C. The characteristic diffraction peaks at $30^\circ$, $36^\circ$, $43^\circ$, $54^\circ$, $57^\circ$, and $63^\circ$ were indexed as the diffractions of the (220), (311), (400), (422), (511), and (440) crystalline planes of Fe$_3$O$_4$ according to the standard spectrum of magnetite and no other crystalline planes was found in the XRD pattern. The binding energy values of 710.8 eV and 724.6 eV were ascribed to Fe 2p$_{3/2}$ and 2p$_{1/2}$, respectively (Fig. S4B, Supporting Information). The analysis data of XPS of Fe 2p$_{3/2}$ spectra (Fig. S4A, Supporting Information) indicated the conversion rate from Fe$_2$O$_3$ to Fe$_3$O$_4$ was as high as 81.5 w% for s-MIL-88A.

The situation for d-MIL-88A was similar to the above one. The diamond-like materials obtained at different temperatures with distinct morphologies and structures were shown in Fig. 5. The bulk crystal was formed at 500 °C (Fig. 5d). At relatively low temperature of 200–400 °C, the morphology of the products was similar to dandelion and retained the size of d-MIL-88A precursor particles (Fig. 5a–c). The TEM images (Fig. 5e,f) of the nanocomposites prepared at 400 °C established a ball-in-dendritic carbon shell structure. The FeO$_x$ crystals were dispersed in the dendritic carbon shell with size of about 20 nm. As shown in the SEM (Figs 3, 4 and 5), the surface of r-MIL-88A at 200 °C was compact while the s-MIL-88A and d-MIL-88A at 200 °C were fluffy. The difference was first related to the absorption of polar solvent. The cell parameter is a direct measurement of distance between Fe and trimeric units and the amplitude of the swelling is influenced by the absorption of polar solvent. Compared with H$_2$O, the stronger polar moment of DMF could make the MIL-88A present bigger cell parameter which indicated the longer distance between the inorganic trimeric units and larger swelling amplitude of s-MIL-88A and d-MIL-88A$^{25}$. The heating would lead to solvent volatilization while the topology of the framework was maintained thus the volatilization of DMF resulted in larger voids than H$_2$O. The voids and burrs formed when s-MIL-88A and d-MIL-88A heated at 400 °C revealing by the TEM further proved the inference. However, the voids and burrs weren't observed during the pyrolysis process of r-MIL-88A due to the smaller cell parameter. On the other hand, the long distance between Fe and trimeric units of
s-MIL-88A or d-MIL-88A played as a buffer for the aggregation of Fe₃O₄ crystal thus led to small particle size. In addition to the volatilization of solvent, the decomposition of organic ligand also attributed to the porosity of the hierarchical nanostructure. According to previous works²⁴,³⁴, we could deduce that the

Figure 3. (a–d) SEM images of r-MIL-88A calcined at different temperature: 200 °C (a), 300 °C (b), 400 °C (c), 500 °C (d). (e,f) TEM images of Fe₃O₄@C by calcining r-MIL-88A at 400 °C. (g) XRD patterns of Fe₃O₄@C by calcining r-MIL-88A at 400 °C. (h) XPS of Fe 2p spectrum of Fe₃O₄@C derived from r-MIL-88A at 400 °C for 30 min.
amorphous carbon generated from the decomposition of organic ligands of MIL-88A served as a temporary framework to distribute FeOx particles. As the temperature increased, the MIL-88A contracted inward and the organic framework further decomposed into carbon and gas (CO₂ and hydrocarbons) under N₂ atmosphere. The adhesive force owing to the volume loss and the release of internally generated

Figure 4. (a–d) SEM images of s-MIL-88A calcined at different temperature; 200 °C (a), 300 °C (b), 400 °C (c), 500 °C (d). (e,f) TEM images of Fe₃O₄@C, by calcining s-MIL-88A at 400 °C. (g) XRD patterns of Fe₃O₄@C, by calcining s-MIL-88A at 400 °C. (h) XPS of Fe 2p spectrum of Fe₃O₄@C, derived from s-MIL-88A at 400 °C for 30 min.
gases prevented the inward contraction of Fe$_3$O$_4$-carbon shell. Finally, for d-MIL-88A, the hierarchical nanocomposites with compact Fe$_3$O$_4$-carbon core and loose shell were formed. While for s-MIL-88A, the smaller diameter didn’t allow the formation of apparent voids between the core and dendritic carbon shell.

Figure 5. (a–d) SEM images of d-MIL-88A calcined at different temperature; 200 °C (a), 300 °C (b), 400 °C (c), 500 °C (d). (e,f) TEM images of Fe$_3$O$_4$@C$_d$ by calcining d-MIL-88A at 400 °C. (g) XRD patterns of Fe$_3$O$_4$@C$_d$ by calcining d-MIL-88A at 400 °C. (h) XPS of Fe 2p spectrum of Fe$_3$O$_4$@C$_d$ derived from d-MIL-88A at 400 °C for 30 min.
The intensive and sharp diffraction XRD peaks (Fig. 5g) revealed the growth of Fe₃O₄ crystallites and the structural evolution at elevated temperatures. The XPS spectroscopy of the products from d-MIL-88A synthesized at 400°C was similar to that from s-MIL-88A at 400°C (Fig. 5h and Fig. S4C in Supporting Information). The XPS indicated the conversion rate of Fe₂O₃ to Fe₃O₄ was 77.5% for d-MIL-88A.

Nitrogen adsorption–desorption isotherms shown in (Fig. S5A Supporting Information) were measured to evaluate the specific surface area and the pore size distribution of Fe₃O₄@C₄₀₀. The curve for Fe₃O₄@C₄₀₀ samples was a little bit similar to the I-type isotherm and suggested the different pore sizes spanning from micro to macropores. The steep increase at low relative pressure pointed the existence of micropores. Hysteresis between adsorption and desorption branches could be observed at medium relative pressure for r-MIL-88A and s-MIL-88A, which demonstrated the existence of mesopores. The steep increase at the tail of the relative pressure near to 1.0 revealed the presence of macroporosity. The majority of the pores were located in the region of mesopore. All the samples displayed very close pore size distribution with a peak centering at ca. 3.0 nm as shown in the pore size distributions curve calculated from the nitrogen adsorption branches (Fig. S5B, Supporting Information). The specific surface area were calculated to be 70.3 cm² g⁻¹, 33.4 cm² g⁻¹ and 20.5 cm² g⁻¹ for r-Fe₃O₄@C₄₀₀, s-Fe₃O₄@C₄₀₀ and d-Fe₃O₄@C₄₀₀, respectively. The specific surface area was higher than many reported metal oxides. We deduce that the high specific surface area of r-Fe₃O₄@C₄₀₀ might result from the small particle size of material. Yan and co-workers have recently discovered that Fe₃O₄ magnetic nanoparticles (MNPs) actually exhibited an intrinsic peroxidase-like activity. A significant amount of research has been focused on imitating peroxidase activity with various noble metals (e.g., Au, Pt and Pd) modified Fe₃O₄ MNPs. The Fe₃O₄@C for amino acid sensor has also been reported. In view of the good electrochemical property, the hierarchical Fe₃O₄/carbon superstructures prepared here were employed to sensing N-acetyl cysteine.

Cyclic voltammograms (CVs) of different modified electrodes (Fe₃O₄@C/GCE (glassy carbon electrode), Fe₃O₄@C₄₀₀/GCE, Fe₃O₄@C₆₀₀/GCE and bare GCE) in 0.1 M NaOH in the presence of N-acetyl cysteine were shown in Fig. 6a–c and Figure S6 When 0.3 mM N-acetyl cysteine was added into 0.1 M NaOH, the catalytic current obtained on Fe₃O₄@C modified electrodes increased obviously and were much larger than that obtained on bare GCE, indicating that Fe₃O₄@C had good catalytic activity for N-acetyl cysteine. The CVs and amperometry were carried out to explore how the morphology affected the electrochemical performance of the three kinds of Fe₃O₄@C/GCE. The CVs of Fe₃O₄@C/GCE at varied scan rate was investigated in 0.1 M NaOH. As shown in Figure S7A-C (Supporting Information), the anodic peak current density increased as the scan rates increased from 10 to 400 mV s⁻¹. The peak current was proportional to the square root of scan rates as shown in the inset of Figure S7A–C (Supporting Information), indicating this process for the three kinds of Fe₃O₄@C/GCE were all diffusion-controlled. Furthermore, the oxidation of N-acetyl cysteine at Fe₃O₄@C were started at about 300 mV then increased as the scan rates increased from 10 to 400 mV s⁻¹. The peak current was proportional to the square root of scan rates as shown in the inset of Figure S7A–C (Supporting Information), indicating this process for the three kinds of Fe₃O₄@C/GCE were all diffusion-controlled. Furthermore, the oxidation of N-acetyl cysteine at Fe₃O₄@C were started at about 300 mV then increased as the scan rates increased from 10 to 400 mV s⁻¹. The peak current was proportional to the square root of scan rates as shown in the inset of Figure S7A–C (Supporting Information), indicating this process for the three kinds of Fe₃O₄@C/GCE were all diffusion-controlled. Furthermore, the oxidation of N-acetyl cysteine at Fe₃O₄@C were started at about 300 mV then increased as the scan rates increased from 10 to 400 mV s⁻¹. The peak current was proportional to the square root of scan rates as shown in the inset of Figure S7A–C (Supporting Information), indicating this process for the three kinds of Fe₃O₄@C/GCE were all diffusion-controlled. Furthermore, the oxidation of N-acetyl cysteine at Fe₃O₄@C were started at about 300 mV then increased as the scan rates increased from 10 to 400 mV s⁻¹. The peak current was proportional to the square root of scan rates as shown in the inset of Figure S7A–C (Supporting Information), indicating this process for the three kinds of Fe₃O₄@C/GCE were all diffusion-controlled.
that the loading amount of Fe$_3$O$_4$ of r-Fe$_3$O$_4$@C$_{400}$, s-Fe$_3$O$_4$@C$_{400}$ and d-Fe$_3$O$_4$@C$_{400}$ was about 82%, 67% and 62%, respectively. It can be easily concluded that the more the loading amount of Fe$_3$O$_4$, the better the catalytic property of the nanocomposite, as shown in Fig. 6f.

Interference is inevitable in the determination of some analyses. So, we have investigated the selectivity of the modified electrode in this work towards several possibly coexisted substances. Fig. S9 (Supporting Information) showed the current responses of the modified electrode toward some chemicals, including BrO$_3$–, IO$_3$–, NO$_2$–, Cl–, NO$_3$–, SO$_4$$_2$–, K$^+$, Na$^+$ and Mg$^{2+}$. We presumed there was no interference if the variance of the catalytic current was smaller than 6% after the injection of other chemicals. It was obvious that chemicals such as saturated BrO$_3$– and IO$_3$–, NO$_2$–, Cl–, NO$_3$–, SO$_4$$_2$–, K$^+$, Na$^+$ and Mg$^{2+}$ in a 10-fold of N-acetyl cysteine concentration did not show obvious interference to 1 mM N-acetyl cysteine detection. The result implied the good selectivity of Fe$_3$O$_4$@Cs/GCE. Similar results were also obtained for both Fe$_3$O$_4$@Cr/GCE and Fe$_3$O$_4$@Cd/GCE.

Chronoamperometry was employed to study the mass transfer kinetics and obtained the heterogeneous catalytic rate constant. Fig. S10A-C (Supporting Information) showed chronoamperograms recording with Fe$_3$O$_4$@C/GCE in the absence and presence (0.5 mM, 1.0 mM, 2.0 mM, 4.0 mM, 6.0 mM, 8.0 mM, 10.0 mM) of N-acetyl cysteine. The applied potential steps were set to 0.60 V and 0.30 V, respectively. Plotting the net current with respect to the minus square roots of time presented linear dependency (inset of Figure S10A-C). Therefore, diffusion-controlled process in the bulk solution was dominated for the oxidation of N-acetyl cysteine. Using the slope of the line, the diffusion coefficient of N-acetyl cysteine could be obtained according to Cottrell’s equation:

**Figure 6.** (a–c) CVs of different electrodes in 0.1 M NaOH in the absence and presence of 0.3 mM N-acetyl cysteine. Scan rate: 50 mV s$^{-1}$ (a) Fe$_3$O$_4$@C$_{400}$, (b) Fe$_3$O$_4$@C$_{400}$ and (c) Fe$_3$O$_4$@C$_{400}$. (d) Typical amperometric responses of Fe$_3$O$_4$@C/GCE to successive injection of N-acetyl cysteine into the stirred 0.1 M NaOH. (e) A segment of the amperometric concentration step response showing sensor response time; (f) The calibration curve of amperometric responses ((a) Fe$_3$O$_4$@C$_{400}$, (b) Fe$_3$O$_4$@C$_{400}$ and (c) Fe$_3$O$_4$@C$_{400}$).
The catalytic rate constant \( (K_{\text{cat}}) \) was calculated based on the slope of the \( I_{\text{cat}}/I_d \) versus \( t^{1/2} \) plot as shown in the inset of Figure S10A-C according to the following equation:

\[
I = \eta FAD^{1/2}C\pi^{-1/2}t^{-1/2} 
\]

The mean value of N-acetyl cysteine diffusion coefficient and the catalytic rate constant \( (K_{\text{cat}}) \) were listed in Table S2 (Supporting Information). These results further confirmed our conclusion that the material with smaller particle size and higher surface area showed better catalytic performance, meanwhile the dendritic shape could promote the diffusion of the electroactive material.

In summary we realized the transformation of Fe-containing MOF, a kind of typical porous material, into Fe\(_2\)O\(_3@C\) with different particle sizes. The different morphologies were determined by the cell dendritic shape could promote the diffusion of the electroactive material.

Preparation of MIL-88A. For the synthesis of nano-sized MIL-88A crystals with different morphology, 4 mmol FeCl\(_3\)·6H\(_2\)O and 4.0 mmol fumaric acid were dissolved in 10 ml ultra–pure water separately. These two solutions were then mixed in equal volume and the mixture was transferred into a teflon reaction kettle, placed in an autoclave, and heated to 100 °C for 4 h. The as-synthesized MIL-88A rods were signed as r-MIL-88A. In order to synthesize MIL-88A with different morphology, the amount of iron source and the solvent were changed. 4 mmol FeCl\(_3\)·6H\(_2\)O and 4.0 mmol of fumaric acid were dissolved in 10ml DMF separately, then the two solutions were mixed in a teflon reaction kettle. The diamond-shaped MIL-88A (hereafter abbreviated as d-MIL-88A) with a average size of 5 μm were successfully obtained after heating for 4 h at 100°C. For spindle-like MIL-88A, 4.0 mmol fumaric acid was dissolved in 10 ml DMF separately, then the two solutions were mixed in a teflon reaction kettle. The spindle-like MIL-88A (hereafter abbreviated as s-MIL-88A) with a average size of 5 μm were successfully obtained after heating for 4 h at 100°C.

\[
I_{\text{cat}} = \lambda^2 \pi^2 \exp(-\lambda) + \exp(-\lambda) 
\]

where \( I_{\text{cat}} \) and \( I_d \) was the current in the presence and absence of N-acetyl cysteine, respectively, \( \lambda = K_{\text{cat}}Ct \) was the argument of the error function, \( K_{\text{cat}} \) was the catalytic rate constant and \( t \) was the consumed time. In the case where \( \lambda > 1.5, \exp(\lambda^{1/2}) \) was almost equal to unity, the above equation could be reduced to:

\[
I_{\text{cat}} = \pi^2 K_{\text{cat}}Ct^{1/2} 
\]
dissolved in 20 mL DMF and added into 2.4 mmol FeCl₃·6H₂O. The mixture was heated for 12 h at 100 °C in a teflon reaction kettle to form spindle-like MIL-88A (hereafter abbreviated as s-MIL-88A). Finally, the raw product was washed by DMF and deionized water for several times, respectively, and dried at 40 °C.

**Preparation of Hierarchical Fe₃O₄/Carbon Superstructures.** The r-/s-/d-MIL-88A were placed in ceramic boats, transferred into a horizontal quartz tube and calcined in the horizontal tube furnace. The thermal treatment was performed at 400 °C for 30 min under N₂ atmosphere with a heating rate of 5 °C/min from room temperature to 400 °C. Then the calcination was followed by natural cooling to room temperature under N₂ atmosphere (the corresponding products were denoted as Fe₃O₄@C, Fe₃O₄@Cₓ, Fe₂O₃@Cₓ, respectively). To study the process of carbonization, the similar experiments were carried out at different target temperature to obtain FeOₓ@C₂₀₀, FeOₓ@C₃₀₀, FeOₓ@C₄₀₀ and FeOₓ@C₅₀₀.

**Preparation of Hierarchical Fe₃O₄/Carbon Superstructures Modified Electrode.** Glassy carbon electrodes (GCEs, Φ = 2 mm) were carefully prepared by 1.0, 0.3 and 0.05 μm Al₂O₃ powder in order. Then, the polished GCEs were scanned in 0.1 M KCl = 5.0 mM K₃Fe(CN)₆. After the same CVs with same peak current and same potential separation were obtained, the polished GCEs were used for the following experiments. The effective surface area of the GCEs was estimated to be about 0.0763 cm². Simultaneously, 3.0 mg hierarchical Fe₃O₄/Carbon superstructures were dispersed into 1.0 mL ultra-pure water to give 3.0 mg/mL homogeneous dispersions followed by adding 10 μL Nafion. Finally 10.0 μL suspensions were dropped on the polished GCE surface and dried in air.

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**Author Contributions**

L.W. and Y.S. wrote the main manuscript text. Y.Z. and X.L. performed the experiments and prepared Figures 2–5. C.W. and Y.X. and J.H. prepared Figure 6. J.Y. prepared Figure 1. All authors reviewed the manuscript.

**Additional Information**

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