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DFT-Elucidated α -ZrP/Phosphorus-Nitrogen Co-Doped Hollow Carbon Spheres

Composite for Highly Sensitive Electrochemical Detection of Moxifloxacin

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Abstract

The widespread use of moxifloxacin (MOX) has raised concerns over its environmental residues, highlighting the need for reliable trace detection methods. Herein, we report an electrochemical sensor based on an α -ZrP/phosphorus-nitrogen co-doped hollow carbon spheres (α -ZrP/PNHC) composite, where PNHC serves as a conductive scaffold to disperse α -ZrP nanosheets and provide abundant transport pathways. DFT computations indicate that phosphorus atoms substitute into the carbon sites at the shoulder position next to pyridinic-N, thereby injecting electrons into the carbon lattice and gently lowering the Lewis basicity of those pyridinic-N centers. For the P-doped pyridinic-N site, the calculated adsorption energy amounts to -0.745 eV, representing a moderate and ideal strength for stable enrichment without active site locking. Importantly, XPS data experimentally corroborate these findings: after P-doping, the fraction of pyridinic-N rises markedly from 29.90% to 38.04%, while pyrrolic-N decreases from 27.50% to 24.80%. This enrichment of pyridinic-N, together with its moderate adsorption energy and open configuration, provides the ideal balance between stable enrichment and active site accessibility. Owing to these synergistic structural and electronic effects, the α -ZrP/PNHC/GCE sensor delivers a broad linear detection interval (0.03–10 μ M), a low limit of detection (0.015 μ M), outstanding selectivity, acceptable reproducibility, and reliable stability. Recovery experiments in tap water and honey give values ranging from 97.29% to 103.70%, verifying the method's practical utility. This work offers a highly sensitive sensing platform for MOX

and provides DFT-guided insights into the rational design of heteroatom-doped carbon-based composites.

Keywords: Hollow carbon spheres; α -zirconium phosphate; Heteroatom doping; Electrochemical sensor; DFT-guided design

1. Introduction

As a fourth-generation fluoroquinolone antibiotic[1], moxifloxacin (MOX) finds wide clinical application in treating respiratory[2], skin-soft tissue[3], and urogenital tract infections[4]. This widespread use is attributed to its broad-spectrum antibacterial activity[5], high bioavailability and favorable tissue permeability[5,6]. However, MOX is not fully metabolized in humans and animals, resulting in significant quantities of the parent compound and its active metabolites being released into environmental water bodies through feces and urine. After entering the environment, these substances may build up along food webs, thereby threatening ecological systems and human wellbeing[7,8]. Studies show that long-term contact with minute MOX concentrations can foster the rise and spread of resistance genes, alter microbial population compositions, and upset the equilibrium of waterborne ecosystems[9–11]. Furthermore, MOX may reach humans through drinking water and dietary routes, heightening the risk of allergic reactions[12], liver damage, and adverse neurological effects[13]. Hence, creating an assay that is sensitive, selective, fast, and simple for detecting MOX at trace levels is of great scientific and practical worth in areas such as water quality

surveillance[14], food safety control[15], and clinical drug concentration assessment[16].

At present, MOX determination mainly depends on conventional methods like HPLC[17], LC-MS, spectrophotometry, and fluorometry[18,19]. Although these techniques offer good precision and reproducibility, they suffer from drawbacks including costly equipment, laborious sample preparation, need for skilled operators, and lengthy analysis durations[20,21]. Such shortcomings make them unsuitable for rapid on-site testing and trace-level quantification. Recently, electrochemical approaches have arisen as attractive options for detecting drug residues, thanks to their merits like high sensitivity, fast response, easy handling, compact instrumentation, and field-deployable nature[22]. Nonetheless, the molecular structure of MOX contains relatively few electrochemically active groups, resulting in slow kinetics for direct electrooxidation reactions. Consequently, traditional bare electrodes typically exhibit broad oxidation peaks, low response currents, and high overpotentials, which collectively limit detection sensitivity[23]. Thus, for effectively boosting MOX's electrochemical signals, developing modifier materials with strong electrocatalytic performance is essential, which constitutes a key scientific task in fabricating high-performance MOX sensors.

Zirconium α -phosphate (α -ZrP), a representative two-dimensional layered inorganic material, has attracted considerable interest in catalysis, adsorption, and electrochemical sensing due to its distinctive layered structure, abundant surface hydroxyl groups, excellent ion exchange capacity, and notable thermal and chemical

stability[24–26]. The layered architecture of α -ZrP offers numerous accessible active sites[27], while its interlayer regions function as microreactors for molecular recognition and enrichment[28], facilitating the pre-enrichment and selective identification of target molecules[29]. Nevertheless, the standalone α -ZrP material exhibits inherent limitations, including poor intrinsic electrical conductivity and a propensity for agglomeration within its layered structure, which severely restrict its practical application as an electrochemical sensing material[30]. Consequently, effectively addressing the issues of inadequate conductivity and agglomeration in α -ZrP, while fully exploiting its structural advantages, has emerged as a critical focus for enhancing its electrochemical sensing performance.

An effective strategy to address the aforementioned challenges involves the integration of α -ZrP with highly conductive carbon materials, which facilitates a dual enhancement in catalytic activity and conductivity through a synergistic effect[31,32]. Among these materials, hollow carbon spheres co-doped with heteroatoms present several advantages in structural and electronic regulation[33,34]. Structurally, the morphology of the hollow spheres and their multi-level pore architecture not only provide efficient pathways for electrolyte penetration and molecular diffusion[35–37], but also possess larger specific surface area enables efficient loading and dispersion of α -ZrP nanosheets[38,39]. This configuration significantly inhibits layered stacking and agglomeration, thereby ensuring high accessibility to active sites[40]. In terms of electronic regulation, heteroatom co-doping disrupts the charge neutrality of the carbon framework, enabling precise modulation of the electronic structure[41,42]. Nitrogen

atoms introduce active configurations, such as pyridine and pyrrole nitrogen, which offer abundant sites for catalytic reactions[43]. The phosphorus atom occupies a carbon atom adjacent to the Pyridinic-N through shoulder substitution[44], injecting electrons into the carbon skeleton and moderately reducing its Lewis basicity[45,46]. This alteration transforms the interaction with the target molecule from excessively strong coordination to a moderately strong hydrogen bond or π - π stacking[47]. It is this synergistic effect of structural shaping and electronic regulation that allows heteroatom-co-doped hollow carbon spheres to exhibit both exceptional enrichment capabilities and favorable electrochemical response characteristics.

Drawing from the foregoing studies, we have built an electrochemical sensing platform using α -ZrP/PNHC composite materials aimed at highly sensitive trace MOX detection. α -ZrP/PNHC composites were prepared by a simple ultrasonic-assisted dispersion method, and their microstructure, crystallographic characteristics, surface chemical composition and electrochemical properties were systematically characterized. By integrating DFT computations, we elucidated at the atomic level the intrinsic mechanism whereby P doping tunes the electronic configuration of Pyridinic-N and improves MOX adsorption strength and electron transfer via shoulder substitution. Experimental findings indicate that the sensor exhibits excellent linear response within the range of 0.03-10 μ M, with a detection limit as low as 0.015 μ M. It also demonstrates outstanding anti-interference ability, reproducibility, stability, and actual sample spiked recovery rate (97.29% - 103.70%). This work offers fresh perspectives on using α -ZrP-based composites in electrochemical sensing and also

supplies dependable technical backing for quickly detecting antibiotic leftovers in environmental waters and foodstuffs.

2. Experimental

2.1 Materials and reagents

The reagents employed in our experiments mainly include the following categories: ZrOCl_2 , H_3PO_4 , NaH_2PO_4 , Na_2HPO_4 , Tris, dopamine, sodium hypophosphite (NaH_2PO_2), and polystyrene (PS) microspheres for material synthesis (Jiangsu Zhichuan Technology Co., LTD.); The target and interfering substances used for electrochemical detection include moxifloxacin (MOX), lomefloxacin (LOM), ofloxacin (OFX), pefloxacin (PEF), ascorbic acid (AA), dopamine (DA), and uric acid (UA). Furthermore, basic reagents such as KCl, $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, absolute ethanol, and ethylene glycol came from Sinopharm Group Chemical Reagent Co., LTD. (Shanghai, China). Except for the PS microspheres, every reagent listed was provided by Shanghai Aladdin Biotech Co., LTD. (China) and used as received (analytical grade) with no additional purification. To prepare 0.1 M phosphate buffer (PBS), accurate amounts of NaH_2PO_4 , Na_2HPO_4 , KCl, and NaCl are weighed, dissolved in deionized water, and finally the pH is adjusted to the target value using 1 M HCl or NaOH.

2.2 Characterization

For comprehensive characterization of the microstructure, crystal phase, and surface chemistry of α -ZrP, PNHC, and the α -ZrP/PNHC composite, we utilized multiple analytical tools in this work. Sample surface morphologies and fine structures were observed using a Sigma 300 SEM (manufactured by Zeiss, Germany) and a JEM-

F200 TEM (supplied by Hitachi, Japan). Crystallographic information was obtained via powder XRD on an XRD-6100 instrument (Shimadzu, Japan) using monochromatic Cu K α radiation ($\lambda = 0.1541$ nm, 40 kV, 25 mA). Surface elemental composition and chemical states were analyzed by XPS (Nexsa, Thermo Fisher Scientific, USA) with monochromatic Al K α excitation at 1486.6 eV. We also measured N₂ adsorption-desorption isotherms using a surface area analyzer (BET-SSA-4200, Boulder, China) and derived specific surface areas via the BET method.

2.3 Preparation of NHC and PNHC

To synthesize N-doped hollow carbon material (NHC), first add 5 mL of commercially available PS microspheres to 60 mL of deionized water, then add 0.6 g of Tris, and adjust the pH of the solution to approximately 8.5 with 1 M hydrochloric acid. Subsequently, 300 mg of dopamine was introduced into this mixture, which is then magnetically stirred constantly at 45 °C over a 24 h period. Once the reaction finishes, the resulting product is rinsed with deionized water, collected by centrifugation, and dried under vacuum at 80 °C for 24 h, yielding the 3D hollow carbon precursor named NHC.

Further phosphating treatment was carried out on the precursors: 200 mg of carbon precursor and 1.0 g of NaH₂PO₂ were respectively weighed and placed in two separate porcelain boats. The porcelain boat containing NaH₂PO₂ was placed upstream of the tube furnace (gas source side), and the NHC precursor porcelain boat was placed downstream. Under an argon flow, the temperature is raised at 5 °C min⁻¹ to 300 °C and kept there for 1 h, then further elevated at the same ramp rate to 800 °C and maintained

for another 2 h. Upon completion, the system is allowed to cool spontaneously to ambient conditions, affording the P,N co-doped hollow carbon spheres designated as PNHC.

2.4 Preparation of α -ZrP and α -ZrP/PNHC composite

Via a simple hydrothermal route, we synthesized the α -ZrP material, which exhibits a nanosheet-like morphology.

The α -ZrP material, characterized by a nanosheet structure, was synthesized using a straightforward hydrothermal method. The specific synthesis steps are as follows: First, 6 g of ZrOCl_2 was introduced into 60 mL of a 15 mol L^{-1} H_3PO_4 solution and stirred continuously to ensure complete dissolution, resulting in a uniform mixed solution. Subsequently, this solution was transferred into a 100 mL PTFE-lined stainless steel autoclave, which was sealed and placed in an oven for a reaction at 200°C for 12 h. After the reaction finishes, the autoclave was left to cool down to ambient temperature on its own. The resulting suspension was then centrifuged at 12,000 rpm for 8 min to harvest the precipitated solids. The collected precipitate is rinsed successively with absolute ethanol (three cycles) and deionized water (three cycles), then dried completely in a vacuum oven at 60°C .

To prepare the α -ZrP/PNHC hybrid, we adopted an ultrasonic-assisted dispersion strategy. The fabrication of the α -ZrP/PNHC hybrid material relied on an ultrasonic-assisted dispersion technique. The specific preparation procedure is as follows: An analytical balance was employed to weigh 3 mg of α -ZrP and 2 mg of PNHC, which were then dispersed into 3 mL of deionized water. Subsequently, we subjected the

mixture to ultrasonication for half an hour to ensure homogeneous distribution. Prior to use, the dispersion receives an extra 30 min of sonication for maintaining uniformity.

2.5 Fabrication of the α -ZrP/PNHC/GCE modified electrode

A glassy carbon electrode (GCE) was polished with 0.3 μm alumina slurry to obtain a mirror-like surface finish (**Scheme 1**). Subsequently, the electrode was washed successively with absolute ethanol and deionized water (three cycles each) for complete removal of residual impurities. Following cleaning, the electrodes were placed under an IR lamp for drying before the modification step. A volume of 6 μL of α -ZrP, PNHC, and α -ZrP/PNHC dispersions was respectively drop-cast onto the pre-treated GCE surfaces. After solvent evaporation under IR lamp irradiation, the modified electrodes α -ZrP/GCE, PNHC/GCE, and α -ZrP/PNHC/GCE were successfully prepared.

2.6 Electrochemical measurements

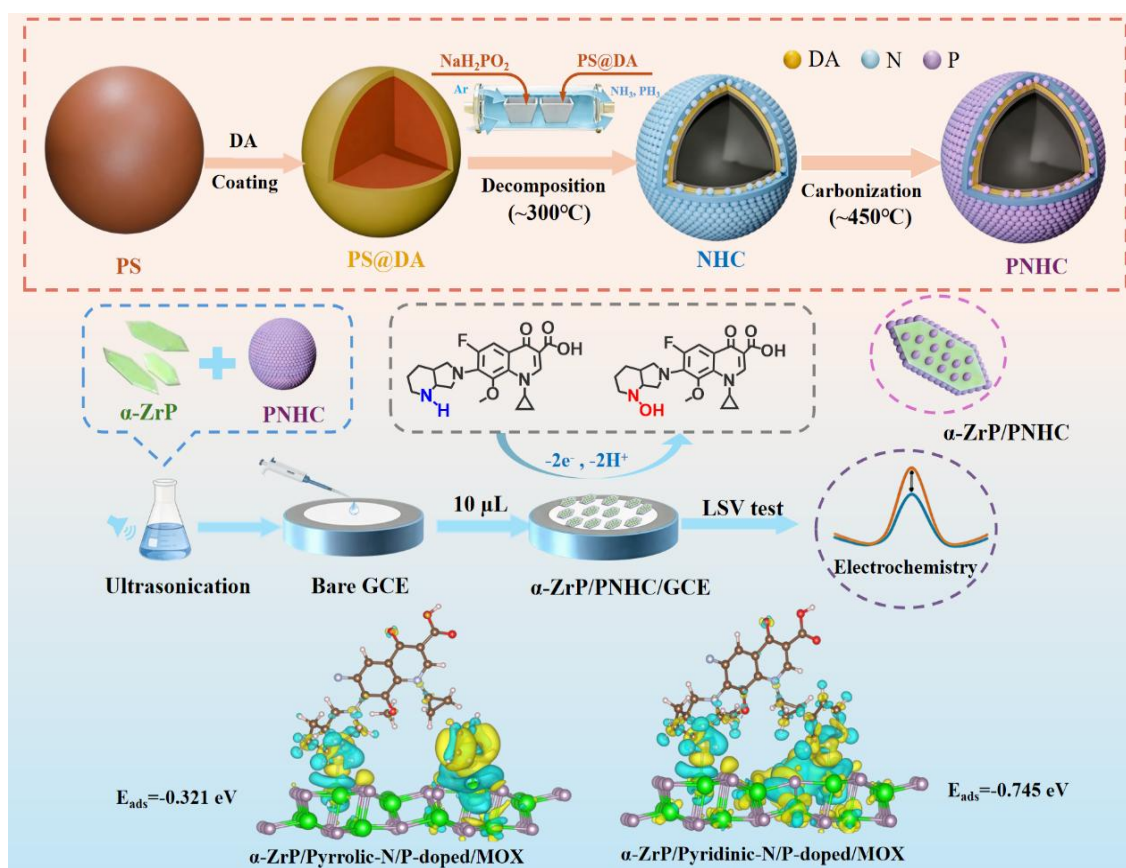
All electrochemical tests were conducted on a CHI 660B workstation (Shanghai Chenhua Instrument Co., LTD.) employing a conventional three-electrode apparatus. The system comprised an SCE reference electrode, a Pt wire auxiliary electrode, and the α -ZrP/PNHC/GCE acted as the working electrode. CV and EIS were used for evaluating the electrochemical behavior of the modified electrodes. EIS measurements were conducted at OCP over frequencies from 100 kHz to 0.1 Hz with an AC signal amplitude of 5 mV. Subsequently, quantification was achieved via LSV, with the potential scanned from 0 to 1.2 V at 0.05 V s⁻¹.

2.7 Real sample preparation

Water samples were filtered through a 0.22 μm membrane, then mixed 1:1 (v/v) with 0.2 M PBS (pH 6.0) before measurement. Honey (purchased from a local supermarket, Zhuzhou, China) was used as a representative complex food matrix. Specifically, 2.0 g of honey was dissolved into 10 mL of deionized water, sonicated for 15 min, and then spun at 10,000 rpm for 10 min. The resulting supernatant was gathered and immediately diluted using pH 6.0 PBS prior to measurement.

2.8 DFT computational methods

DFT-based first-principles computations were performed with the Vienna Ab-initio Simulation Package (VASP). For the exchange-correlation energy, we employed the PBE functional under the GGA framework. Ion-core and valence electron interactions were handled via the PAW approach, together with a 450 eV plane-wave cutoff. Weak van der Waals forces were included by applying the DFT-D3 dispersion correction. Along the surface-normal direction, a vacuum space exceeding 15 Å was inserted to prevent artificial interactions among periodic replicas. Structural relaxations used a Γ -centered Monkhorst–Pack grid at a k-point density of 0.03 Å⁻¹, and spin polarization was included in every calculation. Self-consistency for the electronic energy was assumed once the energy change fell below 10⁻⁶ eV. Convergence of geometry optimization was judged by a force tolerance smaller than 0.02 eV/Å.



Scheme 1. Illustration of the preparation process for the α -ZrP/PNHC/GCE sensor used in sensitive MOX detection.

3 Results and discussion

3.1 Characterization of α -ZrP/PNHC

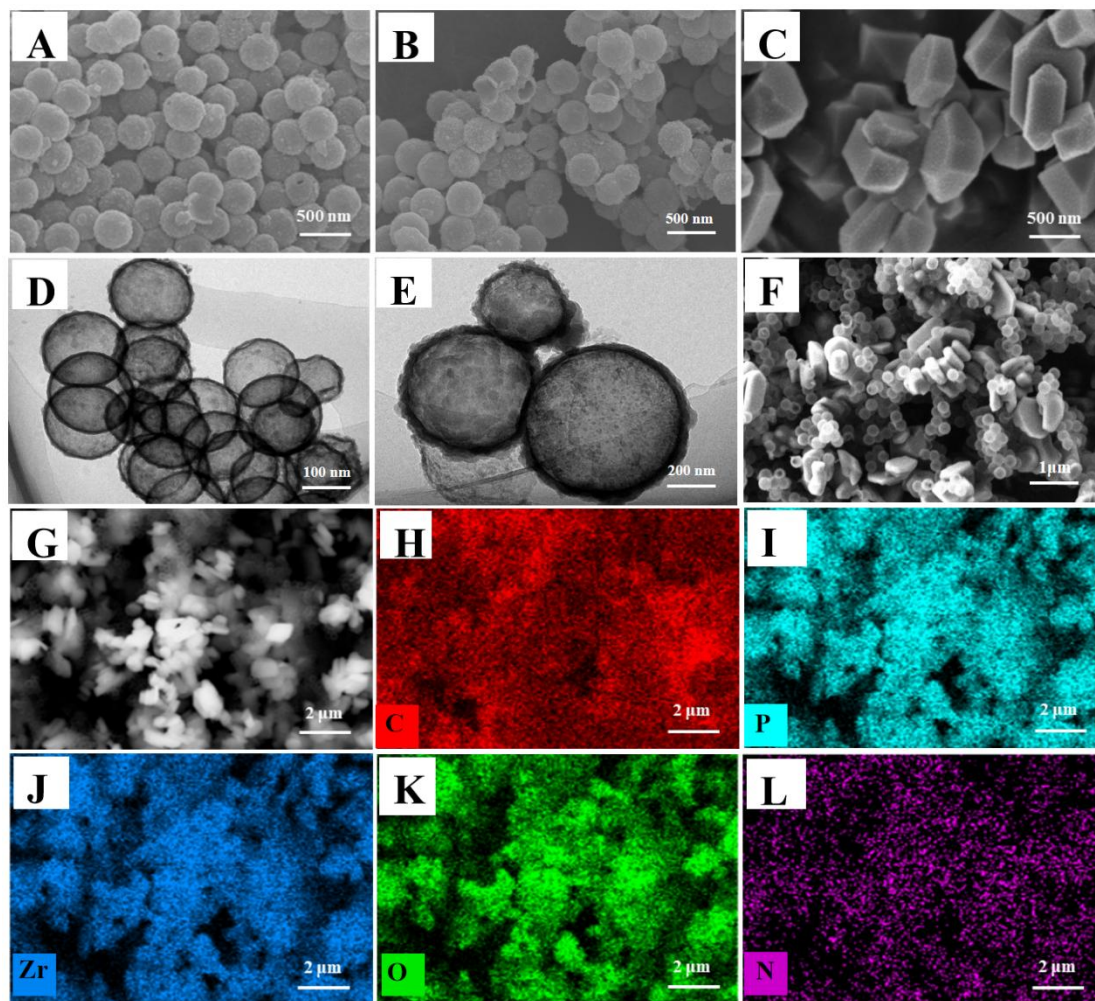


Fig. 1 (A, D) SEM and TEM images of NHC. (B, E) SEM and TEM images of PNHC. (C) SEM images of α -ZrP. (F) SEM images α -ZrP/PNHC. (G-L) EDS mapping showing the elemental distribution (C, P, Zr, O, N) within α -ZrP/PNHC.

As illustrated in **Fig. 1A**, NHC exhibits a regular spherical structure with a diameter of approximately 300 nm. The TEM image in **Fig. 1D** clearly reveals the hollow interior and the well-defined shell, which has a thickness of approximately 20-40 nm. The introduction of nitrogen was crucial in the material formation process. By

precisely controlling the decomposition and carbonization of PS microspheres, the construction of spherical nanomaterials was effectively achieved[48]. Specifically, during high-temperature carbonization, DA releases NH_3 and HCN , which significantly enhance the porosity of the carbon skeleton and contribute to an increase in specific surface area[49,50]. Following phosphorus doping, the PNHC composite material (**Fig. 1B**) retains its original spherical profile; however, its surface morphology becomes markedly rougher. The TEM image in **Fig. 1E** further demonstrates that, compared to NHC, the edge contrast of PNHC is significantly enhanced, the shell thickness increases to approximately 50 nm, and it exhibits a multi-layer shell structure. This indicates that phosphorus has been successfully incorporated into the carbon skeleton, leading to further structural evolution. These findings also confirm that the nitrogen-rich carbon matrix maintains good structural stability during heterogeneous atom doping, this thus provides ideal conditions for the carbon carrier for the subsequent development of functionalized composite materials. **Fig. 1C** illustrates the morphology of pure $\alpha\text{-ZrP}$, which exhibits a characteristic two-dimensional layered structure with smooth lamellar surfaces and distinct edges. This open layered configuration facilitates the exposure of numerous active sites and serves as an optimal anchoring location for subsequent complexation. Following the formation of the composite material (**Fig. 1F**), the $\alpha\text{-ZrP}$ layers were uniformly distributed and integrated within the porous carbon framework of PNHC, resulting in a strong bond between the two components and the establishment of a well-defined heterogeneous interface without significant agglomeration. This structural design is anticipated to facilitate interfacial charge transfer and thereby

enhance the material's overall electrical conductivity.

The elemental composition and spatial distribution of the α -ZrP/PNHC composites were examined using EDS surface scanning analysis (**Fig. 1G-L**). The elemental distribution diagram reveals that the five elements, C, P, Zr, O, and N are uniformly distributed in the composite material. The C and N elements primarily derive from the porous carbon skeleton of PNHC, while the uniform distribution of phosphorus confirms its successful doping. Additionally, the consistent presence of Zr and O indicates that α -ZrP has been effectively integrated into the PNHC matrix. The substantial overlap of each element further substantiates the successful synthesis of the composite material and the uniformity of its composition. The α -ZrP/PNHC composite material exhibits remarkable synergistic benefits in structural design. Notably, the two-dimensional layered architecture of α -ZrP offers numerous accessible catalytic active sites for electrochemical reactions. The porous carbon framework created by PNHC not only effectively supports and disperses the α -ZrP sheets, thereby preventing their agglomeration, but also enhances electrolyte permeability and material transport efficiency through an optimized pore structure. Additionally, the tightly formed heterogeneous interface between the two phases reduces interfacial charge transfer impedance and significantly enhances electron transfer kinetics. The morphological regulation and component synergy inherent in this composite material establish a robust structural and functional foundation for developing an electrochemical sensing platform characterized by high sensitivity, rapid response, and excellent stability.

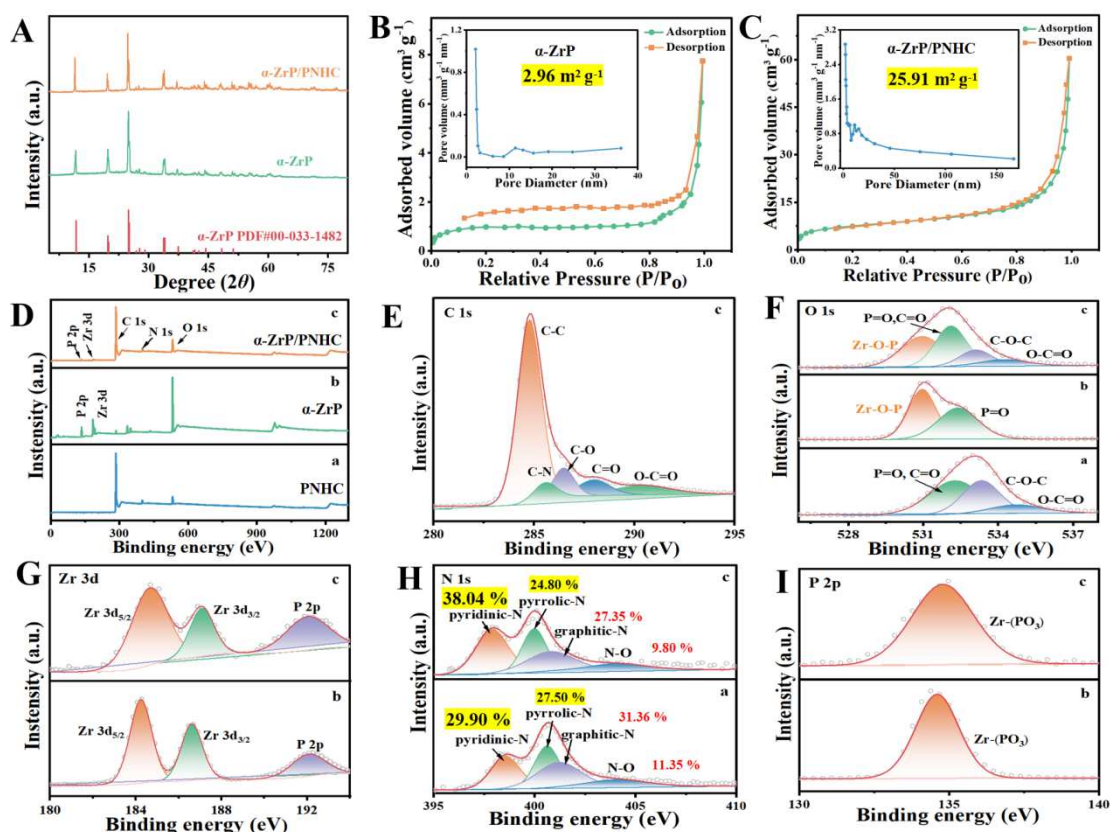


Fig. 2 (A) XRD profiles recorded for (a) PNHC, (b) α -ZrP, and (c) α -ZrP/PNHC. Nitrogen adsorption and desorption isotherms of (B) α -ZrP, (C) α -ZrP/PNHC, and the accompanying insets depict the pore size distributions. (D) Survey XPS scans acquired from (a) PNHC, (b) α -ZrP, and (c) α -ZrP/PNHC. (E-I) High-resolution XPS core-level spectra corresponding to C 1s, O 1s, Zr 3d, N 1s, and P 2p, respectively.

XRD analysis was employed to examine the crystalline phases of PNHC, α -ZrP, and their hybrid material α -ZrP/PNHC, as displayed in **Fig. 2A**. For pristine α -ZrP, distinct XRD reflections are observed at 11.76° , 19.80° , 24.92° , and 33.80° (2θ), which are indexed to the (002), (110), (112), and (020/114) lattice planes, in that order. Notably, the (112) crystal plane exhibits the highest diffraction intensity, indicating that the synthesized α -ZrP possesses a typical monoclinic crystal system structure and exhibits good crystallinity[26]. The XRD pattern of PNHC reveals only a broadened

dispersion peak, characteristic of amorphous carbon, with no discernible crystalline diffraction peaks observed. In the α -ZrP/PNHC composite, all characteristic diffraction peaks of α -ZrP are retained and align closely with the standard card (PDF#00-033-1482)[31]. The lack of extra impurity reflections or noticeable shifts in peak positions indicates that introducing PNHC does not undermine the structural stability of α -ZrP, thereby verifying the effective combination of the two components.

The specific surface area and pore structure of α -ZrP and α -ZrP/PNHC composites were evaluated through nitrogen adsorption-desorption tests, with results presented in **Fig. 2B-C**. The specific surface area of α -ZrP measures only 2.96 m²/g, whereas the α -ZrP/PNHC composite exhibits a significantly higher value of 25.91 m²/g, reflecting an increase of nearly ninefold. Additionally, the pore volume shows a substantial enhancement. The large specific surface area and plentiful mesopores not only offer abundant binding sites for immobilizing MOX molecules but also markedly improve the mass transfer efficiency of substrate molecules within the system, which is highly advantageous for drug loading and subsequent catalytic reactions.

By combining survey and high-resolution XPS measurements (**Fig. 2D-I**), we clarify how P doping modulates the configuration and electrochemical behavior of N-containing species within the α -ZrP/PNHC hybrids. The survey XPS spectrum in **Fig. 2D** verifies the existence of C, N, O, P, and Zr, thereby laying the groundwork for subsequent high-resolution structural analysis. From the C 1s core-level spectrum (**Fig. 2E**), several carbon bonding configurations are observed, including C-C, C-N, and C-O, which suggest that the carbon framework carries numerous functional groups. The

O 1s spectrum (**Fig. 2F**) not only identifies oxygen species, including P=O and C-O-C, but also detects the Zr-O-P bond, providing direct evidence of a robust heterogeneous interface formed between α -ZrP and PNHC via an oxygen bridge. The Zr 3d spectrum (**Fig. 2G**) indicates that Zr exists solely in the +4 oxidation state, while the P 2p spectrum (**Fig. 2I**) displays a characteristic peak associated with Zr-(PO₃), suggesting that the crystal structure of α -ZrP remains intact following recombination.

Most pronounced alterations are observed within the N 1s core-level XPS region (**Fig. 2H**). Relative to the undoped NHC sample, the Pyridinic-N fraction within α -ZrP/PNHC exhibits a marked rise from 29.90% to 38.04%, while pyrrolic-N shows a modest decline from 27.50% to 24.80%. This alteration is not merely a result of component migration; rather, it stems directly from p-doping, as indicated by the presence of P-C and P-N bonds in the P 2p spectrum. The phosphorus atom priority occupies the carbon atom at the shoulder position of both pyridine and pyrrole nitrogen. Through electronic effects and structural stabilization, the configuration of Pyridinic-N becomes thermodynamically more favorable, leading to a substantial increase in its proportion within the composite material.

3.2 DFT calculations

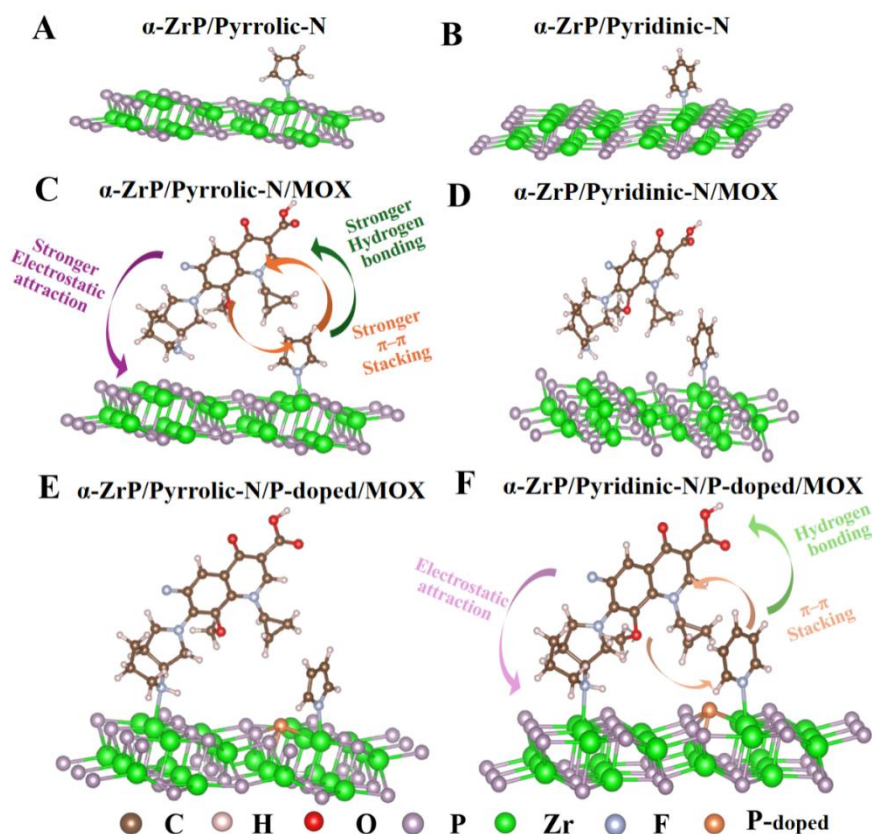


Fig. 3 (A,B) Side-view crystal structures of α -ZrP interacting with Pyrrolic-N (A) and Pyridinic-N (B), respectively. (C) Structural illustration of the α -ZrP/Pyrrolic-N/MOX assembly. (D) Structural illustration of the α -ZrP/Pyridinic-N/MOX assembly. (E) Structure of the α -ZrP/Pyrrolic-N/P-doped/MOX configuration. (F) Structure of the α -ZrP/Pyridinic-N/P-doped/MOX configuration.

To elucidate the role of different nitrogen configurations, through DFT calculations, the adsorption behavior of MOX on the pyridine-N and pyrrole-N sites in phosphorus-doped carbon frameworks was evaluated. Pyrrolic-N resides in a five-membered ring with a highly localized lone pair of electrons, whereas pyridinic-N is located in the edge or defects of the carbon skeleton, exhibiting a more open geometry (**Fig. 3A, B**). In the absence of doping, MOX forms multiple strong interactions

(hydrogen bonds and π - π stacking) with pyrrolic-N, leading to firm anchoring (**Fig. 3C, D**). In contrast, phosphorus atoms insert at the carbon site neighboring pyridinic-N through a shoulder-substitution mechanism, which moderately reduces the electron cloud density of the lone pair on pyridinic-N (**Fig. 3E, F**). This shifts the interaction with MOX from excessively strong coordination to a synergistic effect of moderate-strength hydrogen bonds and π - π stacking, while preserving an open adsorption configuration that facilitates subsequent proton and electron transfer[51].

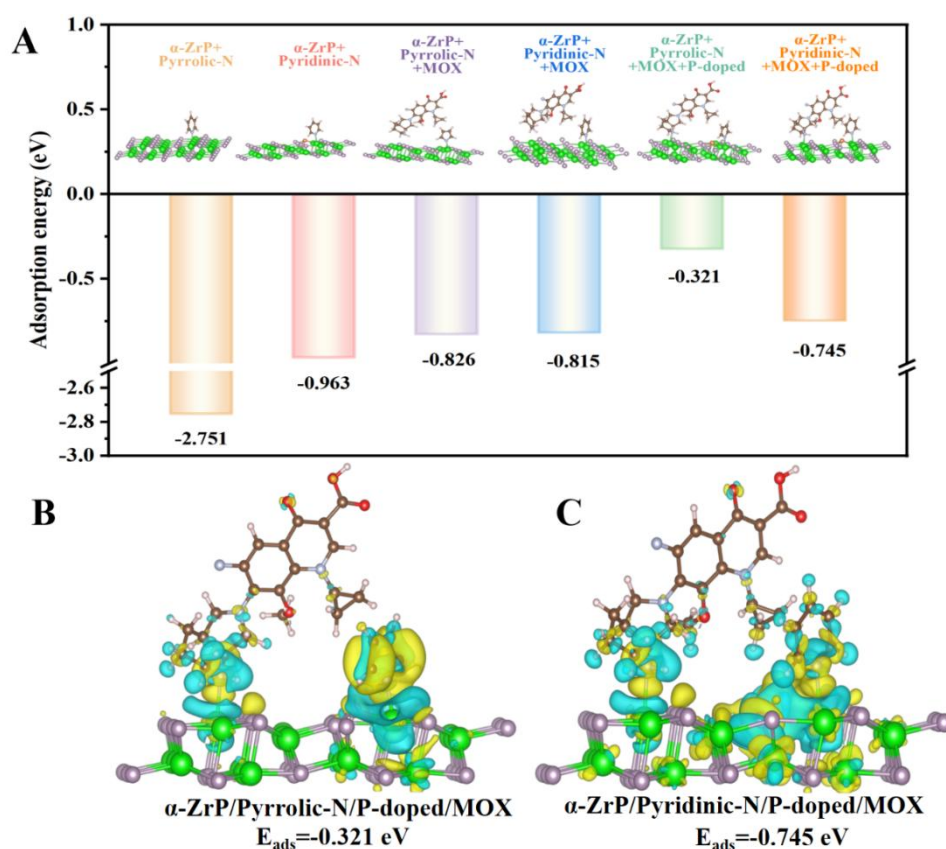


Fig. 4 DFT calculations for elucidating the underlying mechanisms. (A) The adsorption energies of MOX on various nitrogen configurations (pyridinic-N vs. pyrrolic-N) before and after phosphorus doping. (B, C) Charge Density Difference Map of α -ZrP/Pyrrolic-N/P-doped/MOX and α -ZrP/Pyridinic-N/P-doped/MOX system.

Fig. 4 investigates the charge regulation and adsorption performance of various systems through DFT calculations. The adsorption energy data presented in **Fig. 4A** indicate that, in the absence of doping, the adsorption energies of α -ZrP/pyrrolid-N and α -ZrP/pyridine-N were -2.751 eV and -0.963 eV, respectively. Following the introduction of MOX, these values changed to -0.826 eV and -0.815 eV, respectively. After P-doping, the adsorption energies for α -ZrP/pyrrole N/P-doped/MOX and α -ZrP/pyridine N/P-doped/MOX were -0.321 eV and -0.745 eV, respectively. The charge density difference plots in **Fig. 4B, C** reveal that charge distribution primarily occurs at the N and P active centers, as well as on the MOX surface. Furthermore, the interfacial charge recombination in the pyridine N/P-doped system is much stronger than that in the pyrrole N/P-doped system. It should be noted that the absolute value of adsorption energy is not the sole criterion for assessing adsorption behavior; rather, the regulation of the adsorption mode and electronic structure is crucial.

The DFT calculated adsorption energies reveal a clear trend. In the undoped case, the pyrrolic-N site exhibits an excessively strong adsorption energy of -2.751 eV, approaching chemical bond strength, due to its highly localized lone pair electrons, strong Lewis basicity, multi point hydrogen bonding with the MOX carboxyl group, and significant π - π stacking with the quinolone parent nucleus[52,53]. Such overbinding locks the active site, hinders catalyst surface regeneration, suppresses N-hydroxyl intermediate desorption, and ultimately diminishes electrocatalytic efficiency. After P doping, the pyrrolic-N site becomes too weak with an adsorption energy of -0.321 eV, leading to insufficient pre-enrichment and poor signal

repeatability. In contrast, the P-doped pyridinic-N site offers a moderate adsorption energy of -0.745 eV, which is stronger than that of P-doped pyrrolic-N but not excessive. Its charge distribution is more delocalized and its adsorption configuration more open. Phosphorus injects electrons via shoulder substitution, moderately reducing the Lewis basicity of pyridinic-N while enhancing its role as an adsorption center, thus transforming the interaction into moderate strength hydrogen bonding and π - π synergy[54]. Importantly, the XPS data (Fig. 2H) experimentally corroborate these DFT findings. After P-doping, the ratio of pyridinic-N increases from 29.90% to 38.04% while pyrrolic-N decreases. This enrichment of pyridinic-N, together with its moderate adsorption energy and open configuration, provides the ideal balance between stable enrichment and active site accessibility. Consequently, the P-doped pyridinic-N site, combined with an efficient electron transport channel [55,56], serves as the optimal catalytic center for MOX oxidation, enabling both effective preconcentration and rapid electrocatalytic turnover[55,56].

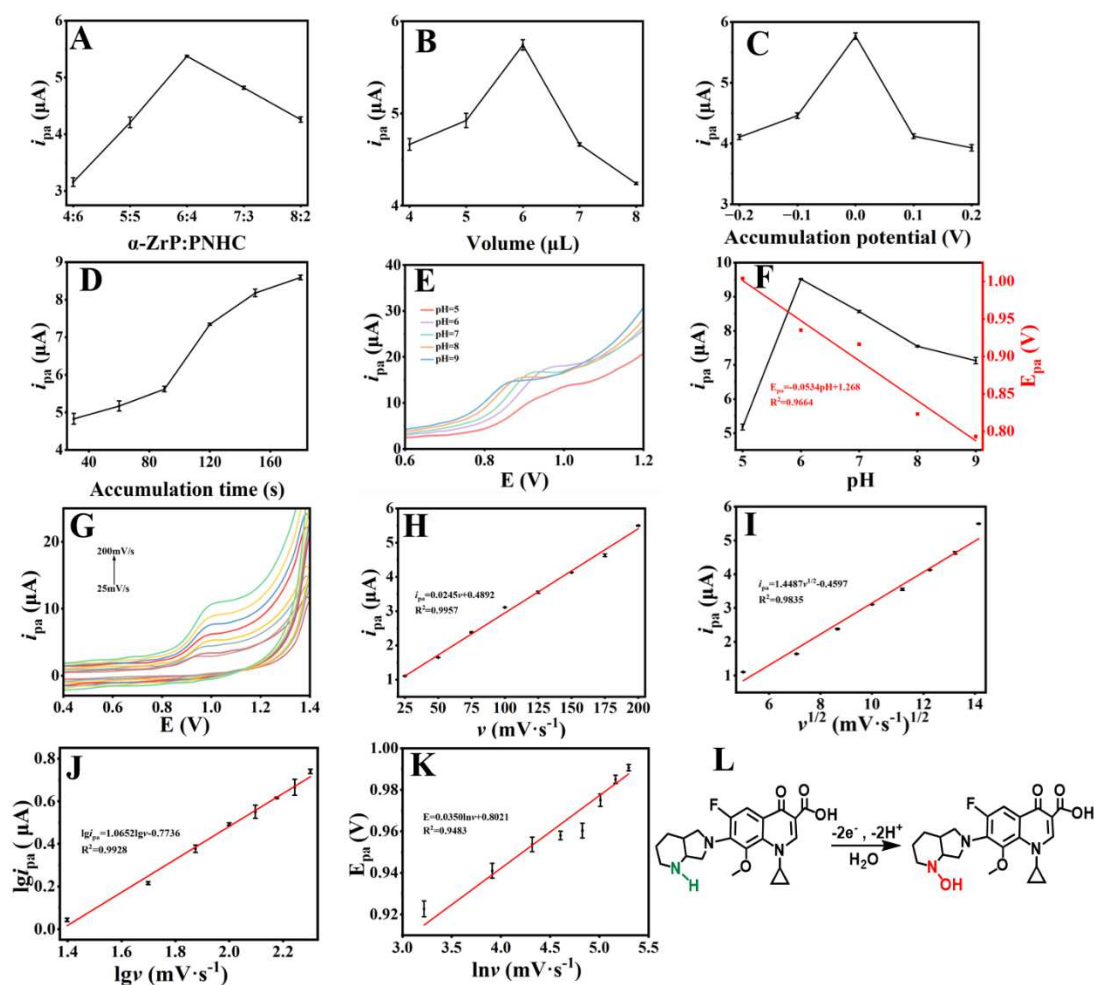


Fig. 5 presents the effects of several experimental parameters on sensor performance: (A) α -ZrP/PNHC mass proportion; (B) modifier volume; (C) accumulation potential; (D) accumulation duration; (E) LSV profiles for 10 μM MOX recorded across various pH values; and (F) linear plots showing how $i_{pa}(\text{MOX})$ and $E_{pa}(\text{MOX})$ vary with pH. The following panels (G–K) address the MOX electro-oxidation pathway at the modified electrode: (G) CV curves of 1.0 μM MOX obtained with varying sweep rates; (H) i_{pa} vs. v linear fitting for MOX; (I) i_{pa} dependence on $v^{1/2}$; (J) logarithmic relationship between i_{pa} and v ; (K) E_{pa} plotted against $\ln v$. Additionally, a scheme illustrating the proposed MOX electro-oxidation process at the α -ZrP/PNHC/GCE surface is also included.

3.3 The LSV responses of MOX across different electrode types

Fig. 5 systematically examines the factors influencing the electrochemical response of α -ZrP/PNHC modified electrodes to MOX and elucidates the underlying reaction mechanism. Initially, **Fig. 5A** illustrates that the oxidation peak current of MOX reaches maximum when the mass ratio of α -ZrP to PNHC is 6:4. This optimal ratio arises from a synergistic balance between conductivity and catalytic activity. PNHC serves as an effective conductive framework, while α -ZrP provides a wealth of catalytic active sites. A lower proportion results in insufficient active sites, whereas a higher proportion may lead to the agglomeration of α -ZrP layers, impeding electron transport[57]. The optimization results presented in **Fig. 5B** indicate that a modification volume of 6 μ L is optimal. A modification layer that is too thin fails to provide complete coverage, while a layer that is too thick increases mass transfer resistance. **Fig. 5C-D** highlight the critical importance of the enrichment process in MOX detection. The optimal enrichment potential is determined to be 0 V. At lower potential, electrostatic repulsion occurs between MOX and the negatively charged modification layer. A shift to a positive potential may induce pre-oxidation. Only at approximately 0 V does the interaction between the two species become strongest, resulting in maximum adsorption efficiency. Furthermore, the enrichment time approaches saturation after 160 s, suggesting that the electrochemically active sites located on the electrode surface near adsorption equilibrium. The influence of pH on the electrochemical response is examined in **Fig. 5E-F**. The maximum anodic current appears at pH 6.0, and E_{pa} shows a linear dependence on pH with a slope close to -53 mV per pH unit. This slope is near

the theoretical Nernstian value of -59 mV/pH (ref. [58]), indicating that MOX oxidation proceeds via an equal proton-electron transfer process.

3.4 Electrooxidation mechanism of MOX

The electrochemical behavior of 1.0 μM MOX across a range of scanning rates (ν) on $\alpha\text{-ZrP/PNHC/GCE}$ was examined using CV (**Fig. 5G-K**). As the sweep rate increased from 25 mV s^{-1} to 200 mV s^{-1} , the i_{pa} exhibited a significant increase, while the E_{pa} shifted slightly in the positive direction, and the peak shape remained well-defined. From these observations, it can be inferred that the electrode process shows good reversibility in terms of kinetics. A robust linear correlation exists between i_{pa} and ν was established (**Fig. 5H**), $i_{\text{pa}} = 0.4923\nu + 0.245$ ($R^2 = 0.9957$), indicating that adsorption predominantly governs the electrode kinetics. Furthermore, a linear correlation is established between i_{pa} and $\nu^{1/2}$ was also observed (**Fig. 5I**), $i_{\text{pa}} = 0.4597\nu^{1/2} + 1.4487$ ($R^2 = 0.9835$), indicating that while diffusion contributes to the reaction, adsorption control remains predominant. Furthermore, a plot of $\lg(i_{\text{pa}})$ versus $\lg(\nu)$ was generated (**Fig. 5J**), yielding a slope of 0.7736 ($R^2 = 0.9928$), approaching the theoretical adsorption-controlled limit of 1.0, thereby reaffirming that the reaction is primarily a surface process[59]. The number of transferred electrons (n) was calculated to be roughly 2 based on the Laviron equation[60], aligning with the pH-dependent relationship and further supporting the two-electron and two-proton process. (**Fig. 5K**).

As illustrated in Mechanism **Fig. 5L**, MOX molecules deposit on the electrode surface via $\pi\text{-}\pi$ stacking forces and hydrogen bonding. The secondary amine groups present in their piperazine rings undergo oxidation, accompanied by the loss of two

electrons and two protons, which subsequently combine with H₂O to yield N-hydroxyl derivatives[61]. Notably, P doping plays a critical role in modulating the electronic properties during this process. The P atom integrates into the carbon framework through shoulder substitution, thereby establishing a conductive channel. This modification moderately reduces the Lewis basicity of pyridine nitrogen, altering its interaction with MOX from excessively strong coordination to a more balanced hydrogen bond/ π - π stacking[62].

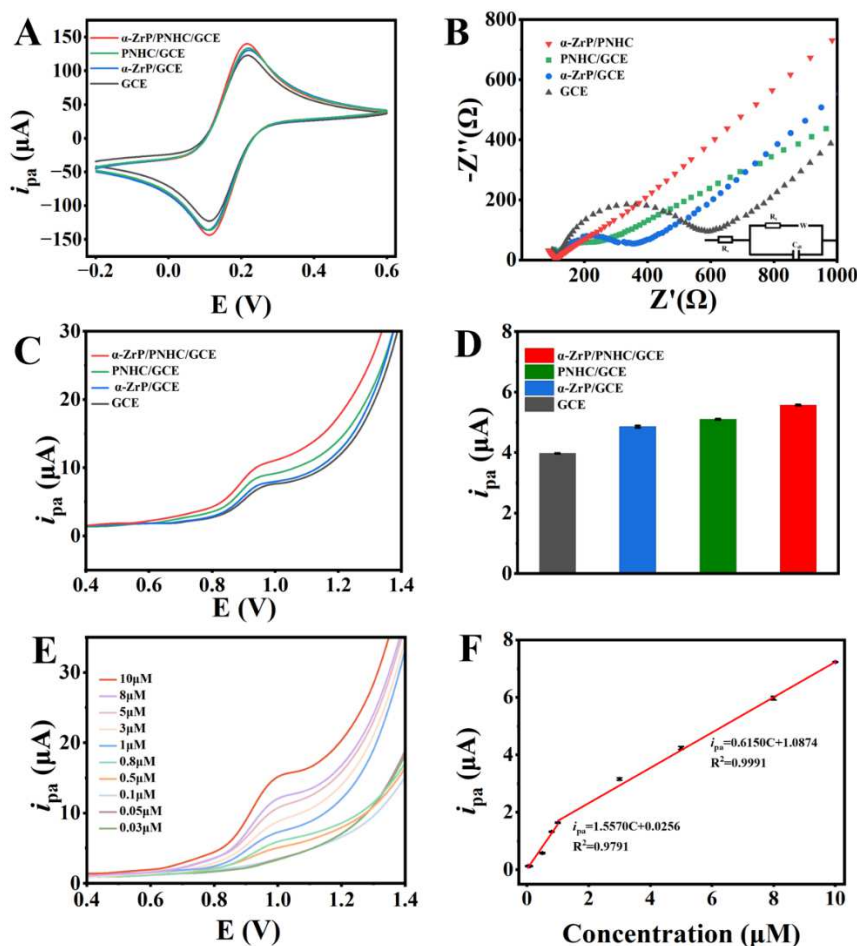


Fig. 6 presents various electrochemical analyses: (A) Cyclic voltammetry diagrams for GCE, α -ZrP/GCE, PNHC/GCE, and α -ZrP/PNHC/GCE systems; (B) The Nyquist plot was obtained in a 0.1 M KCl electrolyte containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$; (C) LSV

recorded on various modified electrodes; (D) i_{pa} of MOX measured on different electrodes; (E) LSV responses of MOX on the α -ZrP/PNHC/GCE under successively higher MOX concentrations; (F) Linear calibration curve representing the correlation between i_{pa} (MOX) and the concentration of MOX.

3.5 Electrochemical properties of α -ZrP/PNHC/GCE

The interfacial characteristics and sensing capability of the α -ZrP/PNHC/GCE are displayed in **Fig. 6**, as evaluated by CV, EIS, and LSV measurements. From the CV data in **Fig. 6A**, the α -ZrP/PNHC/GCE exhibits the largest i_{pa} (160.3 μ A) and i_{pc} (162.1 μ A), substantially exceeding the values obtained at bare GCE, α -ZrP/GCE, and PNHC/GCE. The electrochemically active surface area, derived from the Randles-Sevcik relationship, although only marginally greater than that of PNHC/GCE, demonstrates a current increase that far exceeds the area increase. This suggests that the observed synergistic effect primarily arises from enhanced interfacial catalytic kinetics rather than a mere increase in specific surface area. This enhancement is closely associated with the evolution of nitrogen species within the composite materials. XPS results reveal that the ratio of Pyridinic-N increased substantially different from 29.90% to 38.04% following compounding, while the content of Pyrrole-N experienced a slight decrease. A higher ratio of Pyridinic-N is advantageous, in order to improve the affinity for MOX and its intermediates. This observation aligns with DFT calculations, indicate that the P-doped pyridinic-N site shows off a moderate adsorption energy of -0.745 eV, enabling stable enrichment without active site locking. Additionally, the conductive network formed through p-doping further facilitates electron transfer at the interface.

The EIS results (**Fig. 6B**) corroborate the enhancement in charge transfer kinetics, as shown by the charge transfer resistance (R_{ct}) of α -ZrP/PNHC/GCE, which decreased to 92 Ω , considerably lower than that of bare GCE (470.3 Ω) and PNHC/GCE (112 Ω). The rate constant for charge transfer (K_s) of α -ZrP/PNHC/GCE, determined by the equation $K_s = RT/(n^2F^2R_{ct}AC)$ [63], is notably high, reaching $4.23 \times 10^{-3} \text{ cm s}^{-1}$. This exceptional performance can be attributed to the formation of a robust heterogeneous interface between α -ZrP and PNHC, along with the enhancement of the electronic structure of the carbon skeleton through P-doping.

3.6 Voltammetric behavior on different modified electrodes

The response performance of each modified electrode to 10 μM MOX was evaluated using linear scanning voltammetry (LSV) (**Fig. 6C-D**). The measured value i_{pa} of the exposed GCE was 3.96 μA , while the currents for α -ZrP/GCE, PNHC/GCE, and α -ZrP/PNHC/GCE were 4.89 μA , 5.07 μA , and 5.57 μA , respectively. These values represent enhancements of 1.4, 1.1, and 1.1 times that of the bare GCE, α -ZrP/GCE, and PNHC/GCE, thereby confirming their synergistic effects in the enrichment and catalytic oxidation of MOX.

3.7 Calibration plot

Under optimal detection conditions, the LSV curves of α -ZrP/PNHC/GCE for varying concentrations of MOX were recorded (**Fig. 6E**). As the MOX level raised from 0.03 to 10 μM , the oxidation peak current exhibited a gradual rise, with the peak shape remaining clear and stable. **Fig. 6F** presents the dependence of i_{pa} signal intensity on analyte concentration, revealing two linear segments within the ranges of 0.03-1 μM

and 1-10 μM . Fitting the data separately yields $i_{\text{pa}} (\mu\text{A}) = 1.5570 C + 0.0256$ (μM) ($R^2 = 0.9791$) for the lower concentration range and $i_{\text{pa}} (\mu\text{A}) = 0.6150 C + 1.0874$ (μM) ($R^2 = 0.9934$) for the higher range, resulting in a sensitivity of $S = 1.5570 \mu\text{A } \mu\text{M}^{-1}$.

Based on the linear regression model established at low concentrations, signal-to-noise ratio of 3, the calculated detection limit (LOD) was $0.015 \mu\text{M}$. The summary of the sensing performance of $\alpha\text{-ZrP/PNHC/GCE}$ compared with the previously reported electrodes was presented in **Table 1**. The high sensitivity stems from the composite material's large specific surface area, the abundance of Pyridinic-N active sites, the conductive network formed through p-doping, and the stable heterointerface between $\alpha\text{-ZrP}$ and PNHC. P-doping introduces an electron donor center via shoulder substitution, which moderately weakens the Lewis basicity of Pyridinic-N, facilitating its interaction with MOX to achieve optimal intensity. This process results in a synergistic combination of efficient enrichment and rapid electrochemical response.

Table 1 Comparative evaluation of the electrochemical detection performance for MOX between the $\alpha\text{-ZrP/PNHC/GCE}$ and electrodes from previous publications.

Detection materials	Analytical approach	Linear range	LOD	Samples	Recovery(%)	RSD(%)	Ref.
ZnO-MWCNT/CPE	DPV	0.1~2.4 μM	0.45 μM	Drug/ Urine	99.10~103.50	3.1(n=3)	[16]
Cu-TCPP/rGO	DPV	5~600 μM	1.34 μM	Water samples	100.09~112.02	<6.0(n=3)	[58]
CuNPs/MWCNTs	DPV	5~1000 μM	0.21 μM	Pork	102.75~104.14	< 4.5 (n=3)	[64]
Ag ₂ Se/rGO-ODA	DPV	0.20~425.16 μM	0.1 μM	Urine	98.65~103.3	3.1(n=5)	[65]
HNO/f-CNF/GCE	DPV	0.001~1166 μM	0.034 μM	Environmental waters, artificial saliva	98.15~101.75	/	[66]
$\alpha\text{-ZrP/PNHC}$	LSV	0.03~10 μM	0.015 μM	Honey	97.29~103.70	<4.5(n=3)	This work

3.8 Anti-interfering assay

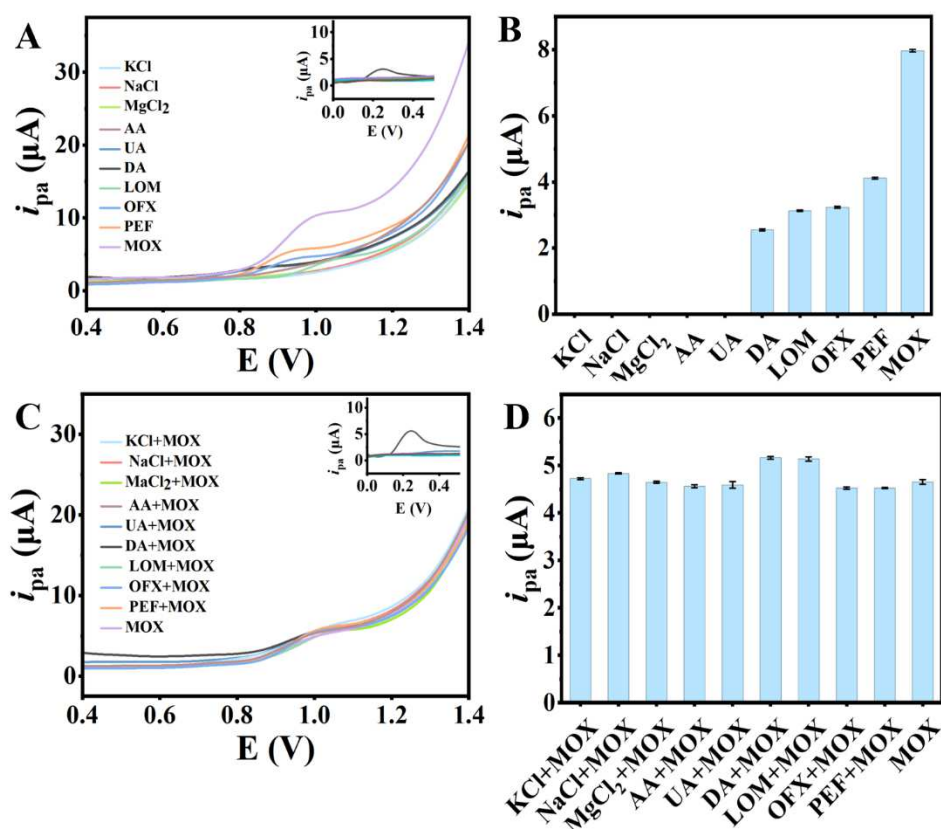


Fig. 7 displays: (A) LSV responses acquired from MOX (10 μ M), UA (100 μ M), NaCl (100 μ M), AA (100 μ M), GLU (100 μ M), $MnSO_4$ (100 μ M), and LUT (100 μ M), together with (C) their respective anodic peak currents; (B) LSV recordings obtained for 10 μ M MOX after adding the identical series of interferents, and (D) the corresponding i_{pa} values under these conditions.

Fig. 7A, B evaluates the selective recognition of α -ZrP/PNHC/GCE for MOX. The excellent anti-interference performance arises from the electronic modulation of pyridinic-N via P-doping. XPS data (Fig. 2H) show that P-doping increases the pyridinic-N proportion from 29.90% to 38.04%, while pyrrolic-N decreases. This enrichment provides more sites with favorable adsorption properties. DFT calculations (Fig. 4A) reveal the origin of selectivity: undoped pyrrolic-N binds MOX too strongly

(−2.751 eV), locking active sites; P-doped pyrrolic-N binds too weakly (−0.321 eV), failing to stabilize enrichment; and P-doped pyridinic-N exhibits a moderate adsorption energy of −0.745 eV with an open configuration, enabling optimal hydrogen bonding and π - π stacking. Structural analogues (LOM, OFX, PEFX) cannot form equally stable interactions, and the weak-binding P-doped pyrrolic-N sites further suppress non-specific adsorption[67]. Consequently, the i_{pa} of MOX (7.98 μ A) is significantly greater than that of other quinolone drugs (3.13-4.12 μ A). Additionally, P-doping enhances conductivity and charge transfer kinetics, favoring MOX enrichment at pyridinic-N sites. Inorganic ions and small biomolecules lack compatible interaction sites, while the porous PNHC structure physically blocks macromolecular impurities. Coexistence tests (Fig. 7C, D) show that with 10-fold excess interferents, the MOX peak current fluctuation remains below 10 % (RSD < 5 %), confirming excellent selectivity.

3.9 Repeatability, reproducibility, and stability

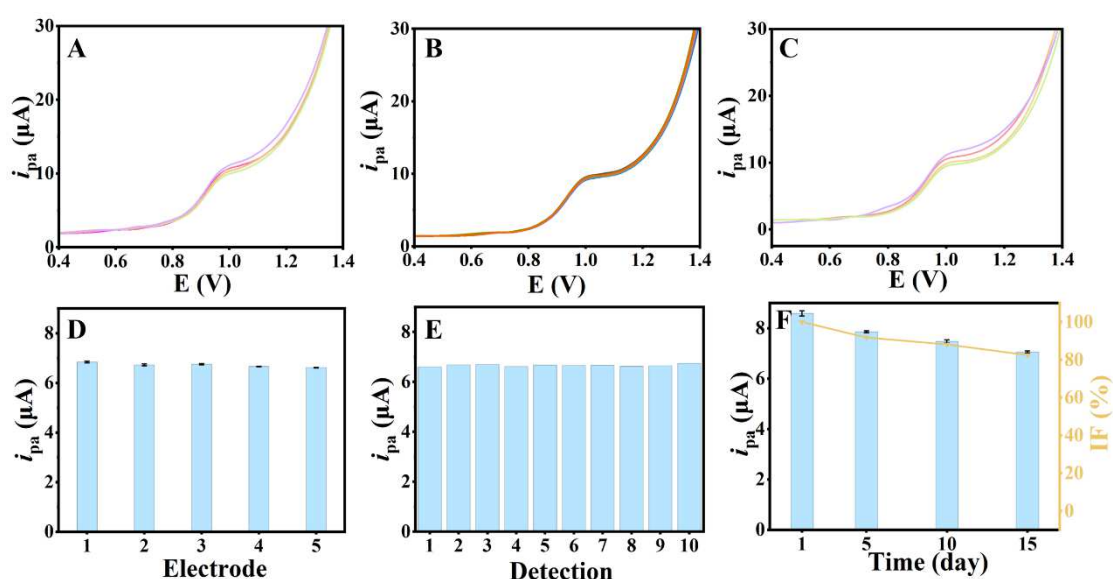


Fig. 8 (A, D) LSV traces and their associated anodic current responses recorded for 10

μM MOX across five separate $\alpha\text{-ZrP/PNHC/GCE}$ electrodes prepared independently. (B, E) LSV scans and the corresponding peak currents obtained over ten consecutive runs using one identical $\alpha\text{-ZrP/PNHC/GCE}$. (C, F) The time-dependent LSV responses and peak current variations for 10 μM MOX recorded across 15 storage days.

Fig. 8 demonstrates the reliability of $\alpha\text{-ZrP/PNHC/GCE}$. The composite exhibits good reproducibility and stability due to its structural synergy and interface bonding. SEM and elemental mapping (Fig. 1F-L) show that $\alpha\text{-ZrP}$ nanosheets are uniformly dispersed within the porous PNHC framework with negligible agglomeration. This uniform distribution ensures consistent availability of pyridinic-N active sites across different electrode batches. As a result, the relative standard deviation (RSD) of the i_{pa} for five independently prepared electrodes was only 1.24 % (**Fig. 8A, D**). The rigid carbon framework of PNHC physically anchors $\alpha\text{-ZrP}$, preventing shedding and agglomeration during repeated measurements, and sustains efficient charge transport through its conductive network. Consequently, ten consecutive scans on the same electrode give an RSD as low as 0.71 % (**Fig. 8B, E**). The Zr-O-P bond detected by XPS (Fig. 2F) confirms a robust oxygen bridge between $\alpha\text{-ZrP}$ and PNHC, enhancing interfacial mechanical stability. Moreover, DFT calculations reveal that the P-doped pyridinic-N site has a moderate adsorption energy of -0.745 eV , which avoids both overly strong binding (which would poison active sites) and too weak capture. This balance contributes to long-term stability: the electrode retained 82.5% of its initial response even after being stored for 15 days (**Fig. 8C, F**). These results confirm that $\alpha\text{-ZrP/PNHC/GCE}$ possesses satisfactory repeatability, reproducibility, and stability for

practical sensing applications.

3.10 Real sample analysis

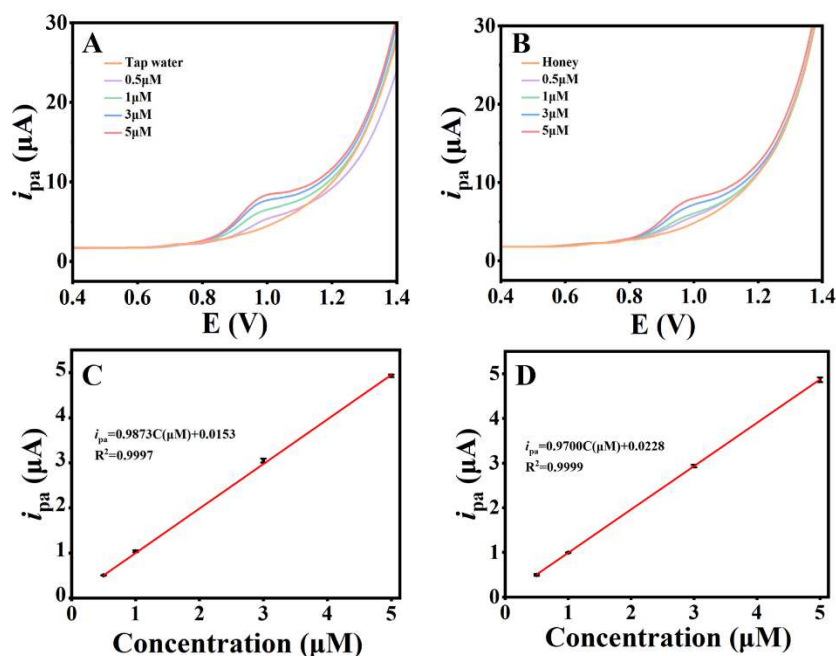


Fig. 9 depicts the application of the sensor for MOX detection in real tap water and honey specimens. (A–B) LSV responses obtained from tap water and honey that were fortified with MOX at different concentration levels. (C–D) Show the respective calibration graphs, which reveal linear correlations between MOX concentration and the corresponding i_{pa} values for tap water and honey, in that order.

Fig. 9 presents the application of α -ZrP/PNHC/GCE for detecting MOX in spiked tap water and honey, confirming its accuracy and reliability in complex matrices. The high specific surface area coupled with a well-defined mesoporous architecture of the composite facilitate rapid diffusion and capture of MOX molecules. In both tap water and honey, the linear correlation between MOX concentration and peak current ($R^2 = 0.9997$ and 0.9999 , respectively) closely matches that observed in pure buffer solution,

indicating minimal matrix interference on mass transfer and adsorption. The sp^2 carbon skeleton of PNHC recognizes the quinolone parent nucleus of MOX through π - π stacking, while α -ZrP provides hydroxyl and Lewis acid sites that support hydrogen bonding and ionic interactions[68]. Additionally, the hierarchical pore structure of PNHC physically blocks macromolecular impurities (e.g., sugars, colloids), preventing competition for active sites[69,70].

Spiked recovery experiments (**Table 2**) yield recovery rates of 97.29–103.70% for MOX in both matrices, with all RSD values below 4.50%. These results are in accordance with the DFT prediction, which the P-doped pyridinic-N site exhibits a moderate adsorption energy of -0.745 eV, which enables stable enrichment without active site blocking, even in the presence of complex sample components[71,72]. Overall, the α -ZrP/PNHC modified electrode effectively mitigates matrix interference and provides accurate, stable detection of trace MOX in environmental water and food substrates, demonstrating promising potential for practical monitoring applications.

Table 2 Quantification outcomes for MOX in both tap water and honey real samples (n = 5).

Samples	Detected (μ M)	Added (μ M)	Found (μ M)	RSD (%)	Recovery (%)
Tap water	ND	0.5	0.5076	0.80	101.53
		1.0	1.0370	2.13	103.70
		3.0	3.0496	1.44	101.66
		5.0	4.9276	0.57	98.55
Honey	ND	0.5	0.4973	4.06	99.47
		1.0	0.9940	0.60	99.40

3.0	2.9330	1.00	97.77
5.0	4.8640	1.10	97.29

ND: not detected.

4. Conclusions

In summary, we have constructed a highly sensitive MOX sensing platform using α -ZrP/PNHC as the electrode modifier. The hollow carbon spheres co-doped with nitrogen and phosphorus serve as a conductive scaffold that uniformly disperses α -ZrP nanosheets, exhibiting abundant binding sites together with efficient diffusion paths. XPS analysis confirms that P-doping significantly increases the proportion of pyridinic-N (from 29.90% to 38.04%) while decreasing pyrrolic-N, which is consistent with DFT predictions of thermodynamic stabilization. DFT calculations reveal that the P-doped pyridinic-N site exhibits a moderate adsorption energy of -0.745 eV and an open configuration, striking an ideal balance between stable enrichment and active site accessibility. Benefiting from these structural and electronic synergies, this sensor demonstrates satisfactory repeatability, enduring stability, exceptional selectivity, a low LOD of 0.015 μ M, and a broad working range from 0.03 up to 10 μ M. The practical feasibility of this sensor is supported by recovery results ranging from 97.29% to 103.70% in drinking water and honey specimens. Limitations include limited interference species tested, no long-term (>1 month) or continuous cycling stability data, and single-analyte capability. The multi-step synthesis with high-temperature carbonization may also hinder scalability. Future research will focus on extending this DFT-guided electronic structure engineering strategy to design heteroatom-doped carbon composites for simultaneous detection of several antibiotic residues. Additionally,

improving the synthesis scalability and exploring regeneration protocols for long-term use are important next steps toward practical deployment.

CRedit authorship contribution statement

Yuan Jin: Conceptualization, Investigation, Methodology, Funding acquisition, writing-original draft. **Yanhong Zhang:** Investigation, Methodology, Formal analysis. **Jinxia Yao:** Investigation, Methodology, Formal analysis. **Nanke Ma:** Funding acquisition, Validation, Visualization. **Guangli Li:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing-review & editing.

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Conflict of Interests Statement

The authors declare that they have no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of Authorship:

This manuscript was prepared entirely by the author without the use of artificial intelligence – based tools or automated text-generation systems.

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