In-situ growth of α -Fe₂O₃ nanorod arrays on 3D carbon foam as an efficient binder-free electrode for highly sensitive and specific determination of nitrite

Yue Ma,^{a,b} Xiangyang Song,^{a,b} Xiao Ge,^{a,b} Haimin Zhang,^a Guozhong Wang,^a Yunxia Zhang^{a,*} and Huijun Zhao^{a,c}

Long-term accumulation and overdose of nitrite ions have been proven to pose a great threat to the ecological environment and public health. It is highly desirable to construct a novel architecture electrode for the accurate quantification of nitrite in a simple and inexpensive manner. Herein, a simple and cost-effective strategy is developed for the construction of three dimensional (3D) α -Fe₂O₃ nanorod arrays (NAs)/carbon foam (CF) architecture, in which CF is initially obtained from direct carbonization of commercially available melamine foam and then α -Fe₂O₃ NAs are grown in-situ on the underlying CF skeleton via simple hydrothermal treatment and secondary pyrolysis. In the unique 3D architecture, α -Fe₂O₃ NAs provide abundant active sites for electrocatalytic reaction; meantime, the CF featured a large amount of interconnected channels to facilitate fast mass diffusion and electron transfers except for good electrical conductivity. Benefiting from these collective effects, the unique 3D architecture is innovatively exploited as a binder-free electrode for the determination of nitrite. As expected, the as-fabricated α -Fe₂O₃ NAs/CF sensor exhibited enhanced electrochemical performance towards the oxidation of nitrite in terms of higher catalytic peak current and reduced oxidation potential as compared with the binder-containing counterparts. Importantly, the as-fabricated sensor demonstrated excellent detection towards nitrite with a fast response time of approximately 3 s, a wide linear range from 0.5 μ M to 1000 μ M, a high sensitivity of 116.8 μ A·mM⁻¹·cm⁻² and a low detection limit of 0.12 μ M, which is dramatically lower than the maximum allowable level of nitrites (~65 μ M) in drinking water set by the World Health Organization (WHO). It is noteworthy that the current electrochemical sensor had a specific recognition capability towards nitrite anions, hardly interfered by the coexisting species in natural waters. Additionally, the proposed sensor can still maintain excellent reproducibility and stability after 30 days of storage in ambient conditions, supported by the neglect decrease in electrocatalytic activity. Furthermore, the α -Fe₂O₃ NAs/CF electrode also shows perspective applications in the determination of nitrite in real samples, as illustrated by satisfactory recoveries in tap water and lake water.

1. Introduction

Nitrite is ubiquitous in the natural environment, food and physiological systems since it is extensively utilized as food preservatives, dyeing agents, chemical fertilizers and corrosion inhibitors. Long-term accumulation and overdose of nitrite ions have been proven to pose a great threat to the ecological environment and public health associated with birth defects, blue baby syndrome, spontaneous abortion, intrauterine growth restriction and potential cancer risk.¹⁻¹⁵ Therefore, the accurate quantification of nitrite is of paramount importance for the supervision of environmental water quality and maintenance of public health because of its high toxicity as well as multiple sources of contamination. To date, numerous analytical strategies have been developed for the determination of trace amount of nitrite, such as ion chromatography,^{1,2} spectrophotometry,^{3,4} chemiluminescence,^{5,6} molecular absorption spectrometry,⁷ fluorescence,^{8,9} Raman spectrometry,¹⁰ electrochemical analysis,¹¹⁻¹⁵ and etc. However, most techniques suffer from more or less major limitations including sophisticated and expensive instruments, time-consuming and tedious sample pretreatment together with professional skill, high cost and limited selectivity, making them incompetent for on-site analysis. By contrast, the electrochemical method has attracted great interest in terms of its outstanding features including quick response, simple operation, high sensitivity, excellent selectivity, cost

effectiveness and ease of miniaturization. Nevertheless, the conventional electrodes usually encounter some obstacles in practical application, e.g. low sensitivity, irreproducibility and surface passivation. Hence, the rational design and fabrication of novel electrode materials with high performance is in urgent demand to improve their electrochemical properties by lowering the oxidation potential and increasing the current response for nitrite sensing.

As reported, an ideal electrode material should have excellent electrocatalytic activity, good electrical conductivity and some extent of mechanical strength and stability.¹⁶⁻²¹ In an effort to achieve these objectives, two effective strategies can be proposed to optimize the electrochemical sensing devices. One is the rational design of the active materials associated with the dimensionality and morphology. As an outstanding representative of electrocatalytic active materials, iron oxide has been recognized as an optimal candidate for the sensing sensors due to low cost, environmentally friendly nature, long-lasting stability, as well as intriguing electrocatalytic property.²²⁻²⁵ Several recent investigations have revealed that micro/nano electrodes possess several advantages over conventional macro electrodes due to more electrocatalytic active sites, pre-concentration of the target ions on the electrode surface, fast mass transport and less electrode fouling problem, thereby resulting in the enhanced sensitivity. Another is the assembly of active materials on 3D conductive substrates. In this regard, CF is extremely attractive for electrochemical sensing application because of chemical

stability, abundant porous structure and open channels, high surface area, remarkable mechanical strength and excellent electrical conductivity, which render it suitable for the ideal supporter of the active materials.²⁶⁻³⁰ The integrated composite electrodes can efficiently suppresses the aggregation of active materials through the special anchoring effect, ensuring full use of the active sites. In addition, the 3D porous frameworks are very beneficial for electron transfer due to the large porosity of CF. Moreover, the synergistic coupling between active nanomaterials and conductive substrates may further improve the sensing performance by decreasing the contact resistance and increasing the electrical conductivity.

Except for the structural design of electrocatalytic materials, the construction means of the electrodes also strongly affects the resulting sensing properties. In traditional composite electrodes, the catalysts are fabricated in advance and then coated onto the surface of conductive substrates with the help of polymer as binder, in which the close packing of catalyst particles may block part of the active sites and thus weaken their electrochemical performance to some extent. Meanwhile, the active materials are probably subjected to the unavoidable exfoliation from the electrodes during the electrochemical reaction due to the poor mechanical interaction between catalysts and conductive substrate, which prevent these modified electrodes from being widely used in practical applications.¹⁷⁻¹⁹ Additionally, it is difficult to obtain a uniform distribution on the surface of the electrode after separate preparation of nanomaterials, hampering the stability and repetition of sensing signals. In view of these limitations, it is highly desirable to explore a facile synthetic strategy to construct a binder-free electrode in order to overcome the inactivation drawbacks caused by the conducting polymer binders.

Based on the above considerations, it is no doubt that the direct growth of one-dimensional (1D) nanostructure arrays on 3D conductive substrates will be favorable for building electrochemical sensors with optimal performance due to the special directional electron transfer. In this work, α -Fe₂O₃ NAs has been directly grown on CF skeleton by simple carbonization of melamine foam and subsequent hydrothermal treatment in the absence of any binder. The structural characteristics of the as-fabricated 3D α -Fe₂O₃NAs/CF architecture are systematically studied via various techniques. The electrochemical properties of the resulting 3D α -Fe₂O₃ NAs/CF electrode are evaluated by anodic stripping voltammetry analysis and electrochemical impedance spectrum. To demonstrate its applicability, the binder-free electrode is utilized for the determination of nitrite based on cyclic voltammetry and amperometric response, in which the sensitivity and selectivity are investigated in detail. Furthermore, reproducibility and stability of the binder-free electrode are also explored in order to gain a better understanding of the feasibility in potential applications for the accurate and reliable determination of nitrite, which is validated by the spike-recovery experiments in various water sources.

2. Experimental

2.1 Chemicals

Melamine foam (MF) was provided by Puyang Green Foam Co. Ltd. Iron(III) chloride hexahydrate (FeCl₃·6H₂O), potassium ferricyanide (K₃[Fe(CN)₆]), potassium ferrocyanide trihydrate (K₄Fe(CN)₆·3H₂O), sodium nitrite (NaNO₂), sodium nitrate (NaNO₃), sodium sulfate (NaSO₄), sodium chloride (NaCl), sodium acetate (NaAc), sodium carbonate (NaCO₃), disodium hydrogen phosphate dodecahydrate (Na₂HPO₄·12H₂O), sodium dihydrogen phosphate dihydrate (NaH₂PO₄·2H₂O), zinc sulfate heptahydrate (ZnSO₄·7H₂O), potassium chloride (KCl), magnesium sulfate heptahydrate (MgSO₄·7H₂O), calcium chloride (CaCl₂), sodium bromate (NaBrO₃), sodium iodate (NaIO₃) and hydrogen peroxide (H₂O₂) were purchased from Sinopharm Chemical Reagent Co. Ltd. Stock solution of NaNO₂ was freshly prepared before experiments. Phosphate buffer solution (PBS, 0.1M, pH 7.0) was prepared by mixing standard stock solutions of Na₂HPO₄ and NaH₂PO₄. Deionized (DI) water with a resistivity of above 18.2 MΩ·cm was obtained using a JL-RO100 Millipore-Q Plus water purifier and used throughout the experiments. All chemicals were of analytical grade and used directly without any further purification during the experiments.

2.2 Preparation of CF

CF was fabricated via a simple pyrolysis process. Briefly, MF was firstly cut into pieces with the size of 0.5 cm × 3 cm × 9 cm. And then the carbonization process was carried out in N₂ atmosphere at the raising temperature rate of 1 °C/min to 900 °C and maintained for 120 min. Finally, the CF with the approximate size of 0.25 cm × 1.5 cm × 4.5 cm was obtained. In order to improve the hydrophilicity of the resulting CF and ensure more oxygen-containing functional groups, the obtained CF was further treated with 3 M nitric acid in a Teflon-lined stainless steel autoclave at 120 °C for 1 h. After cooling down to room temperature, the treated CF were taken out, rinsed with DI water and dried at 60 °C for the following use.

2.3 Preparation of α -Fe₂O₃ NAs/CF composites

α -Fe₂O₃ NAs were directly grown on CF by a facile hydrothermal method. In a typical synthesis, 1.5 mmol of FeCl₃·6H₂O and 1.5 mmol of Na₂SO₄ were dissolved in 35 ml of DI water with constant magnetic stirring for 10 min to obtain a transparent solution. Subsequently, a piece of acid-treated CF (0.25 cm × 2 cm × 3 cm) was immersed into the above solution and further stirred for 60 min. After that, the reaction system was transferred to a 50 mL of Teflon-lined stainless-steel autoclave for hydrothermal treatment at 120 °C for 6 h and then cooled down to room temperature naturally. Afterwards, the resultant monolith was withdrawn from the suspension and washed with DI water for several times to remove the products physically absorbed on CF surface, followed by drying at 60 °C. Finally, the crystalline α -Fe₂O₃ NAs/CF was obtained after annealing in N₂ atmosphere at 450 °C for 2 h, in which the mass loading of α -Fe₂O₃ NAs on CF was found to be about 8 mg/cm³.

For comparison, α -Fe₂O₃ sample was also fabricated via a similar protocol in the absence of CF.

2.4 Characterization

The phase and crystalline structure of the obtained samples was characterized by X-ray diffraction (XRD, X'Pert Pro Super, Philips Co., the Netherlands) with Cu K α radiation (1.5478 Å). The morphology and microstructural observations were carried out on field emission scanning electron microscope (FESEM, SU 8020) at an acceleration voltage of 5 kV and transmission electron microscopy (TEM) on a JEOL-2010 microscope operating at an accelerating voltage of 200 kV. The compositions of resulting products were examined by energy-dispersive X-ray spectroscopy (EDS) attached to SEM. Raman spectra were measured on a Renishaw Micro-Raman Spectroscopy (Renishaw inVia Reflex) using 532 nm laser excitation. X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Thermo Scientific ESCALAB 250 equipped with a focused monochromatic Al K α X-ray source, in which all of the binding energies were calibrated with reference to the C 1s peak (284.8 eV). The compression and release tests were

performed by a mechanical tester CMT-8102 (MTSCHINA, Shenzhen, China) equipped with two flat-surface compression stages and 100 N load cell. For mechanical tests, the CFs were cut into cubic blocks with size of (1 × 1 × 1 cm). The strain ramp rate was controlled to be 5 mm min⁻¹.

2.5 Electrochemical measurements

All electrochemical measurements were performed on a CHI 760E electrochemical workstation (Chen Hua Instrumental Corporation, Shanghai, China) at ambient temperature. A conventional three-electrode system was employed for electrochemical determination, in which the as-synthesized α -Fe₂O₃ NAs/CF was directly used as the binder-free working electrode with the size of 1 cm × 1cm, a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. 0.1 M of PBS (PH=7.0) was used as the supporting electrolyte solution, purged with high purity N₂ for 30 min before each measurement in order to remove the dissolved oxygen. Furthermore, a nitrogen atmosphere was maintained during the whole measurements.

Scheme 1. Schematic illustration of the synthetic route of α -Fe₂O₃ NAs/CF composites

3. Result and discussion

3.1 Morphology and Structure Characterization

The in situ growth of α -Fe₂O₃ NAs on the CF substrate is achieved via a facile two-step process, as illustrated in Scheme 1. First, 3D highly porous CF monolith is synthesized through simple carbonization treatment of the commercially available MF in an inert atmosphere. After pyrolysis at 900 °C for 2 h, the original white sponge becomes black CF, accompanied by the obvious volume shrinkage and mass reduction, i.e. the dimensions from 4.5 × 3 × 3 cm to 2 × 1.5 × 1.5 cm and the mass from 340 mg to 73 mg, which can be attributed to the low carbon yield of the MF precursor. In spite of that, the 3D framework architecture is perfectly retained in the resulting CF sponge. It should be noted that the obtained CF sponge is highly graphitic and hydrophobic. The compression and release tests were carried out to study resilience of the CFs. Fig. S1a

shows the stress–strain curves of the CFs at maximum strains ϵ of 20%, 40%, 60% and 80%. It was revealed that the stress increases slowly with the strain where $\epsilon < 60\%$ because of the dissipation of most of the absorbed energy, and then the stress increases rapidly with the strain at $\epsilon > 60\%$ due to the continuously decreasing pore volume.^{31,32} More importantly, it could recover to its most of original volume with a small residual (plastic) deformation even under compressive strain of 80%, indicating 3D carbon foam is elastic and demonstrating a mechanically robust behavior. Furthermore, the optical images of mechanical properties of 3D carbon foam were also displayed in Fig. S1b. It can be found that the carbon foam can be cut into different shapes and sizes and the 3D carbon foam exhibits excellent flexibility and super mechanical strength. These characteristics are crucial for the application of 3D electrode in field of energy environment. In order to ensure the efficient loading of α -Fe₂O₃, the bare CF sponge is

subjected to further strong acid treatment to provide abundant oxygen-containing groups, which is indispensable for the following wetting of the iron precursors on its surface. Subsequently, the activated CF is impregnated into an aqueous FeCl_3 solution containing Na_2SO_4 , followed by the hydrothermal treatment at 120°C for 6 h and the secondary pyrolysis at 450°C for 2 h. As a result, the composites are converted into red-brown color, suggesting the successful formation of $\alpha\text{-Fe}_2\text{O}_3$ on the surface of CF. Moreover, the as-obtained $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF composites still retained the foam-like shape similar to the original MF or CF. It is noteworthy that the proposed approach in this study is simple, cost-effective and highly reproducible coupled with easy scale-up.

Fig. 1 (a) SEM image of bare carbon foam (CF); (b-d) SEM images of $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF at different magnifications; (e-f) EDS mapping; (g) and (h) TEM and HRTEM images of $\alpha\text{-Fe}_2\text{O}_3$ NAs, respectively.

The surface morphology and structure evolution of the as-prepared samples can be monitored by SEM observations. As shown in Fig. S2 (see †ESI), the commercial MF exhibits 3D network structure with typical pore diameters between 100 and 200 μm and the surface of the framework is quite smooth. After annealing, the original 3D framework structure of the MF sponge is well preserved together with clean and smooth surface, although the obvious shrinkage occurs as compared with that of the pristine MF, which is in good agreement with the microscopic observation. The SEM image (Fig. 1a) further reveals that the as-prepared CF inherits the interconnected network architecture with numerous voids in the range of several to a few tens of micrometers, lower than the pristine MF materials as a result of the volume contraction. Once $\alpha\text{-Fe}_2\text{O}_3$

Fe_2O_3 are immobilized on the surface of sponge substrate, the surface texture of carbon sponge is quite distinct from that of MF or bare CF sponge and becomes much roughened, suggesting the anchoring of $\alpha\text{-Fe}_2\text{O}_3$ NAs on the surface of the

Fig. 2 (a) XRD pattern $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF; (b) Raman spectra of the as-prepared CF and $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF.

CF skeleton. As revealed in Fig. 1b, the whole CF substrate is covered densely and uniformly by the $\alpha\text{-Fe}_2\text{O}_3$ NRs. Another interesting finding is that almost all $\alpha\text{-Fe}_2\text{O}_3$ NAs grow along the direction vertical to the surface of the CF skeleton (Fig. 1c), resulting in the unique 3D hierarchical arrays (the magnified SEM image in Fig. 1d). Furthermore, these nanorods are well separated with a mean diameter of ≈ 70 nm. The element compositions of the resulting 3D sponge are clearly evidenced by EDS spectrum (Fig. S3, see †ESI), in which carbon and nitrogen are derived from carbonization of melamine foam, whereas iron and oxygen are assigned to $\alpha\text{-Fe}_2\text{O}_3$. Moreover, EDS mapping analyses (Fig. 1e and f) reveal the uniform spatial distribution of Fe, O, N and C elements throughout the examined backbone region of 3D frameworks, providing clear support for the formation of $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF composite. To better illustrate the morphology of the as-obtained product, $\alpha\text{-Fe}_2\text{O}_3$ nanorods are detached from CF substrate by drastic ultrasonication and then characterized by TEM (Fig. 1g). Obviously, these nanorods are 60 nm in diameter, in good agreement with the foregoing SEM observation (Fig. 1d). Upon careful high-resolution TEM (HRTEM) analysis of a single nanorod (Fig. 1h), the spacing between adjacent fringes is measured to about 0.27 nm, which can be ascribed to the characteristic spacing between the (1 0 4) planes of $\alpha\text{-Fe}_2\text{O}_3$. Based on above structural characterization, $\alpha\text{-Fe}_2\text{O}_3$ NAs have been successfully synthesized and assembled on the surfaces of the CF. It is noteworthy that each nanorod had well direct contact with the surface of the conductive CF substrate at the

bottom, ensuring the effective participation in the following oxidation reaction. At the same time, the strong adhesion of α -Fe₂O₃ catalyst on the CF current collector minimizes the contact resistance for electron transport, which is crucial for the preparation of a binder-free electrode and improvement of electrochemical performance. The unique porous structures and abundant active sites from dense α -Fe₂O₃ NAs make the resulting α -Fe₂O₃ NAs/CF composites promising electrocatalytic materials.

The crystalline phase of the as-prepared products is further investigated by XRD characterization. As shown in Fig. S4 (see †ESI), for the bare CF, the two peaks located at 26° and 44° can be indexed as the (0 0 2) and (1 0 1) reflections of hexagonal graphite carbon (JCPDS No.75-1621), respectively. After the in-situ growth of α -Fe₂O₃ on the CF substrate, several additional peaks appear at 24.1°, 33.1°, 35.6°, 40.8°, 49.4°, 54.0°, 62.4° and 63.9°, corresponding to the diffraction of (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (2 1 4) and (3 0 0) planes of α -Fe₂O₃ phase, respectively (Fig. 2a), revealing the coexistence of carbon and α -Fe₂O₃ in the obtained samples. Moreover, these peaks had very strong intensity because of high crystalline of α -Fe₂O₃, which is consistent with the TEM observation. In addition, no other peaks have been detected, indicating the high purity of the resulting products. Raman spectroscopy is further employed to characterize the lattice vibrational behavior of pristine CF and α -Fe₂O₃ NAs/CF composites. As illustrated in Fig. 2b, two characteristic peaks at about 1353 and 1553 cm⁻¹ are ascribed to D and G bands of CF, respectively.^{26, 29} As for the α -Fe₂O₃ NAs/CF composites, three new peaks appearing at 217, 280 and 397 cm⁻¹, which can be

assigned to the A_{1g} (217 cm⁻¹) and E_g (280 and 397 cm⁻¹) vibration modes of Fe-O in the hematite phase Fe₂O₃,³³ indicating the successful decoration of α -Fe₂O₃ on the CF substrate. It is well known that the D-band is attributed to the amorphous carbon or deformation vibrations of a hexagonal ring, whereas G-band is associated with the stacking of the graphite hexagon network plane. Therefore, the intensity ratio (I_D/I_G) of D band and G band can directly give useful information about the structural changes of carbon-based materials. Herein, the I_D/I_G value of α -Fe₂O₃ NAs/CF composite is very close to that of bare CF (1.083 vs. 1.032). The result indicates α -Fe₂O₃ NAs/CF composite retains the electronic and structural integrity of the pristine CF, which is favorable for electron transfer in electrochemical reaction.¹¹ Furthermore, the D band of the α -Fe₂O₃ NAs/CF shows a blue-shift by 30 cm⁻¹ in comparison with that of the pristine CF, indicating the strong interaction between α -Fe₂O₃ and CF as well as the formation of α -Fe₂O₃ NAs/CF nanocomposites, consistent with the observations in the literature.³⁴

In order to further elucidate the surface composition of the resulting α -Fe₂O₃ NAs/CF composites and chemical state of various elements, XPS measurements are carried out as shown in Fig. 3. In the survey spectrum of XPS (Fig. 3a), the intense peaks at 297.8, 411.8, 546.8 and 710.7 eV correspond to C 1s, N 1s, O 1s and Fe 2p, respectively, indicating the existence of C, N, O and Fe elements in the as-obtained product, which is exactly consistent with the EDS results. As revealed in Fig. 3b, the high resolution spectrum of C 1s can be divided into three peaks located at 284.7, 286.2, and 288.5 eV, which are

Fig. 3 (a) XPS wide-scan spectrum of the as-prepared α -Fe₂O₃ NAs/CF sample; (b-d) high resolution spectra of C1s, O1s and Fe 2p, respectively.

ascribed to C-C, C-N, and C=O, respectively.²¹ It is worth noting that the presence of C=O bonding at 286.29 eV may be

ascribed to the residual oxygenated functional groups presented in CF subjected to the harsh oxidation, which may

increase the hydrophilicity of the sample and accordingly gain easy access of aqueous electrolyte to the catalytic active sites.³⁵ Additionally, the XPS peak associated with C-N moiety suggests the successful incorporation of nitrogen in the resulting carbon matrix, which will induce enhanced catalytic activity in electron-transfer reactions. The high resolution spectrum of O 1s in Fig. 3c can be deconvoluted into three peaks positioned at 529.9, 531.2 and 533.3 eV, which could be assigned to the metal oxide bond (Fe–O, the lattice oxygen), surface carboxyl (C=O) and adsorbed water (–OH), respectively. The high resolution XPS spectrum of Fe 2p (Fig. 3d) exhibits two prominent peaks of binding energy at 710.7 and 724.5 eV, corresponding to the Fe 2p_{3/2} and Fe 2p_{1/2} spin–orbit coupling of pure α -Fe₂O₃, respectively. Furthermore, two satellite peaks are clearly distinguishable at 718.7 and 732.7 eV,^{36–38} indicating that Fe element is predominantly present in the form of iron(III) in the resultant composite. The aforementioned results provided the powerful support for the formation of α -Fe₂O₃ NAs on the surfaces of the CF substrate.

3.2 Electrochemical characterization of various electrodes

The electrochemical features of various electrodes are investigated using cyclic voltammetry (CV) under identical conditions, in which 5 mM [Fe(CN)₆]^{3-/4-} solution containing 0.1 M KCl is selected as an electrolyte solution. In order to compare with the commercial glassy carbon electrode (GCE), in this section, the as-prepared α -Fe₂O₃ NAs/CF and CF are modified on glassy carbon electrode (GCE, d = 3mm) with the help of Nafion as binder. In addition, α -Fe₂O₃ modified electrode is also fabricated by coating α -Fe₂O₃ sample on the surface of GCE according to the similar method (denoted as α -Fe₂O₃/GCE). As shown in Fig. 4a, a pair of quasi-reversible redox behavior of [Fe(CN)₆]^{3-/4-} is observed at four electrodes. Compared with the bare GCE, the anodic and cathodic peak currents of CF/GCE increased slightly, which indicates that the rate of electron transfer at the electrode surface is accelerated because of the good conductivity of CF. After modification with α -Fe₂O₃ (i.e. α -Fe₂O₃/GCE), however, the peak currents show a large decrease due to poor conductivity of α -Fe₂O₃, which can hinder the electron transfer between [Fe(CN)₆]^{3-/4-} and the electrode surface. In the case of α -Fe₂O₃ NAs/CF, the peaks currents show an obvious enhancement in comparison with α -Fe₂O₃/GCE, revealing that the in-situ growth of α -Fe₂O₃

Fig. 4 (a) Cyclic voltammograms and (b) EIS spectra of different electrodes in the solution containing 5.0 mM [Fe(CN)₆]^{3-/4-} (1:1 molar ratio) and 0.1 M KCl.

NAs on the surface of CF substrate provides more efficient charge transfer at the electrode surface.

Electrochemical impedance spectroscopy (EIS) has been extensively exploited as a useful technique to study interface properties of electrode materials. As we know, the Nyquist impedance plot includes a semicircle in the high frequency region corresponding to electron-transfer-limited process and a linear part at the low frequency representing diffusion-limited process. Therefore, the charge transfer resistance (R_{ct}) can be reflected by the semicircle diameter in the Nyquist impedance plots, and a large semicircle means a high charge transfer resistance of the electrode, implying a low charge transfer rate. Fig. 4b displays the typical Nyquist plots of various modified electrodes in 5 mM [Fe(CN)₆]^{3-/4-} probe solution containing 0.1 M KCl. Obviously, the CF/GCE electrode holds a small semicircle diameter at high frequency, presenting a relative small R_{ct} . As for α -Fe₂O₃ modified GCE electrode (α -Fe₂O₃/GCE), the semicircle diameter increased largely, suggesting high charge transfer resistance originated from non-conductive iron oxide. However, when α -Fe₂O₃ NAs are directly grown on the surface of CF substrate, the R_{ct} value decreased obviously compared to α -Fe₂O₃/GCE, demonstrating the corresponding enhanced charge transfer efficiency.

3.3 Electrochemical determination of nitrite at the free-standing α -Fe₂O₃ NAs/CF electrode

The electrochemistry response of various electrodes has been investigated by CV in neutral solution (PBS buffer solution, pH 7.0) to verify their electrocatalytic activity towards the oxidation of nitrite. It's noteworthy that the as-synthesized α -Fe₂O₃ NAs/CF and bare CF are directly applied as the binder-free working electrodes, whereas α -Fe₂O₃/GCE is also studied for comparison. Fig. 5a shows CVs of the studied electrodes

toward 1.00 mM nitrite in N_2 -saturated 0.1 M PBS buffer solution (pH 7.0) at a scan rate of 50 mV s^{-1} . Obviously, there are almost no obvious current response at the bare CF electrode (red curve) upon the addition of 1.00 mM NaNO_2 , indicating that no redox reaction occurred at CF electrode in the neutral solution. However, after modifying the CF with $\alpha\text{-Fe}_2\text{O}_3$ NAs, a distinct anodic peak appeared at about 0.85 V in presence of 1.00 mM nitrite (blue curve), corresponding to the oxidation of nitrite. Moreover, no associated reduction peak is found in the negative potential sweep, indicating the irreversibility of the electro-chemical oxidation of nitrite. It is reasonable to speculate that $\alpha\text{-Fe}_2\text{O}_3$ NAs is responsible for the electrocatalytic oxidation of nitrite. In addition, the peak current density at $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF is about 1.4 times bigger than that at $\alpha\text{-Fe}_2\text{O}_3$ /GC electrode (the inset in Fig. 5a) under similar conditions. More-over, the oxidation potential of nitrite at the $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF electrode shifts toward more negative (ca. 250 mV) compared to that at the $\alpha\text{-Fe}_2\text{O}_3$ /GC electrode. The higher oxidation peak current and lower onset potential of nitrite oxidation demonstrate that the $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF has higher electrocatalytic activities toward the oxidation of nitrite than $\alpha\text{-Fe}_2\text{O}_3$ /GCE, indicating $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF can be directly employed as binder-free electrode for the efficient determination of nitrite ion.

To explore the application of the $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF in electrochemical sensors for nitrite oxidation, CV experiments are performed by applying a constant potential of 0.85 V in N_2 -saturated 0.1 M PBS buffer solution (pH 7.0) containing various

concentrations of nitrite at a scan rate of 50 mV s^{-1} . As shown in Fig. 5b, in the absence of nitrite, no any obvious redox peak is visible on the surface of $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF electrode, indicating the electrode stability in the investigated potential scan range. However, upon the addition of nitrite, a remarkable anodic oxidation peak appears at the potential of +0.85 V, indicating that a typical electrocatalytic oxidation process toward nitrite occurs. Significantly, the oxidation peak current (I_{pa}) values at $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF electrode increase proportionally with the increase of nitrite concentration from 50 to 1000 μM (the inset in Fig. 5b), which can be used for a quantitative assaying of nitrite and demonstrates the potential capability of the as-fabricated $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF composites to be utilized as an electrode material for the nitrite sensor.

The potential scan rate study is an important factor that might affect the kinetics of the electrode process. To assess the reaction kinetics, CVs of the free-standing $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF electrode are measured in a 0.1 M PBS buffer solution (pH 7.0) containing 1000 μM nitrite at different scan rates from 10 to 100 mV s^{-1} , as shown in Fig. 5c. It is noted that the anodic oxidation peak potential is almost unchanged (about 0.85 V), while the I_{pa} values of nitrite increases linearly with an increase in scan rate and is proportional to the square root of scan rate (v) (Fig. 5d). The corresponding dependent relationship between scan rate and current response of nitrite oxidation may be determined by a linear regression equation as: $I_{pa} (\mu\text{A}) = 15.02v^{1/2} + 5.30$ with a correlation coefficient $R^2 = 0.997$, implying that the overall nitrite oxidation reaction is governed

Fig. 5 (a) Cyclic voltammograms of the $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF, bare CF and $\alpha\text{-Fe}_2\text{O}_3$ /GCE in the presence of 1000 μM NaNO_2 in N_2 -saturated 0.1 M PBS at a scan rate of 50 mV/s; (b) Cyclic voltammograms of the $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF electrode in N_2 -saturated 0.1 M PBS containing 50 ~ 1000 μM NaNO_2 at a scan rate of 50 mV/s; Inset: the linear relationship between the oxidation peak currents and concentration of nitrite; (c) Cyclic voltammograms of $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF in 0.1 M PBS containing 1000 μM nitrite at different scan rates; (d) the linear relationship between the peak currents and the square root of the scan rate.

by the diffusion-controlled electrocatalytic process. Such dependence is consistent with fast charge transfer through the vertical $\alpha\text{-Fe}_2\text{O}_3$ NAs to the CF skeleton. Therefore, the mechanism for the electrocatalytic oxidation of nitrite on the

$\alpha\text{-Fe}_2\text{O}_3$ NAs/CF can be summarized as follows: The interaction between nitrite and $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF to form a complex of $[\alpha\text{-Fe}_2\text{O}_3 \text{ NAs/CF} (\text{NO}_2^-)]$ (eq (1)). The formation of NO_2^- by losing one electron (eq (2)) is followed by the disproportionation of

the nitrogen dioxide to give nitrite and nitrate (eq (3) and (4)). Nitrate is the final product.^{11,42}

In order to achieve the electrochemical detection of the proposed $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF binder-free electrode towards nitrite, the typical chronoamperometric response of $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF electrode is recorded with successive addition of nitrite into PBS buffer solution under stirring at an applied

Fig. 6 (a) Amperometric response of $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF electrode at an operating potential of 0.85 V (vs. SCE) with successive addition of NaNO_2 into 0.1 M PBS buffer solution (pH 7.0) under continuous stirring; (b) Corresponding liner plot of the current response and the concentration of NaNO_2 .

Table 1 Comparison of $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF with other reported modified electrodes towards nitrite sensing

Electrode materials	Techniques	Linear range (μM)	LOD (μM)	References
CoPcF-MWCNTs	Amperometry	0.096 – 340	0.062	11
Hb/Au/GACS	Amperometry	0.05 – 1000	0.01	14
Fe_2O_3 /RGO	DPV	0.05 – 780	0.015	25
Co_3O_4 /RGO	Amperometry	1 – 380	0.14	39
Fe_3O_4 /RGO	DPV	10 – 2882	0.1	40
MOF-GNRs-50	Amperometry	100 – 2500	0.75	41
Pd/RGO	DPV	1 – 1000	0.23	42
Au/ZnO/MWNT	Amperometry	0.78 – 400	0.4	43
Fe_2O_3 @ MoS_2	Amperometry	2 – 6730	1.0	44
$\alpha\text{-Fe}_2\text{O}_3$ NAs/CF	Amperometry	0.5 – 1000	0.12	This work

potential of 0.85 V and the corresponding results are shown in Fig. 6a. It is found that upon injection of nitrite into electrolyte solution, the $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF electrode responds immediately to the oxidation of nitrite and the maximum steady state is achieved within only 3 s after every addition. Such a fast and sensitive response may be attributed to the synergistic effects of $\alpha\text{-Fe}_2\text{O}_3$ NAs and CF skeleton, providing an enhanced conductive pathway to transfer electrons with underlying electrode, which is desired for the real time analysis of samples. Importantly, the increase of the oxidation currents is proportional to the concentration of nitrite in the range of 0.5–1000 μM , as evidenced by the calibration plot in Fig. 6b. The corresponding linear regression equation can be expressed as $I_{\text{pa}} (\mu\text{A}) = 0.1168 C (\mu\text{M}) + 5.524$ with the coefficient of 0.998, where C is the concentration of nitrite. The sensitivity of the as-constructed sensor toward nitrite is found to be ca. 116.83 $\text{mA}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$ from the slope of the linear calibration plot. Additionally, the limit of detection (LOD) is estimated to be 0.12 μM using the

formula: $\text{LOD} = S_B/b$, in which S_B is the standard deviation of the blank signal and b is the sensitivity, which is quite comparable with or superior to other nitrite sensors listed in Table 1 and much lower than the maximum permissible limit of nitrite ($\sim 65 \mu\text{M}$) in drinking water recommended by the WHO and thus sufficient for practical applications. All these findings indicate that $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF electrode can be utilized for the fabrication of high efficient electrochemical sensor toward the determination of nitrite with quick response, wide linear range, and high sensitivity.

The above experimental results uncover that the as-prepared $\alpha\text{-Fe}_2\text{O}_3$ NAs/CF electrode exhibits fast response, high sensitivity, and low detection limit towards nitrite. And the excellent sensing performance can be ascribed to the unique structural features as follows. Firstly, the 3D CF substrate not only guarantees high conductivity but also provides plenty of interconnected channels to facilitate fast mass diffusion and electron transportation. Secondly, the closely packed $\alpha\text{-Fe}_2\text{O}_3$ NAs offer abundant surface active sites

to facilitate the oxidation reaction of nitrite and the separation space between the NRs can provide convenient accessibilities and accelerate the mass diffusion to the active sites.^{45, 46} Thirdly, 1D NAs allow for fast vectorial ions and electrons transport, thus enhancing catalytic efficiency.⁴⁷ Last but not least, in situ growth of α -Fe₂O₃ NAs on the CF substrate allows direct contact between the active α -Fe₂O₃ NAs and conductive CF substrate, which not only avoids the blocking of active sites caused by the conducting polymer binders, but also helps to decrease the charge transfer resistance and thus facilitates electrons flowing from α -Fe₂O₃ to CF.^{19, 21, 48} The synergetic effects based on these features ultimately contribute to the

Fig. 7 Amperometric response of α -Fe₂O₃ NAs/CF electrode upon successive addition of 0.1 mM nitrite and 5.0 mM common species.

Table 2 Determination of nitrites in Dongpu Reservoir and tap water

Real samples	Nitrite spiked (μ M)	Nitrite found (μ M)	Recovery (%)	RSD (% , n=5)
Tap water	50	49.2	98.4	1.25
	100	102.2	102.2	1.74
	200	195.6	97.8	2.56
Dongpu Reservoir water	50	50.8	101.6	1.65
	100	102.9	102.9	2.22
	200	208.6	104.8	1.65

enhanced electrocatalytic activity toward the oxidation of nitrite. More importantly, compared with the existing other methods for the determination of nitrite, the developed α -Fe₂O₃ NAs/CF sensor exhibit several advantages: (i) the low cost and extensively available MF and FeCl₃ are utilized the raw materials, reducing the expense of nitrite sensor; (ii) the fabricated α -Fe₂O₃ NAs/CF monolith can be directly employed as binder-free electrode to determine nitrite level in waters, thus simplifying the assay procedure; (iii) this method do not involve any organic binder that is required in traditional electrode fabrication, which is not only environmentally friendly but also effectively overcomes the inactivation drawbacks.

3.4 Selectivity, stability and reproducibility of the as-fabricated α -Fe₂O₃ NAs/CF electrode

Except for the sufficient sensitivity, an ideal sensor should have the feature of excellent specificity towards the target nitrite ions in an effort to meet the detection requirement in real aqueous environment. The interference measurements are performed by monitoring current response at the proposed α -Fe₂O₃ NAs/CF electrode after the alternate addition of nitrite and interfering species into 0.1 M PBS solution (pH 7.0), in which various ions such as NO₃⁻, CH₃COO⁻, CO₃²⁻, SO₄²⁻, Zn²⁺, Cl⁻, K⁺, Mg²⁺, Ca²⁺, BrO₃⁻, IO₃⁻ and H₂O₂ are selected for interference test with 50 folds concentration

higher than that of nitrite. As displayed in Fig. 7, the current increases immediately upon the introducing of nitrite; whereas the addition of interferents does not produce any significant current alteration, despite very high concentrations. Interestingly, further injection of 0.1 mM nitrite results in the same magnitude of current response as the previous addition. However, as the time goes on, the concentration of nitrite was decreased at an applied potential of 0.85 V and the current gradually decreased. The similar phenomenon was found in the previous reports.^{13,15} These results substantially reveal that the presence of these coexisting species do not affect the quantitative determination of nitrite. In other words, the current electrochemical sensor has a specific recognition capability towards nitrite ions. The excellent specificity combined with high sensitivity makes it possible to utilize the designed α -Fe₂O₃ NAs/CF as a promising candidate for the effective determination of nitrite in real complex waters.

In addition, the reproducibility of the fabricated electrodes is evaluated by recording the CV at six α -Fe₂O₃ NAs/CF electrodes prepared independently under the same conditions (Fig. S5, see †ESI). It is found that the relative standard deviation (RSD) between different electrodes was about 3.05% during the parallel measurements, suggesting the excellent reproducibility of the proposed electrode, which may be correlated with the uniform distribution of α -Fe₂O₃ NAs on CF

substrate. Strikingly, despite no any polymer binder, no detachment of active materials from the binder-free α -Fe₂O₃ NAs/CF electrode can be observed, suggesting its structural stability. At the same time, the storage stability of the designed sensor is also investigated by comparing the electrochemical activity of the same electrode before and after 30 days of storage at ambient temperature. As displayed in Fig. S6 (see †ESI), the electrode is still able to retain ca. 93.5% of its initial oxidation current for nitrite. The long-term stability guaranteed the accuracy of continuous measurements during the electro-chemical process, which can be ascribed to the structural stability as well as strong interaction between α -Fe₂O₃ NAs and CF skeleton. The results mentioned above indicate that the present proposed sensor has satisfactory stability and reproducibility towards the determination of nitrite, which is favorable and reliable for practical applications.

3.5 Real sample analysis

In an attempt to evaluate the feasibility of the developed method for practical applications, the proposed α -Fe₂O₃ NAs/CF electrode is applied to determine nitrite levels in real environmental samples. Herein, two representative water sources with complex background matrices are collected from Dongpu Reservoir (Hefei City, Anhui, China) and tap water, respectively, followed by filtration through Millipore filters (0.22 μ m) to remove the micron sized particles. The initial detection shows no existence of nitrite in the selected two samples. Upon addition of nitrite at three known concentration levels into Dongpu Reservoir and tap water samples, the nitrite concentration in two real samples is quantitatively analyzed by amperometry, in which each measurement is conducted for five times and the average value with relative standard deviation (RSD) is also summarized in Table 2. It can be seen that the values obtained by our electrochemical method are in good agreement with the spiked concentrations in the real water samples and the recoveries of nitrite are found in the range of 97.8 to 104.8%, revealing that the fabricated α -Fe₂O₃ NAs/CF based nitrite sensor is capable of resisting effectively the interference from other coexisting competing species in complicated matrix and thus has great application potential in the practical sample analysis. And the obtained RSD values are less than 3% during five measurements, indicating good reproducibility and accuracy. All the aforementioned results demonstrate the capability of the proposed sensing system for determination of nitrite in the real complex environmental samples with high reliability and accuracy as well as satisfactory recoveries.

4. Conclusions

In summary, a facile strategy has been demonstrated to realize in-situ grown of α -Fe₂O₃ NAs on the surface of 3D CF skeleton. Thanks to abundant active sites from α -Fe₂O₃ NAs, efficient mass/ions transport pathways as well as 3D conductive network inherited from CF substrate, the as-prepared α -Fe₂O₃ NAs/CF composites can be exploited as a binder-free electrode for the efficient determination of nitrite. As a result, the α -

Fe₂O₃ NAs/CF electrode possesses superior electrocatalytic activity towards the oxidation of nitrite than those of the binder-containing α -Fe₂O₃/GCE and bare CF electrode in correlation with higher catalytic peak current and reduced oxidation potential. In particular, the proposed α -Fe₂O₃ NAs/CF nitrite sensor exhibits fast response time, wide linear range, superior sensitivity, low limit detection limit, excellent anti-interference ability and reproducibility as well as long-term stability. Finally, the developed α -Fe₂O₃ NAs/CF sensor has been applied to the determination of nitrite in various real water samples with satisfactory recoveries and low RSD values, highlighting its feasibility for practical applications. Hence, it is reasonably envisaged that the proposed approach paves the way for sensitive and reliable monitoring of nitrite in real environmental samples.

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