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Atomic layer deposition-assisted fabrication of 3D Co-doped carbon framework for sensitive enzyme-free lactic acid sensor

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ABSTRACT

As an important biomaterial, lactic acid (LA) widely exists in human blood and sweat. The development of enzyme-free LA sensors with high-sensitivity and low-cost remains a challenge. We present here a structure of Co-doped porous carbon film derived from zeolitic imidazolate framework-67 (ZIF-67) on 3D carbon frameworks through a pyrolysis process. The conformal coating of ZIF-67 film is realized by a combination of gas-phase and liquid phase growths with the assistance of an induction step from atomic layer deposited-ZnO nanomembrane. In the resultant hierarchical structure with large surface area, Co-doped porous carbon film is closely stacked and firmly attached to carbon skeleton to form Co-doped N-containing carbon framework (Co-NCF). Therein, the Co-doped porous carbon provides catalytic Co nanoparticle, while the carbon skeleton bridges the individual carbon nanoparticle to form a conductive pathway. When adopted as an enzyme-free LA sensor, the Co-NCF composite exhibits excellent electrochemical sensing property in terms of an ultrahigh sensitivity of 1108 μ A mM⁻¹cm⁻² at a liner range from 0.1 to 1 mM with a limit of detection of 13.7 μ M. This work, therefore, presents an efficient strategy to prepare porous carbon structures toward new electrode materials in promising biomedicine systems.

1. Introduction

Lactic acid (LA), as one of the most important biomolecules, widely exists in the human body. LA can be used as a sensitive and reliable indicator of tissue hypoxia, and it is of great significance to the prognosis of patients [1,2]. A traditional blood LA test requires a puncture, and patients are commonly required to go to a hospital for the test. Although the concentration of LA in other body fluid is lower than that in blood, the proven accuracy and undoubted convenience still make highly sensitive LA sensors meaningful in noninvasive tests [3–5]. So far, detection of LA has been realized by several approaches, such as methods of chemically oxidizing lactate, spectrophotometric detection of acetaldehyde, and chromatographic methods [4,6,7]. On the other hand, other techniques use the enzyme kits or biosensors involving enzymes in the detection of LA and by doing so these techniques have replaced the chemical methods in many clinical and analytical laboratories [7,8]. However, the nature of instability and the high cost of LA enzymes limits the wide applications of these biosensors [9,10]. Enzyme-free electrochemical sensor, on the contrary, has become an ideal alternative technique in the clinic and medical-related area [11-13].

The core of the enzyme-free electrochemical sensor is the electrode materials [14,15]. Generally, materials or structures with large surface area, abundant porosity, good conductivity, and high catalytic activity are viewed as promising electrode materials for sensors [14]. Metalorganic frameworks (MOFs) are a series of novel nanoporous materials composed of metal ions together with organic bridging ligands [16], and have drawn tremendous attention in a large variety of fields [17,18]. So far, due to their favorable advantages like outstanding nanoscale porosity, extremely large specific surface areas, and excellent thermal stability, MOFs show great potential in biosensing [19–21]. Especially, zeolitic imidazolate frameworks (ZIFs) are a new class of MOFs with extended three-dimensional structures constructed from tetrahedral metal ions (e.g., Zn and Co) bridged by imidazolate [22]. Cobalt-based zeolitic imidazolate framework-67 (ZIF-67) is an important subclass of ZIF, which is assembled of Co ions and imidazole frameworks [23].

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Received 28 November 2020; Received in revised form 4 February 2021; Accepted 4 March 2021 Available online 10 March 2021 1385-8947/© 2021 Elsevier B.V. All rights reserved. Plenty of researches have confirmed the high catalytic property of the Co component in ZIF-67 [24-26]. For instance, Xu et al. [27] proposed a novel strategy to grow high catalytic ZIF-Co, Zn thin film on ZnO nanowire array for high-performance gas sensor. Due to its unique structure, the fabricated gas sensor shows enhanced selectivity of acetone to humidity, accelerated response and recovery behavior, and decreased working temperature. In addition, ZIF-67 also displays the outstanding stability of inorganic zeolites and the general advantages of MOFs including large surface area, high porosity, and high active sites [28]. ZIF-67 also can be converted into Co-doped porous carbons during the pyrolysis process, resulting in great electrochemical performance [29]. Generally, ZIF-67 is considered to be an ideal start material towards enzyme-free biosensors. However, narrow pore size distributions and poor conductivity hinder the enhancement of electrochemical performance [18]. Several approaches have been developed to integrate MOF nanoparticles on conductive networks to form hierarchical structures [30,31]. Unstable structure of resultant MOF-based composites and poor homogeneity, as well as weak attaching to networks, limit their practical applications [32,33]. Recently, great work has been done by growing ZIFs on foam [34,35]. For instance, Lin et al. [35] adopted a one-step method to prepare a MOF-derived magnetic carbon sponge, and used it for the separation of floating oil from water due to its 3D hierarchical structure with nanoscale porosity. However, there are still challenges to be handled, such as weak attaching and non-uniformity growth. Therefore, we developed an efficient strategy to integrate ZIF film on the flexible conductive substrate via the assistance of atomic layer deposition (ALD) [23,36,37]. ALD can deposit a uniform and conformal oxide nanomembrane with highly controllable thickness on various substrates, including metal, Si wafer, carbon materials, and polymer. Due to the gaseous deposition, the nanomembrane can uniformly grow on complex 3D structures [38]. Through the combination of gas phase and liquid phase reaction, oxide nanomembrane can be converted into the target ZIFs structure, uniformly and firmly attached to the substrates. Three major advantages of this ALD-based approach are noted. Firstly, firm attaching with the substrates endows the composites with excellent structural stability. Secondly, uniform and conformal growth avoids the aggregation of particles. Thirdly, the advantages of ALD make this method highly controllable and can be applied to different kinds of MOFs and substrates. The uniformity and firm attaching as well as hierarchical structure endow the composite with the promoted electrochemical performance [23]. Applications of this strategy in the biosensing field still need to be explored.

Herein, we demonstrate a structure with ultrahigh sensitivity in enzyme-free sensing. The structure was fabricated by growing ZIF-67 layer on ALD pre-treated melamine foam, which was transformed into a Co-doped N-containing carbon framework (Co-NCF) composite after pyrolysis. In the resultant composites, carbon film consisting of Codoped carbon nanoparticles (from ZIF-67) grew on the surface of 3D fiber framework of the foam, forming a hierarchical structure. The carbon framework bridged carbon nanoparticles and provides conductive path for fast electron transportation. Close adhesion between the carbon layer and fiber also ensured improved structural stability. Furthermore, the stack of Co-doped carbon nanoparticles formed a nanoporous structure, which was beneficial to the exposure of active sites and electrolyte penetration. In alkaline electrolyte, the composite exhibited a high sensitivity of 1108 μ A mM⁻¹cm⁻² at a linear range of 0.1 to 1 mM with a limit of detection (LOD) of 13.7 μ M. We believe that this work provides a new idea to realize high-sensitive enzyme-free LA detection, and therefore has a great development prospect in the future.

2. Experimental section

Materials: The melamine foam used in the experiments was obtained from BASF basotect (Shanghai, China). Cobalt nitrate hexahydrate (Co $(NO_3)_2$ ·6H₂O), 2-methylimidazole (2-MI), and nafion (5 wt%) were purchased from Aladdin Ltd. (Shanghai, China). Lactic acid (AR, \geq 99.5%) was obtained from Sinopharm Chemicals. Methanol (AR, \geq 99.5%) was obtained from Sinopharm Chemicals and ethanol (AR, \geq 99.7%) was purchased from Titan Ltd. All the reagents were used as received without further purification. The DI water used throughout all experiments was purified through a Millipore system.

ZnO nanomembrane deposited by ALD: ZnO nanomembrane on foam was prepared through ALD-based technology reported in our previous study [23]. The deposition of ZnO nanomembrane on the exposed surface of foam was performed at 150 °C in a homemade reactor. Diethylzinc (DEZ) and DI water were used as precursors. A typical ALD cycle included DEZ pulse (50 ms), waiting time (2 s), N₂ purge (30 s), DI water pulse (30 ms), waiting time (2 s).

Preparation of ZIF-67 coated foam: $Co(NO_3)_2 \cdot 6H_2O$ (1.45 g) was dissolved in the mixture of methanol (40 mL) and ethanol (40 mL) to form solution A. 2-MI (1.65 g) was dissolved in the mixture of methanol (40 mL) and ethanol (40 mL) to form solution B. Several ZnO coated foam blocks were then placed into a beaker containing solution A. The beaker was sealed at 90 °C for 24 h. After cooling to room temperature, solution B was added and the mixture was aged at room temperature for another 24 h for the growth of ZIF-67 film. After that, the blocks were taken out and washed with ethanol for 3 times. The sample (named as ZIF-67 coated foam) was subsequently dried in vacuum at 60 °C for 12 h.

Preparation of the Co-NCF composites: The ZIF-67 coated foam blocks were heated to 800 °C with a heating rate of 2 °C min⁻¹ and then held at 800 °C for 2 h. The obtained Co-NCF samples were washed with ethanol and dried at 60 °C for 12 h in vacuum.

Structural characterizations: The morphologies of all the products were measured by scanning electron microscopy (SEM, Phenom Prox). The energy dispersive spectrometer (EDS, Oxford X-Max 80 T) was utilized to analyze the composition of the sample. X-ray diffraction (XRD) patterns were measured by an X'Pert Pro X-ray diffractometer (PANalytical Co., Netherlands) equipped with Cu K α radiation (λ = 0.1542 nm). A Quadrasorb adsorption instrument (Quantachrome Instruments) was used to perform the nitrogen sorption/desorption measurements. The specific surface area was calculated using single-point Brunauer-Emmett-Teller (BET) method. The pore size distributions were calculated from nitrogen sorption data using nonlocal density functional theory (NLDFT) methods for slit, cylinder, and sphere pores provided by Quantachrome data reduction software ASiQwin Version 4.01. The Raman spectra were collected from a Raman spectroscope (HR800, Horiba) with a 532 nm laser as the excitation source. X-ray photoelectron spectroscopy (XPS) analyses were made with a VG ESCALAB 220I-XL device. The curve fitting of all XPS spectra was accomplished using XPS Peak 4.1 software. Elemental analysis for Co and Zn was also carried out by using inductively coupled plasma (ICP) mass spectrometry.

Electrochemical characterizations: The electrochemical lactic acid sensing tests were evaluated on a CHI 660E (Chenhua Instrument, China) with three-electrode configuration. In our experiment, an Ag/AgCl (in saturated KCl solution) was used as the reference electrode and a graphite rod was used as the counter electrode. For cyclic voltammetry (CV) tests, the working electrode was prepared by pasting sample on glassy carbon electrode (diameter: 5 mm) by using nafion (5 wt%). For current–time (i-t) tests, the working electrode was prepared by fix the foam sample on graphite paper by using nafion (5 wt%).

3. Results and discussion

The preparation process of the Co-NCF composite is illustrated in Fig. 1 and Figure S1. As shown in Fig. 1a and e, 3D interconnective structure provides stable sites for the growth of active material. A fiber-like branch with a smooth surface can be clearly seen in the corresponding SEM image (Fig. 1i). During ALD process, gas phase precursors penetrate into the deep of foam, leading to the conformal and uniform deposition of a \sim 50 nm-thick ZnO nanomembrane on the framework (Fig. 1b,f and j) [23,38]. Here, the thickness of the ZnO nanomembrane can be measured after high-temperature removal of the melamine foam



Fig. 1. The preparation process of the composite. (a), (e), and (i) Schematic and corresponding SEM images of foam. (b), (f) and (j) Schematic and corresponding SEM images of the sample after ALD pre-treatment. (c), (g), and (k) Schematic and SEM images of sample after the growth of ZIF-67. (d), (h), and (l) Schematic and SEM images of Co-NCF composite.

in O₂ (Figure S2) [39]. As shown in Fig. 1f and j, the obtained ZnO nanomembrane is dense and smooth, without detectable defect, and this uniform coating of ZnO nanomembrane is beneficial to the nucleation of MOF film in the next solution-based growth step. As shown in Fig. 1c, g, and k, dense ZIF-67 film can grow on the surface of the fiber framework uniformly. The SEM images in Figure S3 also demonstrate that the ZIF-67 film consists of regular polyhedron particles that closely stack on the surface of the fiber. Almost all the exposed surfaces of foam are covered with ZIF-67 film (Fig. 1g and k), indicating the effectiveness of this ALD-ZnO nanomembrane induced growth process. According to our previous work [23,36], the mechanism of this growth progress can be described as follows. In the wet chemistry step, ZnO nanomembrane was used as both the induction layer and the reaction layer. Some ZnO attached firmly to the substrate, and other ZnO reacted with cobaltous nitrate hexahydrate to form a (Zn, Co) hydroxy double salt (Zn, Co-HDS, see Figure S4) [23]. After this, when the organic linker (2-MI) was added, the Zn, Co-HDS began to collapse and NO³⁻ and OH⁻ were removed to release Co^{2+} , which coordinated in situ with 2-MI continuously. Zn element makes for the formation of HDS, and promote the anion exchange to further catalyze the formation of target ZIF-67. This process thus led to high uniformity and firm attaching of MOF layer. Due to the presence of = N- in melamine foam, the intimate attachment can be expected compared with MOF film on carbon substrates [23].

Abundant nucleation sites and strong bonds between ZIF-67 and melamine foam are beneficial to the firm adhesion. During the next pyrolysis process, organic linkers transform into carbon, and Co²⁺ is reduced to Co nanoparticle embedded in porous carbon [30]. In addition, the organic compositions of melamine foam are also converted into nanoporous carbon structure, and a highly conductive pathway is constructed [23]. Thus, Co-NCF composite consisting of Co-doped carbon layer (from ZIF-67 layer) and carbon fiber framework (from melamine foam) are produced (Fig. 1d, h, and l). Due to the strong adhesion between ZIF-67 layer and substrate, the initial polyhedron shape of ZIF-67 nanoparticles becomes vague after the pyrolysis process (Fig. 1h and l). The SEM images of Co-NCF with low magnification (Fig. 1h and l) further illustrate the uniformity of the conformal coating. We also noticed that the resultant Co-NCF exhibits a light weight and the sample

can stand on a leaf (Figure S1). In order to further investigate the elemental distribution of Co-NCF, EDS mapping has been measured. As shown in the Figure S5, the results clearly demonstrate that Co and C with high concentrations are evenly distributed over the surface of the composite, implying the uniform growth of ZIF-67 and corresponding complete pyrolysis. The negligible Zn content indicates that the consumption of almost all the ZnO in the conversion process. Considering the semiconducting nature of ZnO [40], the tiny residual ZnO has no observable influence on the electrochemical performance [23]. In order to probe the composition of the sample for more details, we also carried out ICP mass spectrometry analysis, and the results show a high Co concentration in the composite (Figure S6).

We also carried out additional control experiments to elucidate the factors that could influence the fabrication of Co-NCF. For comparison, SEM images of pure melamine foam before and after pyrolysis are shown in Figure S7. There is no observed morphological change and 3D skeleton remains well after pyrolysis, and the stability makes the structure an ideal supporting substrate. To further investigate the effect of pyrolysis temperature of preparing Co-NCF composites, we pyrolyzed ZIF-67 coated foam at 600 °C for comparison. As shown in Figure S8, SEM images of 600 °C-pyrolyzed composite and 800 °C-pyrolyzed composite display no apparent difference, and no crack can be observed in both samples. The phenomenon can be explained by the fact that the current approach produces firm attaching between the foam and the ZIF-67 layer, and the simultaneous carbonization of ZIF-67 and melamine foam exhibits a synchronous shrinkage.

In order to investigate the microstructural properties of the samples, XRD patterns of ZIF-67 coated foam and Co-NCF composite are recorded and shown in Fig. 2a. A broad diffraction band at $\sim 25^{\circ}$ indicates an amorphous nature of melamine foam. After the growth of ZIF-67 film, the XRD pattern shows typical sharp peaks associated with ZIF-67 (plot: ZIF-67 coated foam), indicating the formation of ZIF-67 layer [29], and no other peak can be observed in XRD pattern of ZIF-67 coated foam. With the subsequent pyrolysis process, ZIF-67 nanoparticle was transformed into an amorphous carbon matrix containing Co nanoparticles, as reflected in XRD pattern (plot: Co-NCF), and three diffraction peaks associated with (111), (200), and (220) lattice planes of Co are



Fig. 2. (a) XRD patterns of ZIF-67 coated foam and Co-NCF composite. (b) Nitrogen adsorption/desorption isotherms of the samples. (c) The pore size distributions of ZIF-67 coated foam and Co-NCF. The inset is the corresponding summary of micropore volume, mesopore volume, and total pore volume. (d) High resolution Co 2p XPS spectrum of Co-NCF.

noticeable. In this high-temperature process, the organic melamine foam was also converted into a carbon fiber framework and no distinct diffraction peak can be noticed.

Detailed analyses of the porous structure of the samples were investigated with the help of nitrogen adsorption/desorption isotherms, and the results are shown in Fig. 2b and 2c. Both type I and type IV isotherms can be observed in ZIF-67 coated foam and Co-NCF composite, indicating a co-existence of micropores and mesopores in the two samples [18]. The micropores are inherited from the pores in MOF structure, and the stack of the MOF nanoparticles thus produced mesopores in MOF film. The adsorption/desorption isotherms also demonstrate that ZIF-67 coated foam exhibits a large surface area of $\sim 194~\text{m}^2$ g^{-1} with a large total pore volume of 0.081 mL g^{-1} . After the carbonization process, the obtained composite exhibits a reduced specific surface area of $\sim 121~m^2~g^{-1}$ and a total pore volume of 0.1 mL $g^{-1}.$ The pore size distributions are shown in Fig. 2c. ZIF-67 coated foam exhibits an apparent microporous structure with pore size ranging from ~ 1.1 to \sim 1.5 nm. Meanwhile, a weak mesopore peak at \sim 3.7 nm also can be seen and is attributed to the stack of the MOF nanoparticles. After the pyrolysis process, Co-NCF exhibits a broader micropore peak at \sim 1.3–1.8 nm, and apparent mesopore peaks at \sim 2.7 and 3.8 nm appear. The mesopore peaks should originate from the additional volume caused by the shrinkage of Co nanoparticles and the stack of carbon nanoparticles. The summaries of the pore volume of the samples derived from the NLDFT are shown in the inset of Fig. 2c. The volume ratio of micropores and mesopores in the Co-NCF composite is close to 1:2, and the value varies in the case of ZIF-67 coated foam. The nanoporous structure of the Co-NCF composite should be helpful to the active site exposure and electrolyte penetration, and later we will demonstrate that this feature remarkably enhances the sensing performance. Raman spectra were also measured to further investigate the carbon structures and are illustrated in Figure S9. The ZIF-67 coated foam exhibit bands from the organic linker, while Co-NCF exhibit two typical bands at 1361 and 1594 cm⁻¹, which are ascribed to D and G bands, respectively. The D band represents the defects and disorders of carbon structures, while the G band describes the sp^2 -type carbon in the composite [18]. The intensity ratio of D/G is 1.02, proving the existence of the defects, which is considered to be able to enhance the electrochemical activities [41–43]. In order to investigate the chemical state of Co element, which is closely related to the electrochemical properties of the sample, XPS characterization was carried out and the results are shown in Fig. 2d and S10. The XPS survey scan confirms the presence of C, N, O, and Co (Figure S10), and the high-resolution Co 2p spectrum (Fig. 2d) shows characteristic peaks of metallic Co at 779.8 (Co 2p3/2) and 795.5 eV (Co 2p1/2) [30]. In addition, the existence of Co-N $_{x}$ peak at 783.6 eV and CoC $_{v}N_{z}$ peak at 781.7 eV suggests the chemical coupling among Co, C, and N species, which is believed to be beneficial to improve the electrochemical activity [30].

The electrochemical property of Co-NCF composite was firstly evaluated by cyclic voltammetry (CV) in 0.1 M NaOH aqueous solution at a scan rate of 20 mV s⁻¹ and a potential range of -0.1–0.8 V. As shown in Fig. 3a and Figure S11, two oxidation peaks at \sim 0.27 and \sim 0.43 V and two reduction peaks at \sim 0.1 and \sim 0.35 V are respectively associated with the oxidation and reduction process of Co-NCF composite. Attention should be paid that the current responses of reduction peak and oxidation peak are remarkably enhanced in the electrolyte with 1 mM LA, suggesting that the Co-NCF composite is able to catalyze the oxidation of LA to generate additional currents. Previous literature disclosed that the additional currents should originate from the following revisable reactions [45] :

$$\text{Co} + 2\text{OH}^- \rightarrow \text{Co}(\text{OH})_2 + \text{e}^-$$
 (1)

$$Co(OH)_2 + 2OH^- \rightarrow CoOOH + 2H_2O + e^-$$
(2)



Fig. 3. (a) CV curves of Co-NCF composite in electrolyte with and without the presence of 1.0 mM LA at a scan rate of 20 mV s⁻¹. (b) CV curves of Co-NCF composite at different scan rates (from 10 to 80 mV s⁻¹) in 0.1 M NaOH with 0.5 mM LA. The inset is the linear fitting results of oxidation current (for peak at ~ 0.3 V) and reduction current (for peak at ~ 0.1 V) as a function of the square root of scan rate. CH₃CH(OH)COOH + OH⁻ \rightarrow CH₃CH(OH)COO⁻+ H₂O (3)

$$\mathrm{Co}^{3+} + \mathrm{CH}_{3}\mathrm{CH}(\mathrm{OH})\mathrm{COO}^{-} \rightarrow (\mathrm{CH}_{3}\mathrm{CO})\mathrm{COO}^{-} + \mathrm{Co}^{2+}$$
(4)

In this work, the kinetics of Co-NCF are studied at different scan rates. As shown in Fig. 3b, a successive increase in oxidation and reduction peak currents with the increase of scan rate indicates a well resolved controlled response of the LA. The inset in Fig. 3b shows that the currents of both the anodic oxidation and cathodic reduction peaks increase linearly with the square root of the scan rates from 10 to 80 mV s⁻¹ in 0.1 M NaOH with solution 0.5 mM LA. The good linear relationship indicates a diffusion-controlled electrochemical process in Co-NCF electrode [46].

The sensing behavior of Co-NCF is further studied by CV characterization in 0.1 M NaOH electrolytes containing LA with various concentrations ranging from 0.1 to 1.0 mM. As shown in Fig. 4a, with the increase of LA concentration, the reduction peak at ~ 0.1 V is significantly enhanced. This phenomenon can be attributed to the fact that oxidation of LA leads to a reduction of more Co^{3+} , which provides an additional reduction current. In order to evaluate the electrochemical sensing performance quantitatively, the corresponding calibration plot related to the concentration derived from CV curves is shown in Fig. 4b. The good linear character with a large slope indicates a sensitive response to target LA. The Co-NCF composite exhibits a high sensitivity of 1108 μ A mM⁻¹ cm⁻² with a linear range of 0.1–1.0 mM (linear regression equation: Y = 0.2175 * X + 0.6232; correlation coefficient (R²): 0.99). Here the sensitivity equals to SL/A, where SL is the slope of linear regression equation and A is the surface area of the electrode. In addition, the LOD is also calculated by using the equation $LOD = 3\delta/S$, where δ is the standard deviation of 10 parallel detections of 0.1 mM LA and S is the sensitivity. For current sample, the LOD of 13.7 µM is obtained. We should stress that the sensitivity here is obviously higher compared with other enzyme-free electrochemical sensors in previous reports, and a detailed list of related researches is summarized in Table 1. We further investigate the sensing performance of the Co-NCF composite by current-time (i-t) tests. Fig. 4c exhibits the responses of current with successive addition of 5 mM LA at various applied potentials. Obviously, at a voltage of 0.5 V, Co-NCF composite shows an apparent and stable current response. Therefore, the enzyme-free LA sensing performance of Co-NCF composite is evaluated by i-t test at 0.5 V. Moreover, for comparison, Figure S12 demonstrates that pyrolyzed melamine foam shows negligible current response because it consists of only carbon. This further confirms the sensing function of the composites should originate from Co-related structures. In addition, for pyrolyzed ZIF-67/melamine foam composite without the ZnO induction layer, unstable and low current response to lactic acid can be observed due to the poor structure stability like weak attaching and non-uniform growth (Figure S13), proving the key role of ALD-ZnO nanomembrane.

Fig. 4d illustrates i-t curve of Co-NCF with the successive addition of LA with various concentrations into the electrolyte. With the increasing LA concentration, apparent and rapid current responses can be observed, indicating the realization of real-time sensing of target LA. The corresponding calibration plot related to the concentration is illustrated in Figure S14. The good linear character with a large slope implies the high sensitivity of Co-NCF composite in high concentration within 2-30 mM of target LA. It should be noted that even at such high concentration of LA, our electrode still exhibits good linear property. The selectivity and stability are also important factors for practical LA sensors. To further evaluate the practicality of the Co-NCF sensor, the I-t curve of Co-NCF with consecutive introduction of 5 mM LA and 5 mM NaCl, 5 mM citric acid (CA), 5 mM tromethamine (THAM), 2 mM LA, 5 mM KCl and 5 mM LA was shown in the Fig. 4e. Apparent current response with the addition of target LA is noticeable, while only negligible response can be seen when adding the interferents, indicating the good selectivity and great anti-interference property of the Co-NCF to target molecule. In addition, the stability of Co-NCF sensor is evaluated by testing 5 mM LA after certain periods. When not in use, the sensor was stored in refrigerator at 4 °C. The results are shown in Fig. 4f. The current density of the sensor is quite stable within 7 days, indicating a good stability. The outstanding sensing property of Co-NCF composite can be attributed to the following reasons. Firstly, the unique structure enhances the electron transfer process, which promotes real-time sensing property. Secondly, the ALD-assisted approach endows the samples with uniform and conformal growth of the functional layer and the firm attachment of the functional layer to the 3D fiber frameworks, ensuring excellent structural stability. The close adhesion between Co-doped carbon particles and substrates also prohibits the aggregation during the pyrolysis process, which enhances the catalytic activity and avoids the peeling off of the active materials. Thirdly, the nanoporous structure of the Co-NCF composite helps the penetration of the electrolyte, improving the efficiency of catalytic oxidation. The inherited micropores and mesopores also enhance the active site exposure, while the macropores of the 3D framework with dimensions of hundreds of microns provide large vacancy volume, which maintains the separation of the conductive fiber, thereby further improving the efficiency of the current response. The synergy effects of carbon substrates and the functional carbon layer generate rapid LA oxidation ability. The low-cost preparation, stable and controllable structure, as well as high electrochemical sensing performance of the present Co-NCF composite, can be widely used in practical biomedical areas.

4. Conclusion

The Co-NCF composite has been prepared by growing uniform and



Fig. 4. (a) CV curves of Co-NCF composite within a potential range of -0.1-0.8 V in 0.1 M NaOH containing LA with various concentrations from 0.1 to 1.0 mM at a scan rate of 20 mV s⁻¹. (b) Calibration plot related to the concentration derived from CV curves. (c) The amperometric response of Co-NCF composite with successive additions of 5 mM LA at different potentials. (d) i-t curve of Co-NCF with the successive addition of LA with various concentration in 0.1 M NaOH at a potential of 0.5 V. (e) Current responses of 5 mM LA, 5 mM NaCl, 5 mM CA, 5 mM THAM, 2 mM LA, 5 mM KCl, and 2 mM LA at 0.5 V. (f) Aging test of the sensors toward 5 mM of LA for 7 days. Inset of Fig. 4f, I-t curves of Co-NCF in 0.1 M NaOH with 5 mM LA at 0.5 V.

Table 1	
Comparison of enzyme-f	ee LA sensors and their performances.

Sample ID	Sensitivity μA mM ⁻¹ cm ⁻²	Linear range (mM)	LOD (µM)	Ref
Co ₃ O ₄ Ni(OH) ₂ NiO250 polymer/	/ 35.76 62.35 /	Up to 1 0.01–32.76 0.01–27.27 0.001–100	6 590 27 0.73	[44] [46] [47] [48]
3-APBA ZnO nanotetrapods PEC biosensor Co-NCF	/ 28 1.66 1108	3–1000 0.0036–0.6 0–2.5 0.1–1.0	1500 1.2 0.23 13.7	[49] [50] [51] This work

conformal ZIF-67 on 3D polymer foam with the assistance of an induction step from ALD-ZnO nanomembrane. With the subsequent carbonization process, ZIF-67 was converted into Co-doped nanoporous carbon, and polymer foam became carbon fiber framework that loads the active materials. The resultant Co-NCF shows a unique structure, where a homogeneous Co-doped carbon layer attached firmly to conductive 3D carbon frameworks to form a functional composite. The interconnected conductive pathway with hierarchical structure and high catalytic Co-doped porous carbon film achieve remarkable LA sensing performance, i.e., high sensitivity of 1068 μ A mM⁻¹ cm⁻² in a linear range of 0.1–1.0 mM and a LOD of 14.3 μ M. Therefore, this study provides a strategy for fabricating hierarchical carbon structure applicable in the advanced biomedicine sensing field.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.129285.

References

- [1] W. Liu, M. Chen, L. Duo, J. Wang, S. Guo, H. Sun, B. Menghe, H. Zhang, Characterization of potentially probiotic lactic acid bacteria and bifidobacteria isolated from human colostrum, J. Dairy Sci. 103 (5) (2020) 4013–4025.
- [2] V. Scaravilli, L. Di Girolamo, E. Scotti, M. Busana, O. Biancolilli, P. Leonardi, A. Carlin, C. Lonati, M. Panigada, A. Pesenti, A. Zanella, Effects of sodium citrate, citric acid and lactic acid on human blood coagulation, Perfusion-Uk 33 (7) (2018) 577–583.
- [3] S. Amin, A. Tahira, A. Solangi, R. Mazzaro, Z.H. Ibupoto, A. Vomiero, A sensitive enzyme-free lactic acid sensor based on NiO nanoparticles for practical applications, Anal. Methods 11 (28) (2019) 3578–3583.
- [4] W. Gao, S. Emaminejad, H. Nyein, S. Challa, K. Chen, A. Peck, H.M. Fahad, H. Ota, H. Shiraki, D. Kiriya, D.H. Lien, G.A. Brooks, R.W. Davis, A. Javey, Fully integrated wearable sensor arrays for multiplexed in situ perspiration analysis, Nature 529 (2016) 509.
- [5] F.P. Jadan, Selective determination of lactic acid in dry-fermented sausages using a sensor based on immobilized lactate oxidase, Food Biotechnol. 33 (2019) 272–282.
- [6] L.N. Borshchevskaya, T.L. Gordeeva, A.N. Kalinina, S.P. Sineokii, Spectrophotometric determination of lactic acid, J. Anal. Chem. 71 (8) (2016) 755–758.
- [7] P. Vaňkátová, A. Kubíčková, M. Cigl, K. Kalíková, Ultra-performance chromatographic methods for enantioseparation of liquid crystals based on lactic acid, J. Supercrit. Fluids 146 (2019) 217–225.
- [8] K. Dagar, C.S. Pundir, An improved amperometric L-lactate biosensor based on covalent immobilization of microbial lactate oxidase onto carboxylated multiwalled carbon nanotubes/copper nanoparticles/polyaniline modified pencil graphite electrode, Enzyme Microb. Technol. 96 (2017) 177–186.
- [9] F. Alam, S. RoyChoudhury, A.H. Jalal, Y. Umasankar, S. Forouzanfar, N. Akter, S. Bhansali, N. Pala, Lactate biosensing: The emerging point-of-care and personal health monitoring, Biosens. Bioelectron. 117 (2018) 818–829.
- [10] C.S. Pundir, V. Narwal, B. Batra, Determination of lactic acid with special emphasis on biosensing methods: A review, Biosens. Bioelectron. 86 (2016) 777–790.
- [11] L.L. Jiang, Y.L. Yang, Y.H. Lin, Z.Y. Chen, C. Xing, C.H. Lu, H.H. Yang, S.S. Zhang, An electrochemical sensor based on enzyme-free recycling amplification for sensitive and specific detection of miRNAs from cancer cells, Analyst 145 (2020) 3353–3358.
- [12] B.W. Liu, Z.L. Li, Electrochemical treating of a smooth Cu-Ni-Zn surface into layered micro-chips of rice grain-like Cu/Ni(OH)₂ nanocomposites as a highly sensitive enzyme-free glucose sensor, J. Electroanal. Chem. 855 (2019), 113493.
- [13] H.H. Zhang, X. Cai, H.L. Zhao, W.Q. Sun, Z.X. Wang, M.B. Lan, Enzyme-free electrochemical sensor based on ZIF-67 for the detection of superoxide anion radical released from SK-BR-3 cells, J. Electroanal. Chem. 855 (2019), 113653.
- [14] F. Allahnouri, K. Farhadi, H. Eskandari, M.M. Abarghoui, R. Molaei, Cobalt nanoparticles anchored to porous silicon as a novel modifier for the construction of enzyme-free hydrogen peroxide screen-printed sensor, J. Chin. Chem. Soc. 65 (9) (2018) 1082–1089.
- [15] M. Braik, L.G. Zamfir, L. Rotariu, C. Curutiu, M.C. Chifiriuc, A.M. Ben, C. Bala, An enzyme-free hydrogen peroxide sensor for evaluation of probiotic potential of Enterococcus faecium, Sens. Actuators, B 273 (2018) 298–304.
- [16] Y.X. Tan, F. WangJ., Zhang Design and synthesis of multifunctional metal-organic zeolites, Chem. Soc. Rev. 47 (2018) 2130–2144.
- [17] W.J. Dang, Y.M. Sun, H. Jiao, L. Xu, M. Lin, AuNPs-NH₂/Cu-MOF modified glassy carbon electrode as enzyme-free electrochemical sensor detecting H₂O₂, J. Electroanal. Chem. 856 (2020), 113592.
- [18] Z. Zhao, S.L. Liu, J.X. Zhu, J.S. Xu, L. Li, Z.Q. Huang, C. Zhang, T.X. Liu, Hierarchical nanostructures of nitrogen-doped porous carbon polyhedrons confined in carbon nanosheets for high-performance supercapacitors, ACS Appl. Mater. Interfaces 10 (2018) 19871–19880.
- [19] L.J. Gao, C.X. Jiao, H.M. Chai, Y.X. Ren, G.Q. Zhang, H. Yu, L. Tang, A highly sensitive multifunctional Eu-MOF sensor with pentacarboxylate for fluorescence

detecting acetone, Cu^{2+} and $Cr_2O_7^2$, and electrochemical detection of TNP, J. Solid State Chem. 284 (2020), 121199.

- [20] M. Malekzadeh, A. Mohadesi, M.A. Karimi, M. Ranjbar, Development of a new electrochemical sensor based on Zr-MOF/MIP for sensitive diclofenac determination, Anal. Bioanal. Chem. 12 (2020) 402–414.
- [21] S. Okur, Z.J. Zhang, M. Sarheed, P. Nick, U. Lemmer, L. Heinke, Towards a MOF e-Nose: A SURMOF sensor array for detection and discrimination of plant oil scents and their mixtures, Sens. Actuators, B 306 (2020), 127502.
- [22] A. Phan, C.J. Doonan, F.J. Uribe-Romo, C.B. Knobler, M. O'Keeffe, O.M. Yaghi, Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks, Acc. Chem. Res. 43 (2010) 58–67.
- [23] Z. Zhao, Z.W. Zhang, Y.T. Zhao, J.R. Liu, C. Liu, Z.J. Wang, G.F. Zheng, G.S. Huang, Y.F. Mei, Atomic layer deposition inducing integration of Co, N co-doped carbon sphere on 3D foam with hierarchically porous structures for flexible hydrogen producing device, Adv. Funct. Mater. 29 (2019) 1906365.
- [24] W. Peng, X.X. Yang, L.C. Mao, J.H. Jin, S.L. Yang, J.J. Zhang, G. Li, ZIF-67-derived Co nanoparticles anchored in N doped hollow carbon nanofibers as bifunctional oxygen electrocatalysts, Chem. Eng. J. 407 (2021), 127157.
- [25] Y.R. Bai, J.P. Dong, Y.Q. Hou, Y.P. Guo, Y.J. Liu, Y.L. Li, X.J. Han, Z.G. Huang, Co₃O₄@PC derived from ZIF-67 as an efficient catalyst for the selective catalytic reduction of NO_x with NH₃ at low temperature, Chem. Eng. J. 361 (2019) 703–712.
- [26] Y.B. Li, Z.L. Jin, T.S. Zhao, Performance of ZIF-67-Derived fold polyhedrons for enhanced photocatalytic hydrogen evolution, Chem. Eng. J. 382 (2020), 123051.
- [27] M.S. Yao, W.X. Tang, G.E. Wang, B. Nath, G. Xu, MOF thin film-coated metal oxide nanowire array: significantly improved chemiresistor sensor performance, Adv. Mater. 28 (2016) 5229–5234.
- [28] Y.H. Dong, J.B. Zheng, Tremella-like ZIF-67/rGO as electrode material for hydrogen peroxide and dopamine sensing applications, Sensors and Actuators B-Chemical 311 (2020), 127918.
- [29] Z.W. Zhang, L.J. Deng, Z. Zhao, Y.T. Zhao, J.Y. Yang, J. Jiang, G.S. Huang, Y. F. Mei, Nickel nanograins anchored on a carbon framework for an efficient hydrogen evolution electrocatalyst and a flexible electrode, J. Mater. Chem. A 8 (2020) 3499–3508.
- [30] Z.L. Chen, Y. Ha, H.X. Jia, X.X. Yan, M. Chen, M. Liu, R.B. Wu, Oriented transformation of Co-LDH into 2D/3D ZIF-67 to achieve Co-N-C hybrids for efficient overall water splitting, Adv. Energy Mater. 9 (2019) 1803918.
- [31] Z.L. Chen, R.B. Wu, Y. Liu, Y. Ha, Y.H. Guo, D.L. Sun, M. Liu, F. Fang, Ultrafine Co nanoparticles encapsulated in carbon-nanotubes-grafted graphene sheets as advanced electrocatalysts for the hydrogen evolution reaction, Adv. Mater. 30 (2018) 1802011.
- [32] M.R. Armstrong, K.Y.Y. Arredondo, C.Y. Liu, J.E. Stevens, A. Mayhob, B. Shan, S. Senthilnathan, C. Balzer, B. Mu, UiO-66 MOF and poly(vinyl cinnamate) nanofiber composite membranes synthesized by a facile three-stage process, Ind. Eng. Chem. Res. 54 (2015) 12386–12392.
- [33] W.M. Zhang, X.Y. Yao, S.N. Zhou, X.W. Li, L. Li, Z. Yu, L. Gu, ZIF-8/ZIF-67-derived Co-N-x-embedded 1D porous carbon nanofibers with graphitic carbon-encased Co nanoparticles as an efficient bifunctional electrocatalyst, Small 14 (2018) 1800423.
- [34] N. Huang, H. Drake, J.L. Li, J.D. Pang, Y. Wang, S. Yuan, Q. Wang, P.Y. Cai, J. S. Qin, H.C. Zhou, Flexible and hierarchical metal-organic framework composites for high-performance catalysis, Angew. Chem. Int. Ed. 57 (2018) 8916–8920.
- [35] K.Y.A. Lin, H.A. Chang, B.J. Chen, Multi-functional MOF-derived magnetic carbon sponge, J. Mater. Chem. A 4 (2016) 13611–13625.
- [36] Z. Zhao, Y. Kong, X.Y. Lin, C. Liu, J.R. Liu, Y.Y. He, L.L. Yang, G.S. Huang, Y.F. Mei, Oxide nanomembrane induced assembly of functional smart fiber composite with nanoporosity for ultra-sensitive flexible glucose sensor, J. Mater. Chem. A 8 (2020) 26119–26129.
- [37] Z. Zhao, Y. Kong, C. Liu, J.R. Liu, Z.J. Wang, G.F. Zheng, G.S. Huang, Y.F. Mei, Atomic layer deposition-induced integration of N-doped carbon particles on carbon foam for flexible supercapacitor, J. Materiomics 6 (2020) 209–215.
- [38] Zhe Zhao, Ye Kong, Zhiwei Zhang, Gaoshan Huang, Yongfeng Mei, Atomic layer-deposited nanostructures and their applications in energy storage and sensing, J. Mater. Res. 35 (7) (2020) 701–719.
- [39] Y.T. Zhao, G.S. Huang, Y.L. Li, R. Edy, P.B. Gao, H. TangZ. H. Bao Y. F. Mei, Threedimensional carbon/ZnO nanomembrane foam as an anode for lithium-ion batteries with long-life and high areal capacity, J. Mater. Chem. A 6 (2018) 7227–7235.
- [40] X.L. Wu, S.J. Xiong, Z. Liu, J. Chen, J.C. Shen, T.H. Li, P.H. Wu, P.K. Chu, Green light stimulates terahertz emission from mesocrystal microspheres, Nat. Nanotechnol. 6 (2011) 102–105.
- [41] Y.F. Jiang, L.J. Yang, T. Sun, J. Zhao, Z.Y. Lyu, O. Zhuo, X.Z. Wang, Q. Wu, J. Ma, Z. Hu, Significant contribution of intrinsic carbon defects to oxygen reduction activity, ACS Catal. 5 (2015) 6707–6712.
- [42] Y.Q. Wang, L. Tao, Z.H. Xiao, R. Chen, Z.Q. Jiang, S.Y. Wang, 3D carbon electrocatalysts in situ constructed by defect-rich nanosheets and polyhedrons from NaCl-sealed zeolitic imidazolate frameworks, Adv. Funct. Mater. 28 (2018) 1705356.
- [43] C. Xie, D.F. Yan, W. Chen, Y.Q. Zou, R. Chen, S.Q. Zang, Y.Y. Wang, X.D. Yao, S. Y. Wang, Insight into the design of defect electrocatalysts: From electronic structure to adsorption energy, Mater. Today 31 (2019) 47–68.
- [44] A.S. Chang, N.N. Memon, S. Amin, F. Chang, U. Aftab, M.I. Abro, A.D. Chandio, A. A. Shah, M.H. Ibupoto, M.A. Ansari, Facile non-enzymatic lactic acid sensor based on cobalt oxide nanostructures, Electroanalysis 31 (2010) 1296–1303.
- [45] Y.X. Zhang, J.Y. Xu, J.F. Xia, F.F. Zhang, Z.H. Wang, MOF-derived porous Ni₂P/ graphene composites with enhanced electrochemical properties for sensitive nonenzymatic glucose sensing, ACS Appl. Mater. Interf. 10 (2018) 39151–39160.

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- [46] Sungjin Kim, Kijun Kim, Hyun-Jong Kim, Ho-Nyun Lee, Tae Joo Park, Young Min Park, Non-enzymatic electrochemical lactate sensing by NiO and Ni(OH)₂ electrodes: A mechanistic investigation, Electrochim. Acta 276 (2018) 240–246.
- [47] S. Kim, W.S. Yang, H.J. Kim, H.N. Lee, T.J. Park, S.J. Seo, Y.M. Park, Highly sensitive non-enzymatic lactate biosensor driven by porous nanostructured nickel oxide, Ceram. Int. 45 (2019) 23370–23376.
- [48] T. Alizadeh, S. Nayeri, S. Mirzaee, A high performance potentiometric sensor for lactic acid determination based on molecularly imprinted polymer/MWCNTs/PVC nanocomposite film covered carbon rod electrode, Talanta 192 (2019) 103–111.
- [49] N.V. Zaryanov, V.N. Nikitina, E.V. Karpova, E.E. Karyakina, A.A. Karyakin, Nonenzymatic sensor for lactate detection in human sweat, Anal. Chem. 89 (2017) 11198–11202.
- [50] Y. Lei, N. Luo, X. Yan, Y. Zhao, G. Zhang, Y. Zhang, A highly sensitive electrochemical biosensor based on zinc oxide nanotetrapods for L-lactic acid detection, Nanoscale 4 (2012) 3438–3443.
- [51] B. Cakiroglu, Y.C. Demirci, E. Gokgoz, M. Ozacar, A highly sensitive electrochemical biosensor based on zinc oxide nanotetrapods for L-lactic acid detection, Sens. Actuators, B 282 (2019) 282–289.