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Novel $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}$ with 2D/1D/3D mixed-dimensional heterostructures for enhanced electrochemical sensing of ofloxacin in aquatic products

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ABSTRACT: Rationally engineered mixed-dimensional heterostructures enable synergistic and interfacial effects that are inaccessible to single components. Here we construct a 2D/1D/3D $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs-COOH}/\text{UiO-66}$ nanohybrid and deploy it as an electrocatalytic interface for the differential-pulse-voltammetric (DPV) detection of ofloxacin in aquatic foods. In this architecture, 2D $\text{Ti}_3\text{C}_2\text{T}_x$ MXene acts as a highly conductive scaffold, while 1D carboxyl-functionalized multi-walled carbon nanotubes (MWCNTs-COOH) are intercalated between MXene sheets to suppress restacking and build rapid electron pathways. The 3D metal-organic framework UiO-66, is anchored onto the MXene/MWCNTs network, providing abundant adsorption and recognition sites. resulting in hybrid materials with superior electrocatalytic activity. The mixed-dimensional heterointerfaces promote fast charge transport and strong ofloxacin preconcentration. Under optimized conditions, the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs-COOH}/\text{UiO-66}$ modified electrochemical sensor demonstrated excellent performance for ofloxacin detection, delivering the wide linear range (0.04–50.0 $\mu\text{mol/L}$) and a low limit of detection of 0.018 $\mu\text{mol/L}$ ($\text{S/N} = 3$). The sensor also exhibits excellent anti-interference, repeatability, reproducibility, and stability. Recoveries of 95.9%–110.0% and the agreement with a reference HPLC method in real samples analysis, substantiate its practical utility for monitoring ofloxacin residues in aquatic foods. This work illustrates a generalizable route to leverage mixed-dimensional MXene/MOF architectures for signal amplification in electrochemical antibiotic sensing.

Keywords: Metal-organic framework; $\text{Ti}_3\text{C}_2\text{T}_x$; Hierarchical structure; Electrochemical sensor, Ofloxacin

1. Introduction

Ofloxacin (OFL) is a fluoroquinolone antibiotic with broad-spectrum activity that has been extensively applied in both human and veterinary treatments, have attracted increasing attention due to its persistence, limited metabolic degradation, and widespread residues in aquatic environments and edible tissues ^[1]. Excessive OFL accumulation poses potential teratogenic, carcinogenic, and antimicrobial resistance risks, prompting regulatory agencies worldwide to establish strict maximum residue limits (MRLs) for aquatic food products ^[2, 3]. Conventional analytical methods, such as high-performance liquid chromatography (HPLC) ^[4]

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and ultra-performance liquid chromatography-mass spectrometry (UPLC–MS) ^[5], offer high sensitivity and reliability, but their reliance on sophisticated instrumentation limits their suitability for rapid or on-site monitoring ^[6]. Electrochemical sensing technologies have thus emerged as promising alternatives due to their high sensitivity, low cost, portability, and rapid response characteristics. However, achieving efficient detection of trace-level OFL remains challenging because bare electrodes suffer from limited conductivity, restricted electron transport, and insufficient density of electroactive sites.

Two-dimensional transition-metal carbides and nitrides (MXenes), particularly $\text{Ti}_3\text{C}_2\text{T}_x$, provide an attractive solution owing to their metallic conductivity, hydrophilicity, and abundant surface functional terminations ($-\text{O}/-\text{OH}/-\text{F}$) ^[7]. These features facilitate rapid electron transfer and enable versatile chemical modification. Nonetheless, MXene nanosheets readily undergo restacking driven by van der Waals interactions, hindering ion transport and blocking active sites, which ultimately impairs their electrochemical performance ^[8]. Introducing one-dimensional conductive fillers such as CNTs has proven effective for inhibiting restacking, enlarging interlayer spacing, and constructing multidimensional electron-transport pathways, as evidenced in $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}$ multilayer hybrid materials ^[9]. Nevertheless, CNTs contribute mainly to conductivity enhancement and provide limited molecular recognition, leaving MXene/CNT systems poorly suited for selectively detecting structurally complex antibiotics like fluoroquinolones.

Metal–organic frameworks (MOFs), with well-defined porosity, tunable coordination environments, and abundant functional groups, have emerged as ideal complements for endowing MXene-based electrodes with molecular recognition capability ^[10]. UiO-66, featuring Zr-oxo clusters and terephthalate linkers, exhibits high stability, uniform pore distribution, and abundant interaction sites (coordination, hydrogen bonding, π – π stacking, and hydrophobic interactions), enabling efficient enrichment of aromatic antibiotics including OFL ^[11, 12]. Although UiO-66 can facilitate local electron transfer via Zr–O nodes ^[13], its intrinsic insulating nature restricts long-range charge transport, limiting standalone electrochemical performance.

Recent advances in MOF@MXene heterostructures show that nucleating MOFs on MXene surfaces introduces selective adsorption sites while forming interfacial charge-transfer channels, greatly improving sensing performance for gases, VOCs, and small biomolecules ^[14–16]. For example, Schottky-type MXene–MOF junctions have been shown to accelerate electron migration while the MOF component enriches target molecules through coordination, hydrogen bonding, and π – π interactions. MXene-derived MOFs and 2D conductive MOFs intercalated within MXene layers further illustrate how MOFs can elevate selectivity and provide tailored active sites that CNTs alone cannot offer. These findings highlight the unique advantages of coupling MXenes with MOFs, rather than solely with CNTs, when selectivity and molecular recognition are essential. However, most reported systems are gas-phase oriented, and their liquid-phase electrochemical behavior—especially for antibiotic residues in complex food matrices—remains insufficiently explored. Moreover, mixed-dimensional MXene/CNT/MOF architectures that combine (i) MXene’s high conductivity, (ii) CNTs’ anti-restacking and electron-bridge effects, and (iii) MOFs’ selective enrichment capability, have rarely been utilized for fluoroquinolone detection.

Motivated by these gaps, this work reports a 2D/1D/3D $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs-COOH}/\text{UiO-66}$ heterostructure (Scheme 1), where CNTs intercalate MXene layers to enhance conductivity and structural stability, while UiO-66 provides uniform micropores and diverse interaction sites for OFL preconcentration. This hierarchical design aims to overcome the intrinsic limitations of MXene/MWCNT hybrids and establish a synergistic interface delivering both rapid electron transport and strong molecular recognition, enabling sensitive and reliable electrochemical detection of fluoroquinolone residues in aquatic products..

2. Materials and methods

2.1. Reagents and Materials

Anhydrous sodium sulfate, disodium hydrogen phosphate, sodium hydroxide, sulfuric acid, methanol, anhydrous ethanol, nitric acid, formic acid, ascorbic acid, acetonitrile, and sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) were obtained from Tianjin Kaitong Chemical Reagent Co., Ltd. tetrabutylammonium bromide, 2-Aminoterephthalic acid, N, N-Dimethylformamide (DMF), zirconium chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), and OFL were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. MWCNTs and $\text{Ti}_3\text{C}_2\text{T}_x$ (≥ 98 wt%) were acquired from Nanjing Pioneer Nanomaterials Co., Ltd. Potassium ferrocyanide, potassium ferricyanide, and potassium chloride were sourced from Tianjin Bodhi Chemical Co., Ltd. In contrast, ammonia was purchased from Laiyang Kangde Chemical Co., Ltd. All chemicals employed in this study were of analytical grade and were applied directly without additional purification. All solution preparations utilized ultrapure water, which had a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$.

2.2 Instruments and equipment

The sample surfaces were characterized using a scanning electron microscope (SEM; S4800, HITACHI, Japan). The crystal structure, crystallinity, and chemical composition of the synthesized materials were characterized by powder X-ray diffraction (XRD, D8 Advance, Bruker, Germany) and X-ray photoelectron spectroscopy (XPS, Shimadzu-Kratos, UK). Fourier transform infrared (FT-IR) spectroscopy was employed to analyze the functional groups and assess the purity of the samples. Electrochemical experiments were conducted using a CHI650D workstation (Shanghai Chenhua, China) with a conventional three-electrode configuration. A saturated calomel electrode (SCE) served as the reference electrode, a platinum wire acted as the counter electrode, and a glassy carbon electrode (GCE) functioned as the working electrode.

2.3 Synthesis of $\text{NH}_2\text{-UiO-66}$

According to the literature ^[17], $\text{NH}_2\text{-UiO-66}$ was synthesized via a solvothermal method. Specifically, 1.6 g of zirconium oxychloride octahydrate and 0.8 g of 2-aminoterephthalic acid were first dissolved in 30.0 mL of DMF and mixed at room temperature to form a homogeneous solution. The mixture was then heated to 140°C under continuous stirring, after which 15.0 mL of formic acid was added and the reaction was maintained for 4 h. Afterward, the resulting product was washed with DMF, centrifuged at 8000 r/min for 8 min, and the supernatant was discarded. This washing and centrifugation step was repeated twice to remove

unreacted materials. Finally, the material was placed in a vacuum oven at 60 °C for overnight drying and then finely ground using an agate mortar.

2.4 Preparation of $Ti_3C_2T_x$ /MWCNTs-COOH

Carboxyl-functionalized multi-walled carbon nanotubes (MWCNTs-COOH) were prepared by acid oxidation. Briefly, concentrated HNO_3 and H_2SO_4 were mixed at a volume ratio of 1:3 to obtain 20.0 mL of mixed acid solution. Subsequently, 100.0 mg of pristine MWCNTs were added to the solution and vigorously stirred at room temperature for 2 h. After the oxidation reaction, the product was thoroughly washed with ultrapure water until the pH of the filtrate was close to neutral. Finally, the obtained MWCNTs-COOH were vacuum-dried at 60 °C for further use [18].

Using a sonication method, 60.0 mg of $Ti_3C_2T_x$ was ultrasonically dispersed in 30.0 mL of ultrapure water, and 20.0 mg of MWCNTs-COOH was dispersed in 5.0 mL of DMF. The two dispersions were then combined and subjected to ultrasonic treatment for 2 h. The resulting mixture was dried by centrifugation to yield $Ti_3C_2T_x$ /MWCNTs-COOH powder.

2.5 Preparation of $Ti_3C_2T_x$ /MWCNTs-COOH/ NH_2 -UiO-66 hybrid materials

A total of 20.0 mg of NH_2 -UiO-66 was dispersed in 30.0 mL of DMF and ultrasonicated for 10 min. Subsequently, 20.0 mg of $Ti_3C_2T_x$ /MWCNTs-COOH powder was added, and the mixture was further ultrasonicated for 30 min. The resulting mixture was stirred at room temperature for 12 h, then washed with deionized water and finally vacuum-dried at 60 °C to produce the $Ti_3C_2T_x$ /MWCNTs-COOH/ NH_2 -UiO-66 hybrid materials (hereafter denoted as $Ti_3C_2T_x$ /MWCNTs/UiO-66 for simplicity).

2.6 Preparation of $Ti_3C_2T_x$ /MWCNTs/UiO-66 modified electrodes

The GCEs were polished in sequence using 0.3 μm and 0.05 μm alumina slurries applied on a chamois cloth for 10 min. Next, the electrode was immersed in deionized water and sonicated for 3-5 min to ensure thorough cleaning. After cleaning, the electrodes were air-dried by placing them on a foam plate and set aside. Next, 8 μL of a $Ti_3C_2T_x$ /MWCNTs/UiO-66 nanohybrid materials dispersed in DMF (2 mg/mL) was drop-cast onto the electrode surface and oven-dried for 20 min in preparation for subsequent experiments. The resulting modified electrode was denoted as $Ti_3C_2T_x$ /MWCNTs/UiO-66/GCE. Other electrodes were prepared following the same procedure.

2.7 Actual sample preparation

To assess the sensor's performance in real sample environments, a recovery experiment was conducted. The intrinsic OFL content in the samples was initially determined through a standard HPLC analysis. Then, 1 mL of OFL working solution at concentrations of 0.2, 1.0, and 2.0 $\mu mol/L$ was added to 5.0 g of sample, resulting in final levels of 14.5, 72.3, and 144.6 $\mu g/kg$. Following thorough mixing and equilibration at 4 °C

for 12 h, the fortified samples were subjected to the identical extraction procedure before electrochemical analysis.

In addition, the national HPLC method (GB 31656.3–2021) was applied to further confirm the sensor's precision and reliability in complex matrices, and the detailed analytical procedure can be found in our earlier publication ^[19].

2.8 Statistical analysis

All electrochemical measurements were conducted in triplicate under identical conditions. Experimental results are expressed as the mean $\pm$ standard deviation (SD). Calibration curves were constructed using linear regression analysis, and the correlation coefficient (R^2) was used to assess linearity. The limit of detection (LOD) was calculated based on a signal-to-noise ratio of 3 ($S/N = 3$). All statistical analyses and data processing were performed using Origin software.

3. Results and discussion

3.1 Characterizations of synthesized materials

The morphologies of UiO-66, $Ti_3C_2T_x$, $Ti_3C_2T_x$ /MWCNTs, and $Ti_3C_2T_x$ /MWCNTs/UiO-66 were characterized using SEM. As illustrated in Fig. 1A, UiO-66 exhibits an octahedral structure. In Fig. 1B, $Ti_3C_2T_x$ displays a thin, accordion-like layered morphology. Upon incorporation of the fibrous tubular MWCNTs into the MXene sheets, the resulting MXene demonstrated a more open, multilayered architecture (Fig. 1C). This is attributed to the carbon nanotubes acting as intercalating agents, increasing the distance between the MXene layers and preventing their re-stacking. In Fig. 1D, UiO-66, which maintains its octahedral form, is successfully physical assembly into the $Ti_3C_2T_x$ /MWCNTs material. A small fraction of UiO-66 is embedded within the lamellar structure, thereby enhancing the adsorption and reactive sites for OFL on the electrode. In addition, the $Ti_3C_2T_x$ /MWCNTs/UiO-66 hybrid materials were further characterized using energy dispersive spectroscopy to analyze the elemental distribution (Fig. S1). The elemental mapping results reveal how titanium (Ti), zirconium (Zr), oxygen (O), nitrogen (N), and carbon (C) are spatially distributed throughout the hybrid materials material, confirming the coexistence and relatively homogeneous dispersion of $Ti_3C_2T_x$, MWCNTs, and UiO-66 in the hybrid materials.

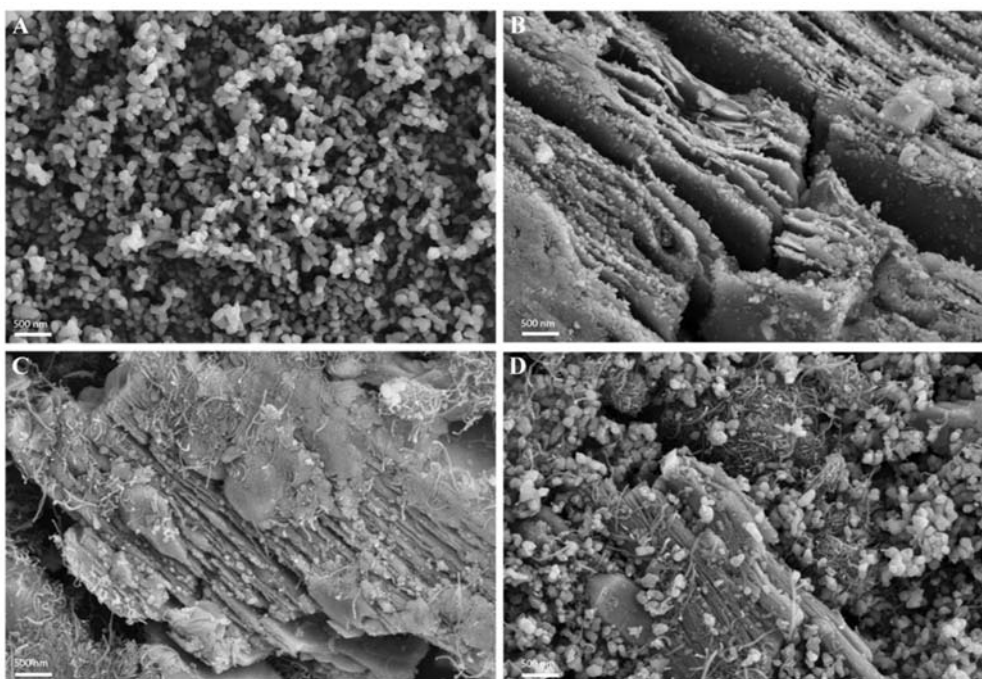


Fig. 1. SEM images of UiO-66 (A), $\text{Ti}_3\text{C}_2\text{T}_x$ (B), $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}$ (C), and $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}$ (D).

XRD was employed to characterize the crystalline structures of UiO-66, $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}$, and $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}$. In Fig. 2A, UiO-66 exhibits high crystallinity, with diffraction peaks at $2\theta = 7.4^\circ$ and 8.5° , which correspond to the (111) and (200) crystal planes, respectively [20]. These peaks indicate the presence of a well-defined skeletal unit in the material, confirming the successful synthesis of UiO-66. $\text{Ti}_3\text{C}_2\text{T}_x$ displays diffraction peaks at 8.6° , 18.5° , 27.8° , 34.2° , and 60.8° , corresponding to the (002), (004), (006), (008), and (110) crystallographic planes, respectively [21]. The diffraction peaks of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}$ appear at the same positions, suggesting that the incorporation of MWCNTs-COOH does not affect the crystalline structure of $\text{Ti}_3\text{C}_2\text{T}_x$. The presence of both UiO-66 and $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}$ characteristic peaks in the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}$ hybrid materials, further confirms each component maintains its crystalline integrity after physical mixing.

The $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}$ nanohybrid materials were further characterized by FTIR spectroscopy. As shown in Fig. 2B, UiO-66 exhibits distinct peaks in the low-frequency region, attributed to the vibrations of the zirconium backbone and aromatic ligands. Specifically, the C-N stretching and N-H bending vibrations of the aromatic amine are observed at 1260 cm^{-1} and 1440 cm^{-1} , respectively. Notably, the symmetric and asymmetric N-H stretching vibrations at 3475 cm^{-1} confirm the successful synthesis of amino-functionalized Zr-MOF [22]. The C-O and C=O vibrations in the -COOH groups of MWCNTs-COOH are observed at 1160 cm^{-1} and 1690 cm^{-1} , respectively. The C-N bond vibration in the benzene ring appears as a strong absorption peak at 1380 cm^{-1} , while the peak at 1430 cm^{-1} corresponds to the C-C bond stretching in the benzene ring. Additionally, the peak at 657 cm^{-1} is assigned to the longitudinal vibration of the Zr-O bond. The absorption peaks near 3450 cm^{-1} in the high-frequency region are assigned to the symmetric and asymmetric N-H stretching vibrations, which exhibit a red shift relative to those of UiO-66. The peak at 1580 cm^{-1} is assigned to the C-O-Zr bond, indicating a coordination linkage between the -COOH group and Zr^{4+} . These characteristic peaks support the coexistence of $\text{Ti}_3\text{C}_2\text{T}_x$, MWCNTs, and UiO-66 in hybrid materials.

The surface functional groups and elemental oxidation states of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ hybrid materials were characterized by XPS analysis. Fig. 2C presents the XPS spectrum of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$, showing the presence of the elements Zr, Ti, C, O, N, and F. The binding energies of the F 1s, O 1s, Ti 2p, N 1s, C 1s, and Zr 3d peaks are 685 eV, 532 eV, 456 eV, 400 eV, 285 eV, and 183 eV, respectively. In Fig. 2D, the Zr 3d binding energy peaks at 183.1 eV and 185.4 eV are attributed to the Zr-O bond, while the peak at 186.0 eV corresponds to the Zr-Zr bond [23]. Fig. S2A presents the XPS O 1s spectrum, in which three distinct peaks appear at 530.8, 531.8, and 533.1 eV, corresponding to C-Ti-O_x, C-Ti-OH, and adsorbed H₂O, respectively [24]. Fig. 2E presents the XPS spectra of the Ti 2p orbitals. The Ti 2p_{3/2} peaks at 455.8 eV and 458.3 eV are attributed to C-Ti-O and C-Ti-OH species, respectively, whereas the Ti 2p_{1/2} peaks at 460.8 eV, 462.4 eV, and 464 eV correspond to Ti-C, C-Ti-OH, and C-Ti-O, respectively [25]. In the XPS C 1s spectrum (Fig. 2F), the peaks at 282.2, 284.0, 285.1, and 288.8 eV are attributed to C-Ti, C-C, C-O, and C=O species, respectively. The N 1s spectrum (Fig. S2B) exhibits a peak at 399.4 eV corresponding to -NH₂, whereas the feature at 400.8 eV is likely associated with protonated amide-related interactions [26].

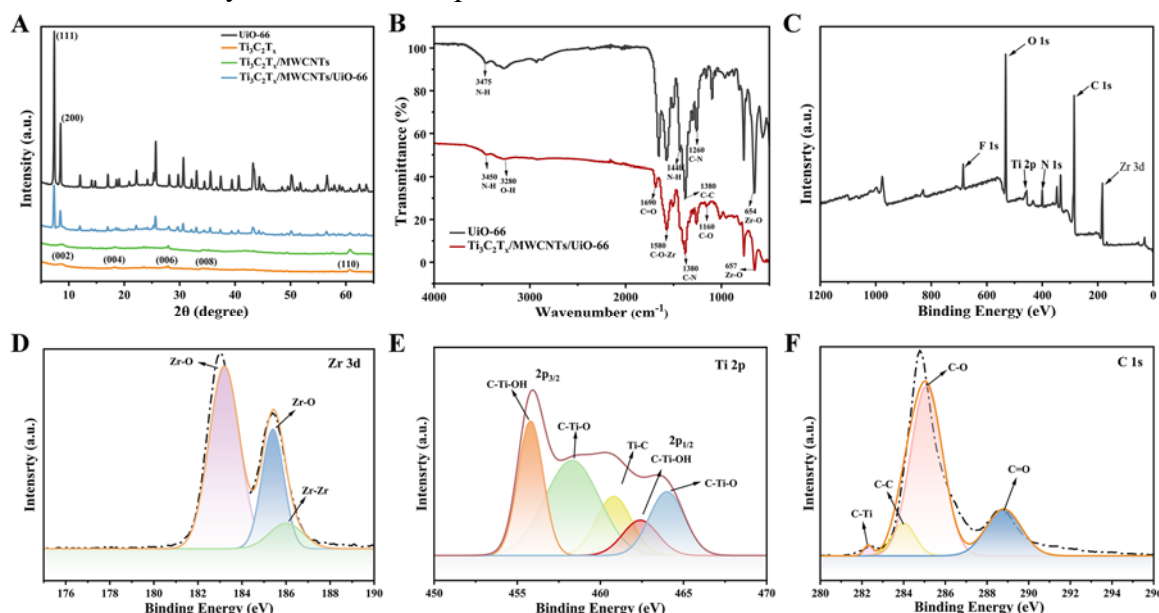


Fig. 2. (A) XRD pattern of UiO-66, $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}$ and $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ (B) FT-IR spectra of UiO-66 and $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ (C) XPS survey spectrum of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ hybrid materials and the core level energies of (D) Zr 3d, (E) Ti 2p, (F) C 1s.

3.2 Electrochemical behavior of electrodes with different modifications

The electrochemical performance of the synthesized materials modified onto the GCE was systematically evaluated using CV and EIS in a 0.1 mol/L KCl solution containing 5 mmol/L $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as a redox probe. As illustrated in Fig. 3A, all modified electrodes displayed a pair of distinct redox peaks, reflecting characteristic reversible electron-transfer behavior. Compared to the bare GCE, the UiO-66-modified electrode exhibited an increased peak current of 68.8 μA and a peak-to-peak separation of 106 mV. Although this suggests a slight enhancement in electron transfer, the improvement was limited, likely due to the intrinsically poor conductivity of UiO-66. In contrast, the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}$ -modified GCE demonstrated a significantly higher redox current, confirming that the integration of MWCNTs into the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene matrix

effectively enhanced the hybrid materials's specific surface area and electrical conductivity, thereby promoting faster electron transfer. Notably, the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}$ hybrid materials-modified GCE demonstrated the highest peak current among all evaluated electrodes. This pronounced enhancement can be attributed to the synergistic effect among the highly conductive $\text{Ti}_3\text{C}_2\text{T}_x$, the high-aspect-ratio MWCNTs, and the porous UiO-66 framework, which collectively provide abundant electroactive sites, facilitate charge transport, and improve electron mobility.

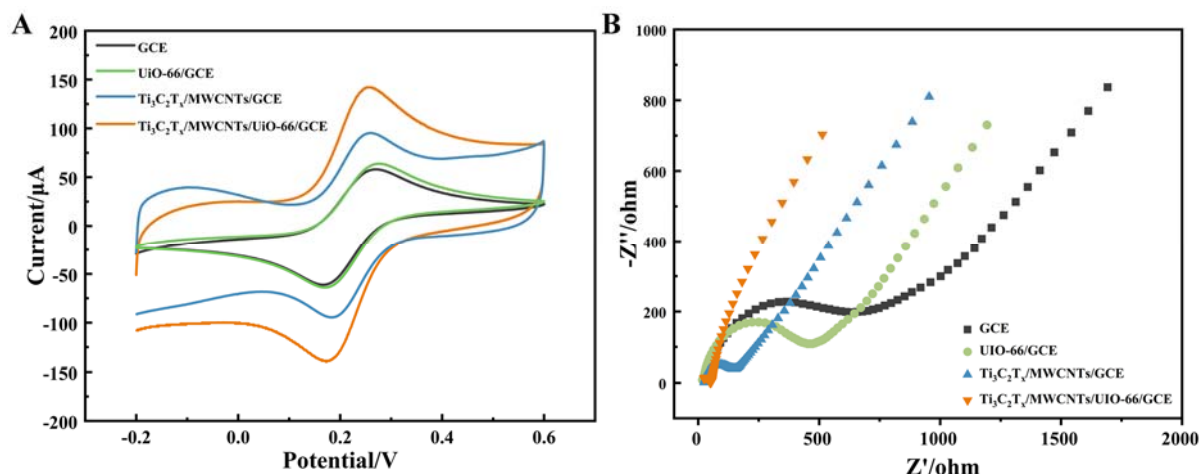


Fig. 3. (A) CV and (B) EIS curves of various electrodes recorded in a solution containing 5 mmol/L $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and 0.1 mol/L KCl: (a) bare GCE, (b) UiO-66/GCE, (c) $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{GCE}$, (d) $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$.

The interfacial electron transfer kinetics were further investigated using EIS. As illustrated in the Nyquist plots (Fig. 3B), the high-frequency semicircular region corresponds to the charge transfer resistance (R_{ct}), while the low-frequency linear region reflects the Warburg impedance associated with ion diffusion. The bare GCE exhibited a large semicircle with an R_{ct} of 676.97 Ω , indicating sluggish electron transfer. Modification with UiO-66 slightly reduced the R_{ct} to 461.6 Ω , reflecting only modest improvement due to its low intrinsic conductivity. A more pronounced decrease in R_{ct} to 153.86 Ω was observed for the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}$ -modified electrode, confirming enhanced conductivity and accelerated electron transfer enabled by the hybrid nanostructure. Remarkably, the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}$ hybrid materials-modified GCE exhibited the lowest R_{ct} of 52.68 Ω , with the semicircle nearly disappearing, indicating significantly improved interfacial charge transfer. This substantial reduction in resistance highlights the excellent electrochemical performance of the hybrid materials, attributed to the efficient integration of conductive pathways and the abundance of electroactive sites provided by the synergistic combination of $\text{Ti}_3\text{C}_2\text{T}_x$, MWCNTs, and UiO-66.

In summary, the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}$ nanohybrid materials demonstrates superior conductivity, reduced charge transfer resistance, and enhanced redox activity, making it a promising material for use in advanced electrochemical sensing applications.

The electrochemically active surface area is a critical parameter for evaluating the performance of modified electrodes, as it represents the quantity of active sites available on the electrode surface to engage in electrochemical reactions. CV measurements of GCE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$ in $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution were performed at various scan rates (10–100 mV/s), as shown in Fig. S3, to assess the role of the hybrid materials in enhancing the electrode's electrically active area. The data shown in Fig. S3A and S3B

indicate that the peak current rises as the scan rate increases at each electrode interface. Fig. S3C and S3D reveal a linear relationship between the anodic peak current and the square root of the scan rate for both the GCE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66/\text{GCE}$, accompanied by the respective slopes. The electroactive surface area of each modified electrode was determined using the Randles–Sevcik equation^[27]: $I_p = 2.69 \times 10^5 \times n^{3/2} \times C_0 \times A \times D_0^{1/2} \times \nu^{1/2}$, where I_p represents the peak current (μA), n is the number of electrons transferred, C_0 denotes the concentration of the redox probe (mol/cm^3), A is the electroactive area (cm^2), ν is the scan rate (mV/s), and D_0 is the diffusion coefficient of the probe species (cm^2/s). The electrochemically active surface areas of GCE and $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66/\text{GCE}$ were calculated to be 0.0696 and 0.1084 cm^2 , respectively. The electroactive surface area of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66/\text{GCE}$ is 1.56 times greater than that of GCE. These findings experimentally confirm that the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ nanohybrid materials significantly enhance the electrochemically active surface area of GCE.

3.3 Electrocatalytic detection of OFL by different modified electrodes

The electrochemical characterization of various modified electrodes was conducted using CV in a 100 $\mu\text{mol}/\text{L}$ OFL solution, with the results presented in Fig. S4. The bare GCE exhibited a weak peak with a current of 6.144 μA . Modification of the electrode with UiO-66 led to a modest increase in the peak current (9.44 μA), indicating that UiO-66 enhances the specific surface area, thereby providing more sites for electrochemical reactions. When $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{GCE}$ was employed as the working electrode, the peak current surpassed that of both the bare GCE and the UiO-66/GCE. This suggests that incorporating MWCNTs into the interlayer of $\text{Ti}_3\text{C}_2\text{T}_x$ sheets not only prevents their aggregation but also significantly enhances the porosity and layered structure of the hybrid materials, creating more ion diffusion channels and exposing additional electrochemically active sites. This mesoporous structure facilitates the rapid mass transfer of OFL in the electrolyte more effectively than the micropores of UiO-66, allowing for better utilization of the increased surface area. Notably, the peak current of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66/\text{GCE}$ in the OFL solution is considerably higher than that of the other electrodes under identical conditions. This improvement is attributed to the synergistic support provided by the three components, which form a stable three-dimensional structure. The MXene and CNTs create a highly conductive skeleton, overcoming the conductivity limitations of UiO-66, and transforming its "inactive surface area" into an "electrochemically active interface," thereby promoting super catalytic activity through interfacial coupling.

3.4 Optimization of experimental parameters

To enhance the analytical performance of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66/\text{GCE}$ sensor, the electrode fabrication procedures and experimental conditions were carefully optimized in phosphate-buffered saline containing 50 $\mu\text{mol}/\text{L}$ OFL. The effect of each variable on sensor behavior was assessed using the anodic peak current (I_{pa}) as the evaluation metric. During optimization, individual parameters were examined separately while all remaining conditions were kept unchanged, allowing for a reliable determination of their specific contributions.

3.4.1 Optimization of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ dispersant concentration

The effect of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ dispersion concentration on the I_{pa} of the modified electrode for OFL was examined. In Fig. 4A, increasing the dispersion concentration from 0.5 to 2.0 mg/mL resulted in a gradual increase in I_{pa} , from 14.3 μA to 36 μA . This increase was primarily due to the fact that, at lower concentrations, the drop-coated hybrid materials material did not fully cover the electrode surface, forming a sparse and discontinuous film, which significantly reduced electron transfer efficiency. At a concentration of 2.0 mg/mL, the loading per unit area increased, exposing more catalytically active sites and enhancing the OFL oxidation reaction rate. However, when the concentration was further increased to 3.0 mg/mL, I_{pa} decreased to 29.2 μA , likely due to the high concentration blocking the mesoporous channels of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$, which hindered the diffusion of OFL molecules to the internal active sites. Consequently, a concentration of 2.0 mg/mL was chosen as the optimal amount of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ for the subsequent experiments.

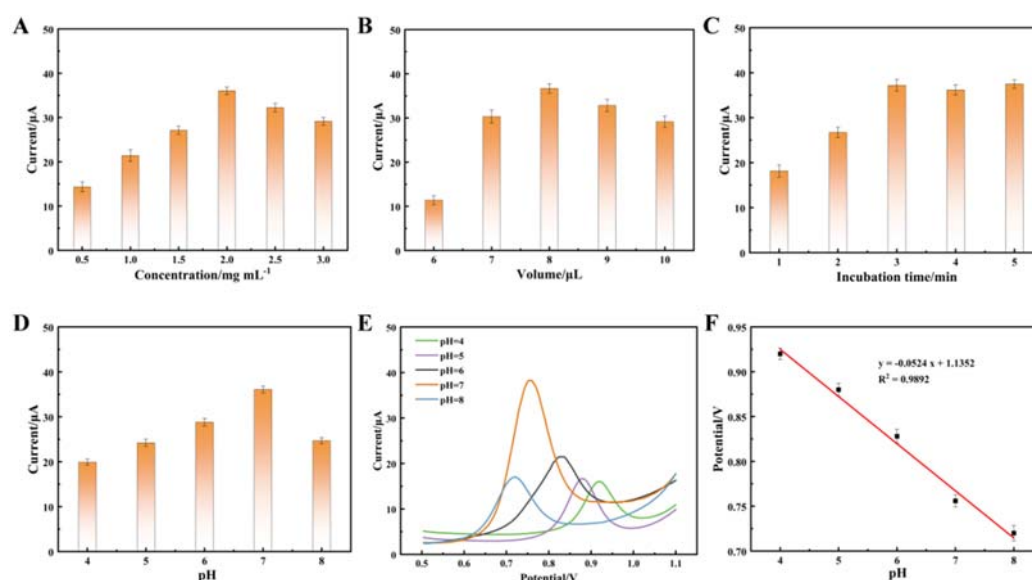


Fig. 4. Optimization of fabrication and application conditions for the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66/\text{GCE}$ sensor: (A) concentration of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$; (B) loading volume of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$; (C) incubation time in OFL solution; (D) effect of pH on the anodic peak current of OFL; (E) DPV response curves of OFL at different pH values; (F) Linear relationship between peak potential of OFL and pH.

3.4.2 Optimization of the loading volume of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ on GCE

Fig. 4B depicts how varying the deposition volume of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ influences the anodic current response of OFL. Increasing the modifier volume from 6 to 8 μL resulted in a progressive increase in I_{pa} from 11.4 to 36.7 μA , which can be attributed to the greater number of electroactive sites available for OFL oxidation. However, when the volume was further increased to 10 μL , the peak current decreased to 29.2 μA , likely because an excessively thick coating hindered efficient electron transfer. Consequently, 8 μL was selected as the most suitable deposition amount for subsequent measurements.

3.4.3 Optimization of incubation time

The duration of incubation is critical for influencing the OFL detection performance of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$ sensor. To identify the optimal duration, DPV measurements were performed to ensure sufficient OFL accumulation on the electrode surface while avoiding unnecessary time consumption. As shown in Fig. 4C, when the OFL concentration was fixed at $50\ \mu\text{mol/L}$, the I_{pa} increased from $18.2\ \mu\text{A}$ to $37.2\ \mu\text{A}$ with prolonged incubation, eventually reaching a stable value at approximately 3 min. This stabilization indicates that the adsorption capacity of the electrode had been fully utilized. Extending the incubation time beyond this equilibrium did not produce further enhancement in binding and could reduce analytical efficiency.

3.4.4 Optimization of electrolyte pH

The pH of the background electrolyte is a critical factor influencing the electrochemical behavior of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$ toward OFL. As shown in Fig. 4D, variations in pH markedly affect the oxidation response of the modified electrode. The anodic peak current gradually rises as the pH increases from 4.0 to 7.0, but it starts to decline when the pH exceeds 7.0. At acidic pH, the protonation of the nanohybrid materials cavity weakens the hydrogen bonding between the OFL molecule and the grafted acceptor functional group. In contrast, at alkaline pH, electrostatic repulsion inhibits the accumulation of OFL molecules on the electrode surface, thereby hindering its oxidation and diminishing the electrocatalytic performance of the sensor. These findings suggest that an optimal pH of 7.0 is necessary to maximize OFL oxidation on the proposed electrode system by promoting effective charge distribution.

3.5 Electrooxidation mechanism of OFL

The electrochemical oxidation of OFL is highly dependent on pH, consistent with a proton-coupled electron transfer (PCET) mechanism. In buffered solutions, increasing the pH from 4 to 8 (Fig. 4E) results in an approximately linear negative shift of the anodic peak potential (E_{pa}), a characteristic feature of proton-involved redox reactions. Under alkaline conditions ($\text{pH} > 7.0$), electron transfer is hindered by limited proton availability, resulting in a decreased I_{pa} . Conversely, higher proton concentrations under acidic conditions ($\text{pH} < 7.0$) facilitate oxidation, leading to an increased I_{pa} . These results suggest that the concentration of protons is a key factor in regulating the oxidation kinetics of OFL, with the optimal electrochemical response observed near pH 7.0. Moreover, as illustrated in Fig. 4F, E_{pa} shows a linear relationship with pH. The fitted equation, $E_{pa}(\text{mV}) = -52.4 \cdot \text{pH}(\text{mV/pH}) + 1135.2$, exhibits excellent linearity ($R^2 = 0.9892$). The slope of $-52.4\ \text{mV/pH}$ is close to the theoretical Nernst value of $-59.2\ \text{mV/pH}$, indicating a stoichiometric 1:1 proton-to-electron ratio in the oxidation step.

The kinetic behavior of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$ was investigated by CV at different scan rates in PBS containing $50\ \mu\text{mol/L}$ OFL. As illustrated in Fig. 5A, the I_{pa} increases progressively as the scan rate rises from 10 to $90\ \text{mV/s}$. Moreover, a strong linear correlation between the redox peak current and the scan rate is observed (Fig. 5B), with the fitted regression equation $I_{pa}(\mu\text{A}) = 1.5089\ \text{V}(\text{mV/s}) + 2.4355$ ($R^2 = 0.9932$). This linear dependence confirms that the electrochemical oxidation of OFL on the

Ti₃C₂T_x/MWCNTs/UiO-66/GCE is governed by an adsorption-controlled mechanism. In addition, Fig. S5 displays a linear relationship between the oxidation E_{pa} and the natural logarithm of the scan rate ($\ln v$), consistent with the Laviron equation [28]:

$$E_{pa} = E^{\theta} - \frac{RT}{(1-\alpha)nF} \ln \frac{RTK}{(1-\alpha)nF} + \frac{RT}{(1-\alpha)nF} \ln v$$

In this equation, n denotes the number of electrons transferred, and E^{θ} represents the standard potential, and α is the charge transfer coefficient reflecting the symmetry of the energy barrier for electron transfer. The parameter K corresponds to the heterogeneous electron transfer rate constant. For a fully irreversible electrode reaction, it is common to assume $\alpha = 0.5$, R as the universal gas constant, T is the absolute temperature ($T = 298$ K), v is the scan rate (mV/s) and F as the Faraday constant. Under these assumptions, the calculated value of n is approximately 2. Because the number of electrons and protons involved in the electrooxidation process is equivalent, the electrooxidation of OFL on the Ti₃C₂T_x/MWCNTs/UiO-66/GCE is inferred to involve the transfer of two electrons and two protons. Based on the molecular structure of OFL, we infer that the oxidation likely occurs at the piperazine moiety. In agreement with previous experimental and computational evidence, a plausible mechanism for OFL oxidation on the Ti₃C₂T_x/MWCNTs/UiO-66/GCE surface is proposed. In this process, OFL undergoes a two-electron and two-proton loss and subsequently reacts with water molecules to generate its oxidation products.

3.6 Analytical performance of the Ti₃C₂T_x/MWCNTs/UiO-66/GCE sensor

Under the optimized conditions, the I_{pa} of the Ti₃C₂T_x/MWCNTs/UiO-66 modified GCE was recorded by DPV at different OFL concentrations. As illustrated in Fig. 5C, I_{pa} increases proportionally with increasing OFL concentration. A strong linear correlation is obtained within the range of 0.04–50.0 $\mu\text{mol/L}$ (Fig. 5D), described by the regression equation $I_{pa} (\mu\text{A}) = 0.685 \cdot C (\mu\text{M}) + 0.9627$ ($R^2 = 0.9985$), confirming the broad dynamic range of the sensor. The LOD, calculated using $\text{LOD} = 3\sigma/k$, is 0.018 $\mu\text{mol/L}$. These results suggest that the Ti₃C₂T_x/MWCNTs/UiO-66/GCE provides high sensitivity, maintains a broad linear range, and achieves a low detection limit for the determination of OFL.

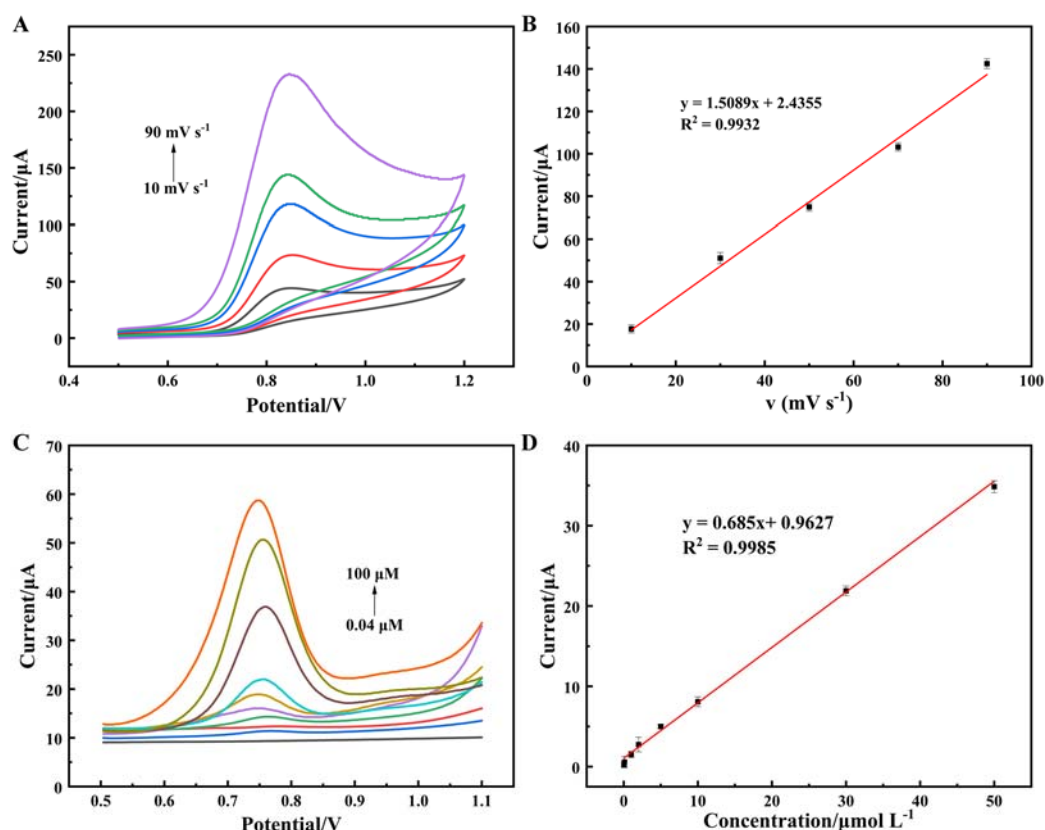


Fig. 5. (A) CV curves of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$ at various scan rates; (B) plot of anodic current versus scan rate; (C) DPV curves of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$ at different OFL concentrations; and (D) corresponding linear relationships between OFL concentration and peak current for $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$.

Compared with previously reported electrochemical sensors (Table 1), including binary hybrid materials such as $\text{Ce-MOF}/\text{Ti}_3\text{C}_2\text{T}_x/\text{GCE}$ and $\text{HP-UiO-66@Ni-BDC}/\text{GCE}$, as well as ternary composites such as $\text{MXene@NiCo-LDH}/\text{CS}/\text{GCE}$, $\text{CS-MWCNT}/\text{AuNPs}/\text{GCE}$, and $\text{MXene}/\text{g-C}_3\text{N}_4/\text{Au-COOH}/\text{GCE}$, the sensor developed in this study exhibited excellent analytical performance, achieved a low detection limit while maintaining a moderate linear range.

Table 1 Comparison of the proposed electrochemical sensor with other reported sensors in terms of linear range and LOD

Electrode	Linear range ($\mu\text{mol/L}$)	LOD ($\mu\text{mol/L}$)	Analyte and reference
$\text{Ce-MOF}/\text{Ti}_3\text{C}_2\text{T}_x/\text{GCE}$	0.2–139	0.190	L-Tryptophan ^[29]
$\text{HP-UiO-66@Ni-BDC}/\text{GCE}$	10–160	0.328	P-Chlorophenols ^[30]
$\text{MXene@NiCo-LDH}/\text{CS}/\text{GCE}$	1–3998	0.210	Glucose ^[31]
$\text{CS-MWCNT}/\text{AuNPs}/\text{GCE}$	1–100	0.050	mycophenolic acid ^[32]
$\text{MXene}/\text{g-C}_3\text{N}_4/\text{Au-COOH}/\text{GCE}$	0.1–480	0.029	Guanosine 5'-monophosphate ^[33]
$\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$	0.04–50	0.018	ofloxacin, this work
Electrode	Linear range ($\mu\text{mol/L}$)	LOD ($\mu\text{mol/L}$)	Analyte and reference
$\text{Ce-MOF}/\text{Ti}_3\text{C}_2\text{T}_x/\text{GCE}$	0.2–139	0.190	L-Tryptophan ^[29]
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3.7 Analytical performance of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ sensor

3.7.1 Anti-interference of the sensor

To assess the sensor's anti-interference performance in real samples, its response to 10 $\mu\text{mol/L}$ OFL was examined in the presence of various potential interfering substances. As shown in Fig. 6A, the introduction of common coexisting species, including Ca^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , CO_3^{2-} , glucose, ascorbic acid, ciprofloxacin (CIP), enrofloxacin (ENR), norfloxacin (NOR), levofloxacin (LEV), and enoxacin (ENO) at a tenfold higher concentration (100 $\mu\text{mol/L}$) resulted in only minimal changes in the OFL oxidation current. The relative current deviation remained below 5%, indicating the excellent anti-interference capability of the sensor. This strong selectivity is primarily attributed to the synergistic structural features of the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66$ hybrid materials, which enhance adsorption affinity and electrocatalytic activity toward OFL while reducing non-specific interactions with interfering species.

Overall, these findings confirm that the $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66/\text{GCE}$ exhibits robust anti-interference performance and is highly suitable for selective and reliable OFL detection in complex matrices.

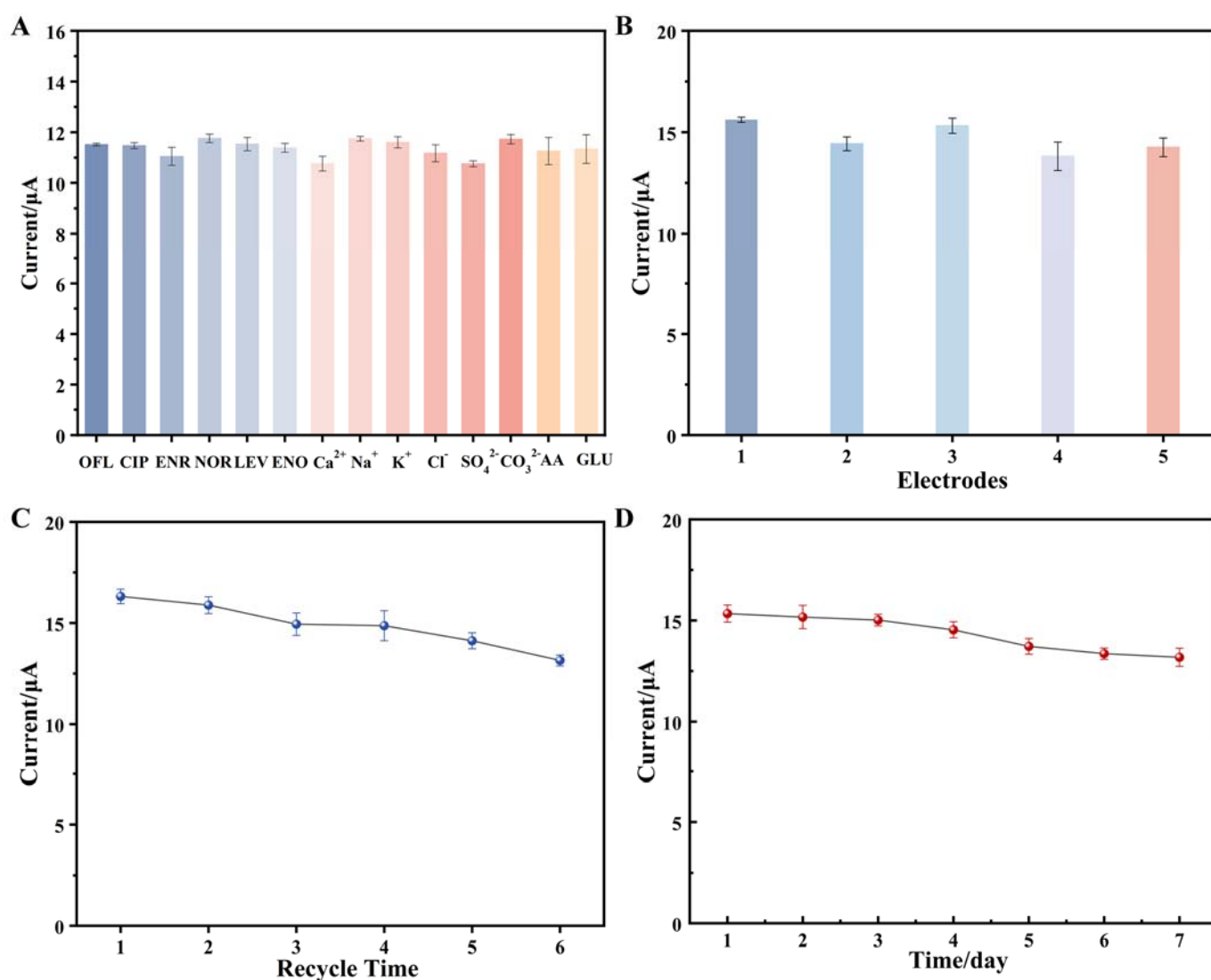


Fig. 6. (A) I_{pa} response of $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66/\text{GCE}$ to OFL and some ions and common interferences; (B) reproducibility of the sensor; (C) repeatability of the sensor; and (D) stability of the sensor.

3.7.2 Reproducibility of the sensor

Reproducibility describes the degree of consistency obtained when multiple electrodes are used to measure a fixed concentration of OFL (10 $\mu\text{mol/L}$) under identical conditions. High reproducibility enhances the reliability of the detection and ensures consistent analytical outcomes. Five electrodes were fabricated under the same preparation conditions. As shown in Fig. 6b, electrode 1 exhibited the highest I_{pa} (15.6 μA), whereas electrode 4 showed the lowest (13.8 μA). The resulting RSD of 4.2% demonstrates that the sensor possesses excellent reproducibility.

3.7.3 Repeatability of the sensor

Fig. 6C illustrates the reusability of the sensor by performing six consecutive OFL measurements with the same electrode. The I_{pa} decreased progressively from 16.31 μA in the first cycle to 13.15 μA in the sixth cycle. This decrease is primarily attributed to the loss of active sites on the electrode surface. Nevertheless, after six consecutive desorption–adsorption cycles, the electrode retained 80.6% of its initial response, indicating good reproducibility and confirming its suitability for OFL determination.

3.7.4 Stability of the sensor

Storage stability indicates the sensor's ability to maintain its performance during long-term storage. A stable storage behavior prolongs the sensor's operational lifespan and reduces maintenance costs. We evaluated this by monitoring the electrochemical response toward 10 $\mu\text{mol/L}$ OFL after the sensor had been stored at 4 $^{\circ}\text{C}$ for seven days. As illustrated in Fig. 6D, the sensor displayed an initially high oxidation peak current of 15.34 μA , which gradually decreased over the storage period. After 7 days, the sensor maintained 86% of its initial response, indicating that its electrochemical activity remained stable. The observed decrease in current is likely attributable to partial oxidation or structural degradation of the $\text{Ti}_3\text{C}_2\text{T}_x$ and MWCNT components, as well as surface fouling or passivation of the hybrid materials film, which reduces the number of accessible active sites and impedes the charge-transfer efficiency. Nevertheless, the relatively minor current decrease during the testing period confirms that the sensor maintains acceptable stability under refrigerated conditions and demonstrates its suitability for practical OFL quantification.

3.8 Electrochemical sensing detection of OFL in actual samples

To assess the practical applicability of the developed $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO}-66/\text{GCE}$ sensor, spiked-recovery tests and real-sample analyses were performed using aquatic food samples.

The spiked-recovery experiments utilized the standard-addition protocol, in which three levels of OFL (14.5, 72.3, and 144.6 $\mu\text{g/kg}$) were added to yellow croaker, crucian, perch, shrimp samples, as summarized in Table 2. The method demonstrated excellent recovery values (95.9–110.0%) with RSDs below 4.8% ($n = 3$), indicating that the sensor provides high analytical reliability and accuracy in complex aquatic food samples.

Table 2 Recoveries of OFL in real samples with different spiked concentration

Sample	Spiked ($\mu\text{g/kg}$)	Original ($\mu\text{g/kg}$)	Found ($\mu\text{g/kg}$)	Recovery (%, $n=3$)	RSD (%, $n=3$)
Yellow croaker	14.5	17.2	31.1	95.9	4.8
	72.3	17.2	88.2	98.2	2.9
	144.6	17.2	164.4	101.8	1.8
Crucian	14.5	26.3	40.5	97.9	2.7
	72.3	26.3	98.3	99.6	2.1
	144.6	26.3	173.8	102.0	1.9
Perch	14.5	6.1	20.2	97.2	3.8
	72.3	6.1	75.9	96.5	2.3
	144.6	6.1	153.2	101.7	1.7
shrimp	14.5	1.8	15.9	97.2	3.2
	72.3	1.8	73.0	98.5	2.5
	144.6	1.8	160.8	110.0	1.8

Subsequently, the sensor was used for the precise quantification of OFL in yellow croaker and crucian samples. As illustrated in Table 3, the OFL concentrations determined by the sensor were $17.7 \pm 0.8 \mu\text{g/kg}$ and $26.0 \pm 1.6 \mu\text{g/kg}$, respectively, which are in excellent agreement with those obtained using the Chinese standard HPLC method ($17.2 \pm 0.3 \mu\text{g/kg}$ and $26.3 \pm 0.6 \mu\text{g/kg}$), with no statistically significant difference ($P > 0.05$). These results indicate that the prepared $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$ constitutes a robust platform for OFL detection in aquatic products, highlighting its potential for routine surveillance of antibiotic residues in food products.

Table 3 Determination of OFL in real samples by the proposed $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}$ sensor and the standard HPLC method

Samples	OFL content detected by the proposed sensor ($\mu\text{g/kg}$, $\pm$ SD)	OFL content detected by HPLC method ($\mu\text{g/kg}$, $\pm$ SD)	p
yellow croaker	17.7 ± 0.8	17.2 ± 0.3	0.36
crucian	26.0 ± 1.6	26.3 ± 0.6	0.77

4. Conclusions

This study reports a novel $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}/\text{UiO-66}/\text{GCE}$ electrochemical sensor for the determination of OFL. $\text{Ti}_3\text{C}_2\text{T}_x$, featuring abundant surface functional groups and superior conductivity, serves as the substrate. The integration of MWCNTs not only increases the surface area but also enhances the material's structural stability. UiO-66 combined with $\text{Ti}_3\text{C}_2\text{T}_x/\text{MWCNTs}$ offers efficient adsorption and catalytic sites for OFL in hybrid materials. This approach represents a novel strategy for designing sensors targeting OFL or other less stable nanomaterials. The sensor demonstrates a broad linear range ($0.04\text{--}50.0 \mu\text{mol/L}$) and a low LOD of $0.018 \mu\text{mol/L}$. It also exhibits outstanding stability, reproducibility, and repeatability, rendering it a highly effective sensor for OFL detection and broadening the scope of high-sensitivity electrochemical antibiotic analysis. The successful application of this sensor in aquatic products suggests it constitutes a promising platform for OFL quantification in real food matrices. This sensing platform shows promise for rapid food safety monitoring and early risk identification, which are critical for safeguarding consumer health and promoting human wellness. Future efforts may extend this strategy to other antibiotics and more complex food matrices, as well as portable on-site applications.

Declaration of interests

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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