

Screen-Printed Electrode-Based Sensing of L-Ascorbic Acid Using Metal–Organic Framework Supported Carbon–Palladium-Doped MXene Quantum Dots in Human Serum and Artificial Sweat

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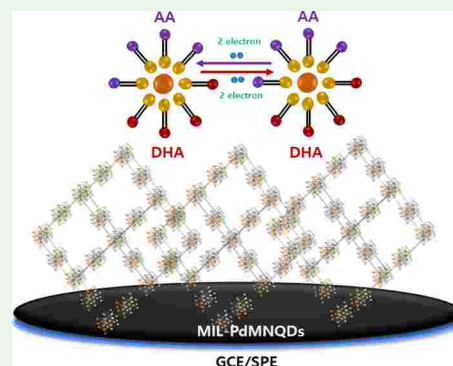
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ABSTRACT: Carbon-doped MXene quantum dots (MNQDs) were synthesized through a hydrothermal reaction involving citric acid and ethylene diamine in the presence of MXene. Palladium nanoparticles were subsequently incorporated into the MNQDs and integrated into an iron-based metal–organic framework, forming MIL-PdMNQDs. The successful synthesis of MIL-PdMNQDs was confirmed by PXRD, SEM, TEM, XPS, and FTIR analyses. Modified glassy carbon and screen-printed electrodes with MIL-PdMNQDs were used to measure L-ascorbic acid concentrations in a phosphate buffer solution, ranging from 10 to 100 nM. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) revealed a linear anodic peak current between 52.05 and 82.44 μA , with a linear regression (R^2) value of 0.9885. In human serum diluted with PBS (5 mL of serum in 95 mL of PBS), the MIL-PdMNQDs-SPE₁ detected ascorbic acid concentrations from 10 to 50 μM , illustrating a DPV redox peak current between 124.39 and 152.54 μA , with an R^2 of 0.9901. Additionally, in artificial sweat, the DPV sensor detected ascorbic acid concentrations ranging from 100 to 1000 μM , with current readings between 11.132 and 64.83 μA and an R^2 value of 0.9903, demonstrating its selective sensing capability. The limit of detection (LOD) for ascorbic acid in PBS using MIL-PdMNQDs-GCE was determined to be 4.705 nM. The MIL-PdMNQDs-GCE and SPE sensors exhibited high stability and exceptional selectivity for ascorbic acid detection.

KEYWORDS: Ascorbic acid, Carbon, Cyclic voltammetry, Differential pulse voltammetry, Metal–organic framework, MXene



INTRODUCTION

Vitamin C is the L-enantiomer of ascorbic acid (AA), and its oxidized form, dehydroascorbate (DHA), is a weak sugar acid structurally analogous to glucose (GL) and lactone.^{1–3} In humans, the inactivation of the L-gulonolactone oxidase (GLO) gene prevents ascorbate synthesis from GL. The antioxidant properties of AA significantly contribute to scavenging reactive oxygen species (ROS), positively impacting malignant tumors.^{4,5} Additionally, AA acts as a pro-oxidant, generating hydrogen peroxide.^{6,7} Using vitamin C as a preventive measure can reduce the duration of the common cold. As a result, it is essential to obtain AA through our diet or supplements to maintain normal metabolism and physiological health. Moreover, vitamin C is water-soluble and easily lost through urine, it requires daily supplementation. To avoid stomach upset from excessive intake of AA and prevent deficiency diseases like scurvy, precise analysis and medication are essential. An adequate concentration of AA in the blood is recognized at 50 μM , while levels below 20 μM are symptomatic of AA deficiency. Colorimetric, fluorescence, and electrochemical techniques are widely used for detecting AA. In the colorimetric approach, the oxidized form of AA serves as the reaction center, binding with a suitable reagent to produce visible light-emitting dyes. A colorimeter is then

employed to measure the color intensity, which varies according to the concentration of AA.^{8,9} Fluorescence detection relies on changes in the intensity of quenched emissions from AA and the prepared material.¹⁰ The interaction involving charge transfer between AA and DHA in the buffer solution and modified electrodes is pivotal in detecting AA through the electrochemical method.^{11–15} Compared to the previously mentioned sensing methods, the electrochemical approach is easier to handle, faster, reagent-free, and cost-effective.^{16,17}

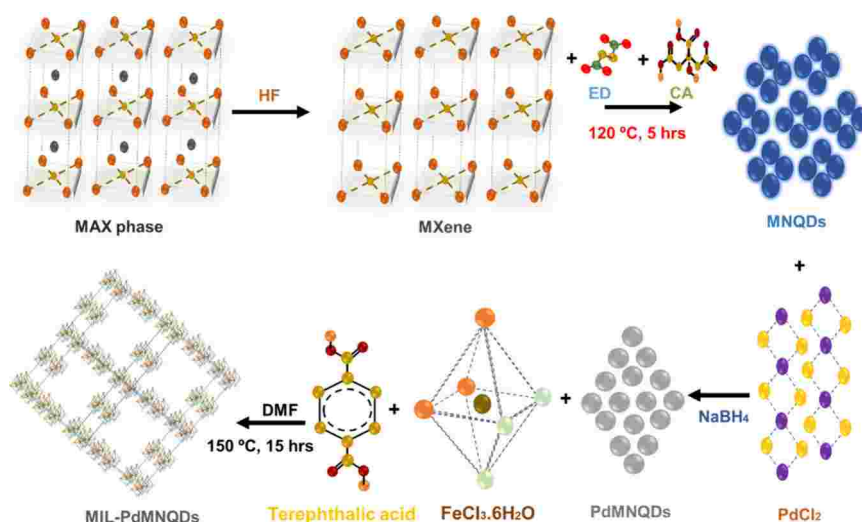
We conducted electrochemical experiments using glassy carbon (GCE) and screen-printed (SPE) electrodes. The practical application of SPE provides a more profitable and portable probe for biological analysis. Therefore, our goal was to develop a highly selective material that is sensitive to AA and capable of detecting it specifically in human serum. For

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Scheme 1. Solvothermal Mode of Synthesis of MXene, MNQDs, PdMNQDs, and MIL-PdMNQDs



selective sensing, composites must be highly conductive, able to adsorb AA selectively, and stable. Materials such as MOFs, MXene, and quantum dots have been proven to be highly effective in detecting AA.^{15,18–21} However, when it comes to selectivity, many materials face challenges due to the presence of chemical analogues of AA like glucose (GL), lactone (LC), uric acid (UA), and dopamine (DA). In this study, we prepared palladium (Pd) supported carbon-doped MXene quantum dots (MNQDs), collectively referred to as Pd-MNQDs.²² The nanostructured MNQDs increase surface area and enhance the interaction and electron transfer during AA sensing.²³ MXenes are two-dimensional (2D) layered inorganic materials with transition metal carbides, nitrides, or carbonitrides. The most common one, Ti_3C_2 , is highly hydrophobic, possesses good mechanical strength, and is flexible.^{24,25} It is used in various applications such as energy storage, water purification, catalysis, and sensors. Despite their potential for diverse applications, the main challenge faced by Ti_3C_2 -based MXenes is their chemical stability. In aqueous and aerobic environments, Ti_3C_2 undergoes oxidation and degradation. In highly acidic and alkaline environments, MXenes degrade, which limits their use in extreme conditions.

Surface functionalization is one of the most effective methods to increase the stability of MXenes. Functionalization using antioxidants can slow down the oxidation process. The chelating effects of citric acid and ethylene diamine protect the MXene surface from further chemical oxidation. Additionally, the physical functionalization of MXenes with conductive metals such as Pd can enhance their stability and improve electrical conductivity.

Similarly, Pd, a member of the platinum family, is characterized by its low density and noble metallic properties.^{26,27} Pd's excellent electrical conductivity and stability will offer additional support for MNQDs during their incorporation. The composite described earlier was integrated into a Fe-based MIL-53 MOF to detect AA specifically. Inspired by prior research on the sensitivity of MIL-53 MOFs to AA, we developed a MIL-53, incorporating Pd-supported MNQDs (MIL-PdMNQDs) for the selective detection of AA. The high porosity and large surface area of MIL-53 enable the incorporation of PdMNQDs into its pores. The breathing effect of MIL-53 induces the pore adjustment, allowing better

integration of PdMNQDs. This structural flexibility enhances AA adsorption and improves the overall sensing mechanism by expanding the active surface area. Furthermore, the ionic Fe framework in MIL-53 facilitates charge transfer during AA sensing. The developed composite demonstrated exceptional selectivity, sensitivity, and stability for the electrochemical sensing of AA using both a GCE and an SPE.

The carbon and palladium-coated MXene quantum dots (MNQDs) increase the chemical stability of MXene, and the combination supported on MIL-53 provides enhanced charge transfer and high chemical and thermal stability. MNQDs exhibit spatial confinement of electron–hole pairs or excitons in one more dimension known as quantum confinement.²⁸ In quantum confinement, the charge transfers more efficiently, which is highly useful in electrochemical sensing applications and probe development. The nanoscale dimensions of MNQDs increase the available active site for the analyte interaction. Surface terminal groups on the MNQDs can form a stable interaction with the other components during the composite preparation. The interaction between the nanosized MXene and carbon-doped palladium lowers the Fermi energy level, improving charge transfer.²⁹ The MIL-PdMNQDs system is highly stable and selectively senses AA at deficient concentrations, making it suitable for practical applications using screen-printed electrodes (SPE).

The redox characteristics of the synthesized MIL-PdMNQDs were initially assessed using the conventional three-electrode system with a glassy carbon electrode (GCE). Subsequently, we performed the sensing experiments, interference studies, and real sample analysis using GCE and SPE. A portable, user-friendly SPE-based probe is much easier than a three-electrode system. The selective detection of AA using SPE demonstrates our material's effectiveness, specificity, portability, and user-friendliness. We analyzed our materials' morphology, physical properties, and chemical composition using various characteristic tools. Voltammetry measurements were performed using a WIZMAC voltammeter.

EXPERIMENTS AND RESULTS

Electrochemical Probes and Equipment. The study examined the electrochemical sensing of AA using three electrode systems: a conventional glassy carbon electrode (GCE) setup, a Metrohm DropSens 250AT screen-printed electrode (SPE_1), and a SPE_2 from

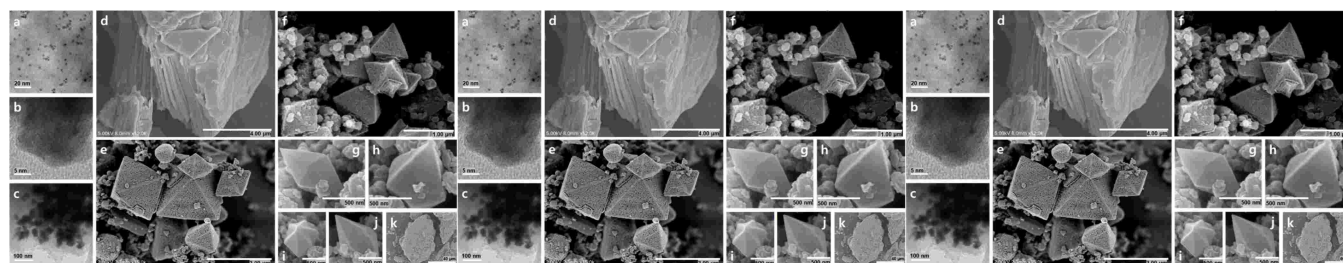


Figure 1. (a) TEM image of MNQDs, (b) TEM image of PdMNQDs, (c) TEM image of MIL-PdMNQDs, (d) SEM image of MXene, (e&f) SEM image of MIL-53, and (f-k) SEM image of MIL-PdMNQDs.

Shenzhen More-Suns Electronics Co., Ltd. (Figure S1(c-e)). The conventional GCE system, with its glassy carbon working electrode (WE) (0.07 cm^2), Ag/AgCl reference electrode (RE), and platinum counter electrode (CE), was chosen for mechanism studies due to its cost-effectiveness. For practical analysis in PBS and human serum, we opted for the Metrohm DropSens 250AT SPE₁, which includes a gold WE, platinum CE, and Ag RE. The Shenzhen SPE₂, incorporating carbon paste for both the working and counter electrodes alongside an Ag reference, was utilized for interference analysis and cost-sensitive applications.

Preparation of MXene. The MXene is prepared from the MAX phase through an etching process (Scheme 1). Ten grams of MAX phase is dispersed in 200 mL of concentrated HF and stirred for 36 h. The acidic mixture was subsequently washed with distilled water and centrifuged at 6000 rpm for 5 min. This washing and centrifugation process was repeated until the pH of the supernatant liquid dropped below 5. The MXene was dispersed in DMSO and stirred continuously for 24 h to achieve delamination. The filtrate was then dried in a vacuum oven at 60°C overnight, and the resulting black MXene powder was stored in a vacuum desiccator for further experiments and analysis.

Preparation of MNQDs. We prepared MXene and C-doped MXene quantum dots (MNQDs) following the methods described in previous studies.²² Ten mg of MXene was dispersed in 10 mL of distilled water. We then added 10 mg citric acid (CA) to this mixture and sonicated it for 10 min to ensure thorough dispersion and delamination of the MXene. We added 500 μL of ethylene diamine (ED) to this mixture and sonicated it again for 10 min. The well-dispersed sample was heated in a Teflon-lined autoclave at 120°C for approximately 5 h. The cooled mixture was subsequently filtered using 0.22 μm syringe filters. The MNQDs filtrate was then stored in the refrigerator at -4°C for future use.

Preparation of PdMNQDs. Ten mg of PdCl_2 was added to the MNQDs filtrate, and the mixture was sonicated for 30 min. The mixture was then stirred for 30 min, after which 100 mM sodium borohydride in 5 mL of distilled water was gradually added drop by drop over 30 min.³⁰ The entire solution was then stirred for about 2 h.

The black-colored PdMNQDs were centrifuged at 4000 rpm for 5 min. The residue was washed three times with water to separate the dispersed PdMNQDs, using centrifugation. Subsequently, it was dried in a vacuum oven at 60°C for around 24 h. The collected sample was stored in a vacuum desiccator for further experiments.

Preparation of MIL-53. The solvothermal method using DMF is adopted to prepare Fe-based MIL-53. 135 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 83 mg of terephthalic acid (TPA) were dissolved separately in 35 mL of DMF.^{31–33} First, the ferric solution was transferred into a 100 mL Teflon tube, and the ligand solution was added to the same tube. The mixture was then autoclaved at 150°C for approximately 15 h to carry out the solvothermal synthesis of MIL-53. The prepared sample was washed three times with DMF, dried in a vacuum dryer for about 24 h, and then stored in a vacuum desiccator for further analysis.

Preparation of MIL-PdMNQDs. The PdMNQDs prepared earlier were dispersed in 20 mL of DMF using sonication (Scheme 1). Following this, 135 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in the same solution, and 83 mg of TPA was added to the reaction mixture. The entire mix underwent thorough sonication for 10 min. The reaction mixture was transferred into a Teflon-lined autoclave and heated to 150°C for 15 h. The resulting black-colored MIL-PdMNQDs were washed with DMF and dried under vacuum for 24 h. After drying, the samples were stored in a vacuum desiccator for subsequent analysis and electrochemical applications.

Morphological Investigation of the Prepared Materials. Morphologically, MNQDs are yellow in the aqueous phase and turn solid after freeze-drying (Figure S1a). Both PdMNQDs and MIL-PdMNQDs are black, while MIL-53 appears yellowish-orange after preparation and purification. MNQDs is fluorescent and emit blue in a fluorometer, while the other composites are nonfluorescent (Figure S1b). We prepared MXene and MNQDs using acidic etching and hydrothermal methods (Scheme 1). The SEM morphology of MXene demonstrates a two-dimensional, layered sheet-like structure (Figure 1d & Figure S2a). TEM analysis reveals that the MNQDs are around 5 nm in size (Figure 1a & S1a), and the SAED pattern indicates they are polycrystalline (Figure 2a). TEM EDX analysis confirms the presence of C, N, O, and Ti in the synthesized MNQDs (Figure S3).

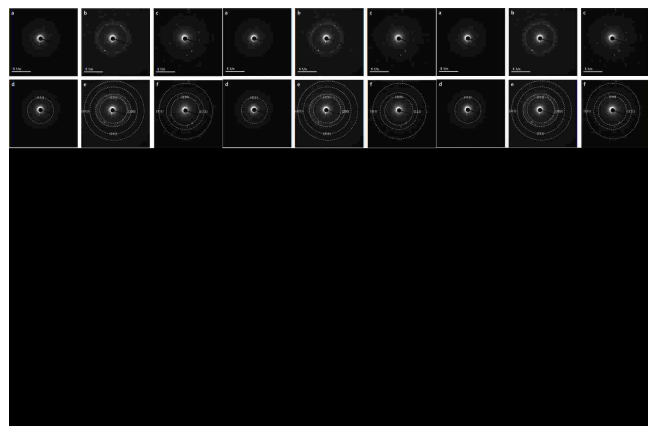


Figure 2. (a&d) SAED pattern of MNQDs, (b&e) SAED pattern of PdMNQDs, and (c&f) SAED pattern of MIL-PdMNQDs.

We used TEM & SEM (Figure 1b & S4) to assess the nanolevel shapes of PdMNQDs. TEM analyses confirm that the PdMNQDs are fine polycrystalline particles, about 15–20 nm in size. SEM and TEM EDX analysis confirmed that these particles have evenly distributed Pd and MNQDs (Figure S4 & S5). The SEM images represent that MIL-S3 has a rough surface and octahedral shape with edge lengths of about 500 and 250 nm (Figure 1e&f and S6). The morphology of MIL-S3 is primarily octahedral, though some irregular structures are also present in the sample, indicating that occasional uneven shapes are observed while the dominant shape is octahedral. MIL-PdMNQDs have an octahedral shape with a smoother surface than MIL-S3, suggesting successful composite formation without Pd oxidation (Figure 1(g–k) & S2(b–d)). Like MIL-S3, twinned octahedra are the most prominent shapes observed in the sample, along with some irregular forms in the MIL-PdMNQDs. TEM imaging of MIL-PdMNQDs reveals a structure closely resembling MIL-S3, as illustrated by SEM analysis, with a smooth octahedral morphology (Figure 1c and S8(a)). The TEM image of single octahedra indicates that MIL-PdMNQDs have edge lengths of

approximately 500 and 250 nm, consistent with the SEM morphology (Figure 1(g–j) and S8(a)). SEM and TEM analyses confirm the presence of Ti, Pd, and N along with Fe, C, and O in the synthesized MIL-PdMNQDs (Figure S7), verifying the successful preparation of the composite.

The crystallinity of the synthesized MNQDs was assessed using Selected Area Electron Diffraction (SAED) pattern analysis (Figure 2a&d). The spot pattern in the SAED confirmed the polycrystalline structure of the MNQDs. The measured d -spacing from the prominent rings in the SAED pattern, at 2.55 Å, corresponded to the (111) lattice plane of the MNQDs (Figure 2d). For the PdMNQDs, the SAED pattern also indicated a polycrystalline nature, confirming that the PdMNQDs have an FCC (face-centered cubic) structure (Figure 2b&e).³⁴ The interplanar distances obtained from the four prominent rings in the SAED pattern were 2.45 Å, 2.01 Å, 1.45 Å, and 1.25 Å, corresponding to the (111), (200), (211), and (221) lattice planes of the PdMNQDs (Figure 2e). For MIL-PdMNQDs, the SAED pattern revealed a polycrystalline orthorhombic structure, consistent with a BCC (body-centered cubic) arrangement (Figure 2(c&f)).^{35,36} This structure originates from the parent $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ metal node, which crystallizes in an orthorhombic form. In this parent structure, Fe^{3+} is octahedrally coordinated by water molecules and surrounded by Cl^- ions. The interplanar distances derived from the three prominent rings in the SAED pattern were 2.18 Å, 1.33 Å, and 1.1 Å, corresponding to the (110), (111), and (220) lattice planes of the MIL-PdMNQDs (Figure 2f). The presence of the (110) plane confirms the crystallinity of MIL-S3, in agreement with previous studies. Additionally, the (111) and (311) planes indicate the presence of PdMNQDs in the composite material.

HRTEM was employed to examine the lattice fringes of PdMNQDs and MIL-PdMNQDs (Figure S(8b&c)).³⁷ Incorporating PdMNQDs into MIL-S3 significantly enhances electrical conductivity, especially in detecting AA. The HRTEM analysis revealed that PdMNQDs displayed a lattice fringe spacing of 0.224 nm, corresponding to the (111) plane (Figure S8b). The SAED pattern already demonstrated diffraction at (111), confirming the presence of palladium in the PdMNQDs. Additionally, the HRTEM analysis of MIL-PdMNQDs displayed a fringe width of 0.202 nm, which

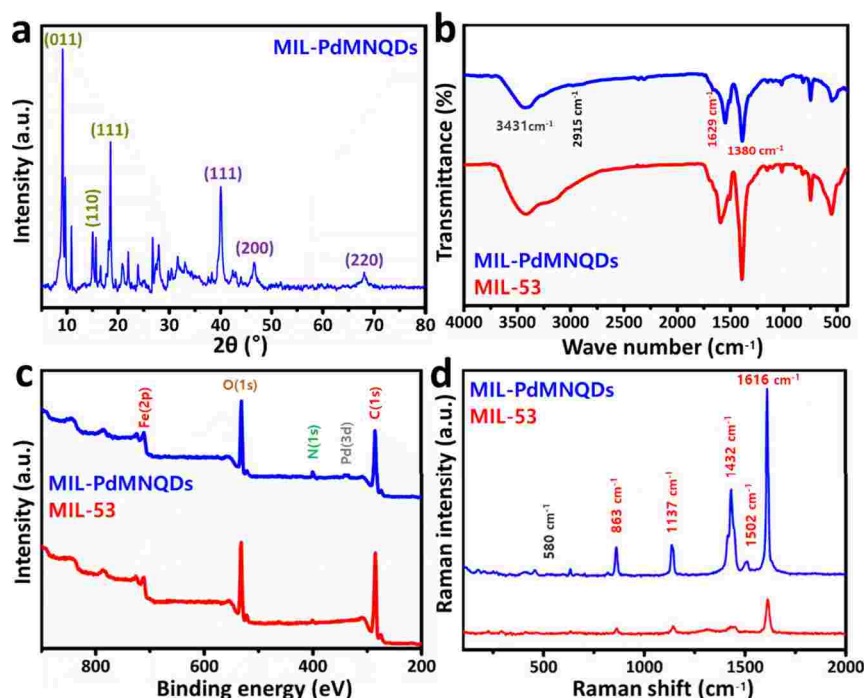


Figure 3. (a) XRD spectra of MIL-PdMNQDs, (b) FTIR spectra of MIL-S3 & MIL-PdMNQDs, (c) XPS total survey spectra of MIL-S3 & MIL-PdMNQDs, and (d) Raman spectra of MIL-S3 & MIL-PdMNQDs

produced a SAED pattern at (110), verifying the successful synthesis of MIL-53 with the inclusion of PdMNQDs (Figure S8c).

PXRD of the prepared sample is crucial for determining its phase composition, orientation, and crystallinity. In our research on developing a composite for selective AA sensing, we conducted PXRD analysis on MIL-53, MXene, PdMNQDs, and MIL-PdMNQDs (Figure 3a & Figure S9(a-d)). The bonding in MIL-53 and MIL-PdMNQDs is characterized by coordinated interactions between Fe^{3+} or iron oxide to the terephthalate anion. The high dipole moment of DMF facilitates an ideal environment for the deprotonation of terephthalic acid to terephthalate at higher temperatures. The PXRD plot's sharp peak strongly supports the prepared material's crystalline nature. The successful synthesis of MIL-53 and MIL-PdMNQDs MOF is demonstrated by characteristic peaks at 9.5° , 12.5° , and 18.2° in the PXRD patterns (Figure 3a & S9(a&b)) attributed to the (011), (110), and (111) planes of MIL-53 MOF. The persistence of the 9.5° peak indicates that the crystalline structure of MIL-PdMNQDs remains unchanged, preserving the integrity of the original MOF. XRD analysis of the synthesized MXene and PdMNQDs was also conducted for crystallographic assessment (Figure S9(b&c)). The distinct peaks at around 9.6° and 18.6° , corresponding to the (002) and (004) planes of Ti_3C_2 , confirm the successful transformation of MXene from its MAX phase precursor (Figure S9b). The PdMNQDs diffraction pattern displays characteristic peaks at 40° (111), 46° (200), and 67° (220), aligning with the face-centered cubic (FCC) structure of Pd nanoparticles (Figure S9d). The presence above three peaks in the XRD pattern of MIL-PdMNQDs confirms the successful integration of PdMNQDs into the MIL-53 structure (Figure S9(c&d)). The peaks at 18.5° and 30.44° degrees indicate the diffraction from (111) and (202) planes of iron oxide in the MIL-PdMNQDs. The SEM and TEM images reveal some irregular shapes other than the octahedra is from the oxides of iron.

Notably, the Miller indices from the SAED pattern analysis align with the XRD findings for PdMNQDs and MIL-PdMNQDs (Figure 2 & Figure S9d). The three prominent rings in the SAED pattern of MIL-PdMNQDs, measured at 2.18 Å, 1.33 Å, and 1.1 Å, correspond to the (110), (111), and (311) lattice planes. The 14.9° and 20.84° peaks are attributed to the (110) and (311) plane of the MIL-53 MOF, while the diffraction peaks for the (111) plane confirm the inclusion of PdMNQDs in the composite. Also, the Miller indices derived from the HRTEM analysis are consistent with the XRD data (Figure S8b&c). The diffraction pattern of PdMNQDs illustrates distinct peaks at 40° (111), 46° (200), and 67° (220), corresponding to the FCC structure of palladium. The presence of these three peaks in the XRD pattern of MIL-PdMNQDs confirms the successful incorporation of PdMNQDs into the MIL-53 framework. Furthermore, the XRD diffraction peak associated with the fringe width of MIL-PdMNQDs was determined to be 0.202 nm, which produced a SAED pattern at (110) and revealed a peak at 14.9° in the XRD spectrum (Figure S8c & Figure S9d). This supports the successful synthesis of MIL-53 with incorporated PdMNQDs.

Chemical Investigation of the Prepared Material. To evaluate the nature of chemical bonding, we conducted the FT-IR on MIL-53, MXene, PdMNQDs, and MIL-PdMNQDs (Figure 2b and S10 (a-d)). The strong absorption band 3431 cm^{-1} is from the adsorbed water moiety in the prepared sample. The peak at 1629 cm^{-1} is from the stretching vibration of the $-\text{COO}-$ bond in the MIL-53 and MIL-PdMNQDs, confirming the presence of terephthalate in the MOF (Figure S10(c&d)). The symmetric and asymmetric stretching vibrations of the $-\text{C}-\text{O}-\text{C}$ bond result in two peaks at 1524 cm^{-1} and 1380 cm^{-1} , respectively, indicating the presence of the terephthalate group in the structure. The $-\text{C}=\text{O}$ bond stretching vibration in the carboxylate group produces a peak at 1671 cm^{-1} . The bending vibration of the OH group in $\text{Fe}-\text{O}(\text{H})-\text{Fe}$ gives a peak at 863 cm^{-1} , while the peak at 747 cm^{-1} corresponds to the C-H bending from the benzene ring of terephthalate. Additionally, the $\text{Fe}-\text{O}$ vibration shows an absorbance of 532 cm^{-1} in both MIL-53 and MIL-PdMNQDs. The peak at 574 cm^{-1} corresponds to the Ti-O stretching, confirming the successful

synthesis of Ti_3C_2 from Ti_3AlC_2 (Figure S10(a)). The C-H stretching observed at 2915 cm^{-1} in both PdMNQDs and MIL-PdMNQDs confirms the presence of $\text{sp}^2\text{ C}$ in both composites (Figure S10(b&d)). These results indicate the successful incorporation of PdMNQDs into MIL-53, forming the MIL-PdMNQDs composite.

We conducted XPS analysis on the synthesized MXene, PdMNQDs, MIL-53, and MIL-PdMNQDs to evaluate their chemical stability and verify successful synthesis (Figure 3c& S11(a-g)). The total survey spectrum of MXene reveals peaks for Ti ($2p_{1/2}$ & $2p_{3/2}$) and C at 456.72 and 285.5 eV, respectively (Figure S11a). The lack of an Al peak at 398.3 eV confirms the effective transformation of Ti_3AlC_2 to Ti_3C_2 through the etching process (Figure S11a). The XPS peak of Pd, N, and C at 336, 399.65, and 285.5 eV in the total survey spectrum further supports the successful synthesis of PdMNQDs (Figure S11a). The surface modification of Pd around the MNQDs accounts for the absence of a Ti peak, likely due to the surface-sensitive characteristics of XPS. For MIL-53, the total survey spectrum indicates the presence of Fe, O, and C at 712.1, 531.79, and 285.5 eV, respectively, confirming the successful synthesis of MIL-53 (Figure 3c). In the final product, the peaks corresponding to Fe, Pd, N, C, and O in the survey spectrum validate the successful formation of MIL-PdMNQDs (Figure 3c).

For a more in-depth analysis, we concentrated on the deconvolution spectra of the prepared samples (Figure S11(b-g)). The presence of the N(1s) peak in both PdMNQDs and MIL-PdMNQDs confirms the incorporation of MNQDs in the prepared samples (Figure S11(b&c)). The peaks at 334 and 340 eV in PdMNQDs and MIL-PdMNQDs confirm the presence of Pd(3d) in the samples (Figure S11(d&e)). The deconvolution spectra from MIL and MIL-PdMNQDs illustrate two peaks at 712 and 725 eV, corresponding to Fe ($2p_{2/3}$) and Fe ($2p_{1/2}$), which confirms the successful preparation of the MIL-53 and MIL-PdMNQDs (Figure S11(f&g)). Consequently, the retained binding energy observed for Pd in both MIL-PdMNQDs and PdMNQDs confirms that Pd maintained its zero-oxidation state even after incorporation into MIL-53, verifying the successful integration of PdMNQDs within the MIL-53 structure. Furthermore, the surface atomic percentages for MIL-53 were determined as 40.12% C(1s), 11.52% O(1s), 1.27% Fe(2p), and 0.83% N(1s). For PdMNQDs, the atomic composition was found to be 31.05% C(1s), 3.81% N(1s), 3.01% Pd(3d), and 15.92% O(1s). In the case of MIL-PdMNQDs, the composition is 37.12% C(1s), 12.26% O(1s), 2.14% N(1s), 1.65% Fe(2p), and 0.21% Pd(3d). XPS analysis confirms that PdMNQDs is integrated into MIL-53 without altering the oxidation state or chemical nature of the PdMNQDs.

We conducted Raman spectroscopy on MXene, MIL-53, and MIL-PdMNQDs to examine the prepared materials' bonding characteristics and crystalline structure (Figure 3d & S12(a-c)). The presence of sharp absorption peaks in the Raman spectra verifies the crystalline nature of the synthesized materials. The A_{1g} (205 cm^{-1}) and E_g (255 cm^{-1}) peaks in the MXene Raman spectra reflect the vibrations of fluoride groups on the titanium surface (Figure S12a).³⁸ Meanwhile, the E_g and A_{1g} peaks at 580 and 725 cm^{-1} represent carbon vibrations within the MXene structure (Figure S11a). The presence of six peaks in the spectra confirmed the successful synthesis of MIL-53 and the MIL-PdMNQDs composite (Figure 3d & S12(b&c)). The peak at 634 and 863 cm^{-1} confirms the presence of aromatic C-H bonds in the synthesized materials. The peak at 1137 cm^{-1} confirms the bonds between two sp^2 hybridized carbon atoms in the benzene ring and carboxylate groups. The 1432 and 1502 cm^{-1} peaks are attributed to the asymmetric and symmetric stretching vibrations of the $-\text{COO}-$ linkers. The peak confirms the stretching of the aromatic $\text{C}=\text{C}$ bond at 1616 cm^{-1} . The light peak at 580 cm^{-1} in MIL-PdMNQDs is attributed to carbon vibrations from Ti_3C_2 . Although Raman spectroscopy is typically insensitive to neutral Pd, the presence of Pd enhances the Raman signal in MIL-PdMNQDs relative to MIL-53 through surface-enhanced Raman scattering (SERS), serving as an indirect confirmation of Pd incorporation.

Porosity Studies. As illustrated in Figure S13, adsorption isotherms for MIL-53 and MIL-PdMNQDs were performed at 77

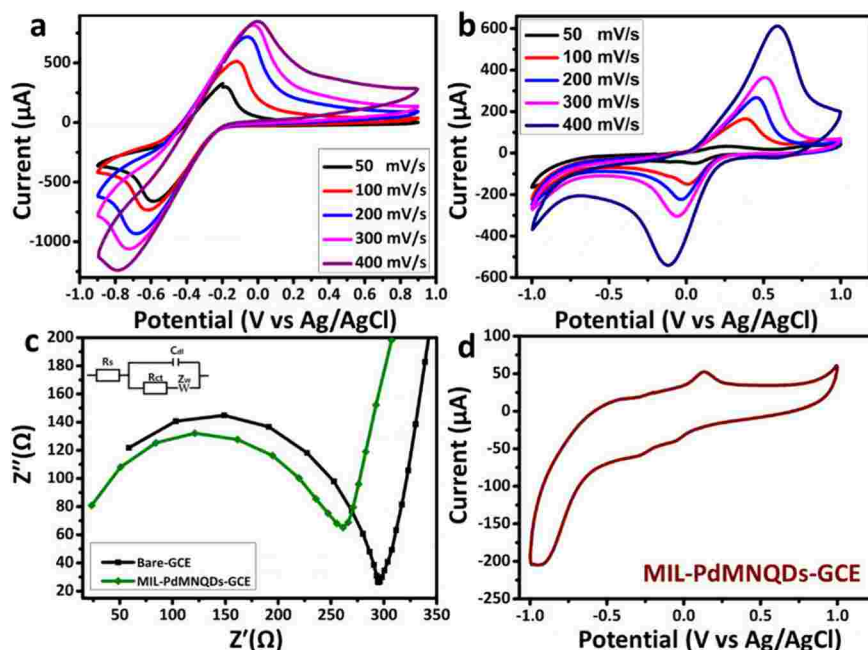


Figure 4. (a) CV at various scan rates using MIL-PdMNQDs-GCE in $[\text{Ru}(\text{NH}_3)_6]^{3+}$, (b) CV at various scan rates using MIL-PdMNQDs-GCE in $[\text{Fe}(\text{CN})_6]^{3-/4-}$, (c) Nyquist plot in PBS comparing bare GCE and MIL-PdMNQDs-GCE, and (d) CV at a scan rate of 100 mV/s in the presence of 10 nM AA using MIL-PdMNQDs-GCE.

K and up to 1 bar. Before the adsorption experiments, 0.0858 g of MIL-53 and 0.0684 g of MIL-PdMNQDs were degassed overnight at 200 °C. In both cases, the BET curve displays an initial concave phase at low pressure, a linear phase, and a convex phase at high pressure along the x -axis. The material isotherm graph demonstrates a gradual increase in adsorption and illustrates a plateau peak at high-pressure reign, confirming the mesoporous nature of the prepared sample (Figure S13a&c). The H3-type hysteresis loop suggests irregular pore sizes in both MIL-53 and MIL-PdMNQDs. For MIL-53, the BET surface area is 383.9 m²/g, with a pore volume of 0.3489 cm³/g and an average pore size of 3.43 nm (Figure S13b). When PdMNQDs are incorporated, the resulting MIL-PdMNQDs illustrate a BET surface area of 249.61 m²/g and a pore volume of 0.1904 cm³/g, with a slightly smaller pore size of 2.96 nm (Figure S13d). The decrease in surface area and pore volume in MIL-PdMNQDs, compared to MIL-53, is due to the inclusion of PdMNQDs.

Electrochemical Optimization and Sensing Experiment in PBS and Human Serum. We developed various materials for AA sensing and investigated its electrochemical activity using different modified GCEs. MIL-PdMNQDs is the best composite for selectively detecting AA among various interferents and can detect it at very low concentrations. As part of our electrochemical optimization, we assessed the zeta potential and conductivity of MIL-PdMNQDs (Figure S14a&b). The zeta potential represents the potential difference between the Stern layer and the slipping plane. We used an ELSZ zeta potential analyzer to measure the zeta potential and conductivity of MIL-PdMNQDs. By dispersing MIL-PdMNQDs in ethanol at very low concentrations, we found that the zeta potential was 7.31 mV, and the conductivity was 0.0181 mS/cm.

The complexes $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ are well-known and widely used in research to optimize the electrochemical properties of various novel electrodes. $[\text{Ru}(\text{NH}_3)_6]^{3+}$ is positively charged, while $[\text{Fe}(\text{CN})_6]^{3-/4-}$ is negatively charged. For a preliminary comparison, we performed single-electron charge transfer studies using the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ complexes (Figure S15(a-d)). A 1 mM solution of each complex was prepared in Milli-Q water as the solvent, and CV was conducted on both the bare electrode and the MIL-PdMNQDs modified GCE. The peak current increased from 40.73 to 510.88 μA , and the electrochemically active surface area (ECSA) for the MIL-PdMNQDs-GCE was determined

to be 0.31 cm², compared to 0.025 cm² for the bare GCE with $[\text{Ru}(\text{NH}_3)_6]^{3+}$ as the analyte (Figure S15a&b). A similar trend was noted in the analysis of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ complex, where the modified GCE demonstrated a peak current of 166.72 μA , an increase from 73.16 μA (Figure S15c&d). The ECSA rose from 0.045 to 0.103 cm². These preliminary results prove that the prepared MIL-PdMNQDs-GCE is highly effective for charge transfer.

The ECSA was calculated from the peak current using the Randles-Sevcik equation (eq 1). Here, (I_p) represents the peak anodic current, (n) is the number of electrons transferred in the charge transfer process, (A) is the ECSA, (D) is the diffusion coefficient of the redox species (cm²/s), (C) is the concentration (mol/cm³), and (γ) is the scan rate (V/s).

$$A = \frac{I_p}{(2.69 \times 10^5) n^{3/2} \times D^{1/2} \times C \times \gamma^{1/2}} \quad (1)$$

The ECSA indicates the surface area available for electron transfer between the electrode and electrolyte during an electrochemical process. We compared the ECSA of bare GCE, MNQDs, Pd, MIL-53, PdMNQDs, and MIL-PdMNQDs modified GCE using CV (Figure S16(a-f)). The CV experiment utilized a 1 mM redox couple $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in distilled water as the solute-solvent system. Using the Randles-Sevcik equation (eq 1), we calculated the ECSA from the bare GCE to MIL-PdMNQDs modified GCE as 0.045, 0.046, 0.061, 0.063, 0.0294, and 0.103 cm², respectively. Carbon and palladium-coated MXene quantum dots embedded within the pores of MIL-53 enhance the chemical stability of MXene.³⁹ This combination, supported by MIL-53, facilitates improved charge transfer and offers high chemical stability. The interaction between the nanosized MXene and carbon-doped palladium within the MIL-53 framework reduces the Fermi energy level. Altogether, an increase in the ECSA, which in turn enhances the single-electron charge transfer in $[\text{Fe}(\text{CN})_6]^{3-/4-}$.

The surface charge and defects in MXene, PdMNQDs, and MIL-PdMNQDs are crucial in determining their electrochemical performance. HF-etched MXene typically carries a negative charge due to F[−] ions, which helps improve its dispersion in aqueous solutions. In contrast, palladium generally has a neutral or slightly positive charge in its pure form. When palladium is functionalized on the negatively charged MXene, it forms PdMNQDs. MXene helps to cover the

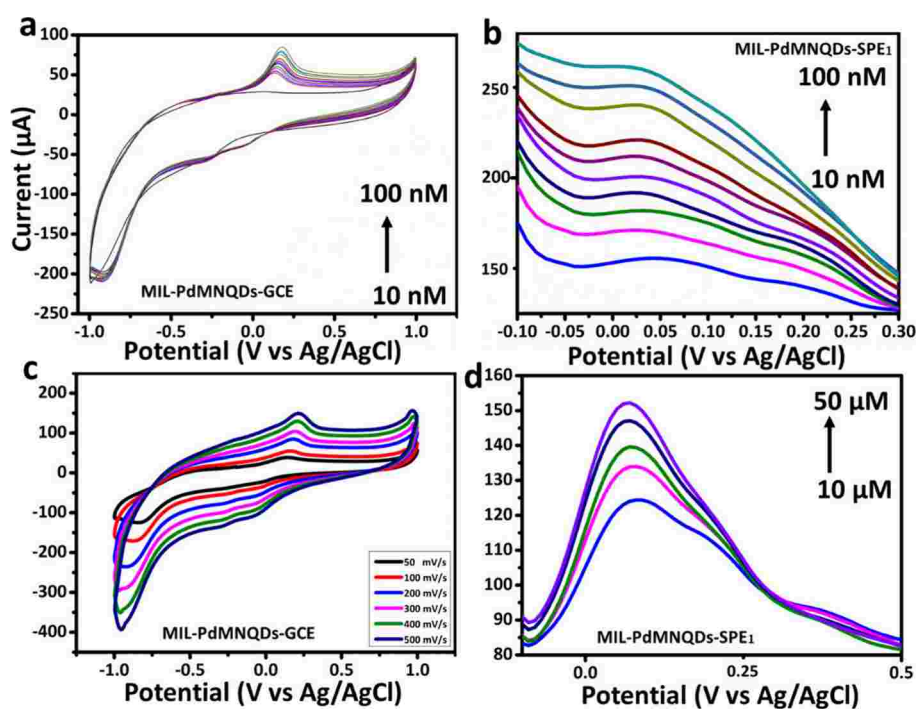


Figure 5. (a) CV plot for MIL-PdMNQDs-GCE in concentrations ranging from 10 to 100 nM in 1 mM PBS at pH 7.4, (b) DPV plot for MIL-PdMNQDs-SPE₁ in the same concentration range in 1 mM PBS at pH 7.4, (c) CV at various scan rates for MIL-PdMNQDs-GCE in the presence of 20 nM AA, and (d) CV plot for MIL-PdMNQDs-SPE₁ across concentrations of 10 to 50 μ M in 1 mM human serum-PBS at pH 7.4.

structural defects in palladium. The increase in peak current observed for PdMNQDs-GCE compared to MNQDs-GCE indicates improved defect correction and enhanced hopping mode of charge transport, supporting single-electron charge transfer in the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ system. The breathing effect in MIL-53 leads to pore adjustment in the presence of PdMNQDs within the reactant mixture, enabling their successful incorporation into the pores of MIL-53 to form MIL-PdMNQDs. The increased peak current for MIL-PdMNQDs-GCE compared to PdMNQDs-GCE alone confirms the single-electron charge transfer in the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solute. In this process, PdMNQDs serve as charge carriers through a hopping mechanism within MIL-53, creating an efficient composite for charge transfer.

A kinetic investigation of a single electron transfer reaction involving $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and $\text{Fe}(\text{CN})_6^{3-/4-}$ was performed using MIL-PdMNQDs-GCE (Figure 4(a&b)) at various scan rates. We optimized the redox reaction using a 1 mM metal complex in PBS at pH 7.4. A strong correlation was found between $\log(\text{scan rate})$ and $\log(\text{anodic current})$ for both complexes. For the positively charged ruthenium complex, the correlation coefficient (R^2) was 0.9721, with a slope of 0.5049, indicating a diffusion-controlled charge transfer mechanism (Figure S17a). Similarly, for the negatively charged iron complex, the R^2 was 0.9966, with a slope of 0.2047, also confirming a diffusion-controlled mechanism (Figure S17b).

The charge transfer resistance (R_{ct}) of Bare, MIL, MNQDs, PdMNQDs, MIL-PdMNQDs, and MXene-modified GCEs was evaluated using Nyquist plots derived from their electrochemical impedance spectra (Figure 4c and S18(a-f)). R_{ct} measures the charge transfer resistance between the electrolyte and the electrode surface. The Nyquist plot confirms that the MIL-PdMNQDs-GCE has a lower semicircular curvature, indicating higher electron conductivity than the other modified GCEs. The MIL-PdMNQDs-GCE exhibit a lower R_{ct} value of 238.14 Ω , demonstrating superior conductivity to the other modified GCEs (Figure 4c). The MIL-PdMNQDs-GCE illustrates a lower R_{ct} value of 238.14 Ω , indicating better conductivity than the other modified GCEs.

In comparison, the bare GCE has R_{ct} value of 285.3 Ω , reflecting a higher electron transfer resistance between the electrolyte and the bare GCE. This decrease in charge transfer resistance is due to the

hopping mechanism involved in the conductivity. The PdMNQDs incorporated into MIL-53 act as charge carriers, which reduces the charge transfer resistance between the MIL-PdMNQDs-GCE and the electrolyte.

We optimized the redox performance of bare GCE, MNQDs-GCE, MIL-53-GCE, PdMNQDs-GCE, MIL-MNQDs-GCE, and MIL-PdMNQDs-GCE for detecting 10 nM AA in PBS (Figure 4d & S19(a-f)). As expected, only MIL-PdMNQDs-GCE gives a response to AA at such a low concentration, producing an anodic peak current of 51.51 μ A at 0.141 V. This result validates the combined sensing mechanism utilizing Fe-based MIL-53 MOF, Pd, and MNQDs. The carbon and palladium-coated MNQDs enhance MXene's chemical stability, while their support on MIL-53 increases charge transfer and boosts chemical and thermal robustness. MNQDs display quantum confinement, where spatial restriction of electron-hole pairs in one or more dimensions enables efficient charge transfer, making them ideal for electrochemical sensing and probe development.^{28,40,41} The nanoscale size of MNQDs increases active sites for analyte interaction, and surface terminal groups on the MNQDs establish stable interactions with other composite components. The interaction between the carbon-doped palladium and nanosized MXene lowers the Fermi energy level, enhancing charge transfer. MIL-53's high porosity and large surface area accommodate PdMNQDs within its pores, and the material's "breathing" effect can facilitate better PdMNQDs integration. This structural flexibility amplifies AA adsorption, increasing the active surface area improves the sensing mechanism. Additionally, the ionic Fe framework in MIL-53 supports effective charge transfer during AA sensing.

A pH of 7.4, often identified as physiological pH, typically ranges from 7.35 to 7.45. Physiological pH is crucial for most metabolic reactions in human serum, supporting the stability of enzymes and protein structures essential for cellular and metabolic responses.⁴⁰ Artificial sweat, with a slightly acidic pH, ion content, and molecular composition similar to human sweat, is an ideal medium for trialing wearable sensors that monitor diagnostic biomarkers. Urine, containing critical diagnostic markers, offers a convenient sampling method for regular health monitoring, making it valuable for early disease detection. In our study, we performed CV, DPV, and

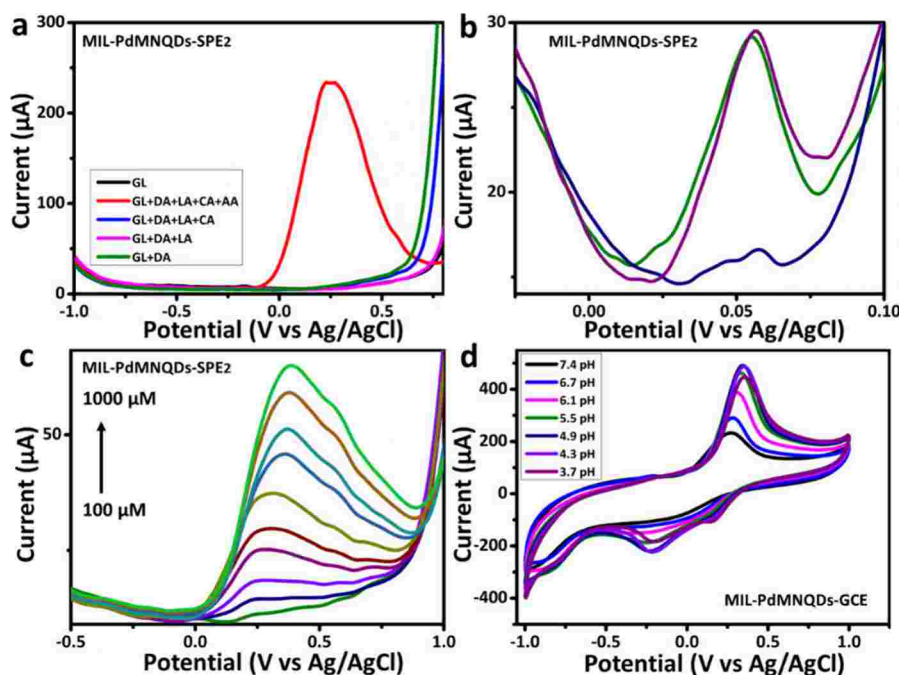


Figure 6. (a) Interference response of MIL-PdMNQDs-SPE₂ toward various interferents in 1 mM PBS at pH 7.4, (b) comparison of interference responses of 200 nM AA and UA with MIL-PdMNQDs-SPE₂ in PBS, (c) sensing response of MIL-PdMNQDs-SPE₂ to AA in concentrations from 100 to 1000 μ M in artificial sweat solution, and (d) effect of pH variation on MIL-PdMNQDs-GCE in 1 mM PBS at 500 nM AA.

chronoamperometry in human serum and artificial sweat across a pH range from 7.4 to 6.5. These experiments aimed to analyze the electrochemical performance of MIL-PdMNQDs-GCE and SPE for AA sensing, encompassing both basic and acidic conditions, including the physiological pH range.

We attempted to detect AA in PBS within the 10 to 100 nM range using the CV and DPV technique with MIL-PdMNQDs-GCE (Figure 5a) and MIL-PdMNQDs-SPE₁ (Figure 5b). The CV sensing experiment generated a linear anodic peak current ranging from 52.05 to 82.44 μ A. The mathematical linearity derived from the sensing experiment gives an R^2 value of 0.9885 (eq 2) along with a slope equation of (Figure S20a).

$$y = 0.3269x + 47.825 \quad (2)$$

$$\text{LOD} = 3.3S_y/S \quad (3)$$

By employing eqs 2 and 3, we calculated the detection limit as 4.705 nM, where S_y represents the standard deviation and S denotes the slope of the linear graph.

We conducted the AA sensing from 10–100 nM using a Metrohm DropSens electrode (SPE₁), consisting of a gold WE, a platinum CE, and a silver RE. The DPV sensing using MIL-PdMNQDs-SPE₁ generated a linear anodic peak current ranging from 156.32 to 261.42 μ A (Figure S20b). The mathematical linearity derived from the sensing experiment gives an R^2 value of 0.9952 (eq 4) along with a slope equation of (Figure S20b).

$$y = 1.1484x + 145.64 \quad (4)$$

By employing the eqs 4 and 3, we calculated the detection limit as 7.53 nM.

The sensing mechanism of AA using MIL-PdMNQDs-GCE was investigated through scan rate experiments. Scan rate refers to the rate of potential change over time. We conducted scans ranging from 50 to 500 mV/s, resulting in an anodic current range of 37.66 to 152.83 μ A (20 nM AA in PBS) (Figure 5c). To verify whether the mechanism of AA sensing is controlled by adsorption or diffusion, we plotted a log graph of scan rate versus current (Figure S20(c)). The slope of 0.5632 from the log–log graph confirms that adsorption predominates in the sensing mechanism of AA using MIL-PdMNQDs-GCE. Double layer capacitance (C_{dl}) refers to the stored charges aligned between the

electrolyte and the modified GCE surface. C_{dl} can be calculated from the slope of the current density versus the scan rate plot, which is 0.0034 μ F/cm² (Figure S20d).

SPEs are cost-effective, easy to fabricate, portable, require minimal samples for analysis, and are disposable. These advantages make them a preferred choice for sensing biomolecules over the traditional three-electrode system. We used Metrohm DropSens SPE₁ to study the redox response of AA in human serum (HS) mixed with PBS in the physiological range. A solution of 5 mL HS in 95 mL PBS (pH 7.4) was prepared, and the redox response of AA, ranging from 10 to 50 μ M, was evaluated using MIL-PdMNQDs-SPE₁. The MIL-PdMNQDs-SPE₁ demonstrated redox peak currents ranging from 124.39 to 152.54 μ A, with an R^2 value of 0.9901 (Figure 5d & S21(a)). This linear range verifies the detection of AA in HS-PBS, aligning with the normal threshold range for adequate AA levels.

AA Sensing Mechanism with MIL-PdMNQDs-SPE: Interference and pH Effects. The electrochemical method is the most commonly utilized probe system globally due to its simplicity of operation, portability, and high sensitivity. In electrochemical sensing, the primary mechanism involves the redox conversion of AA to dehydroascorbic acid (DHA) at a specific potential, releasing two electrons and two protons. For the MIL-PdMNQDs-GCE, this AA-to-DHA conversion occurs at 0.41 V, while for the Metrohm-based probe with MIL-PdMNQDs-SPE₁, it takes place at 0.05 V. AA, also known as ketolactone, contains two ionizable hydroxyl groups in its furan-2-one ring. At physiological pH (7.4), AA is the monoanion (AscH^-) with a pK_1 value of 4.2. AscH^- donates an electron upon oxidation, forming the ascorbate radical ($\text{Asc}^\cdot$), which subsequently converts to the keto derivative DHA, with a pK_2 value of 11.6. The electron released from AA is detected by the MIL-PdMNQDs-GCE or SPE₁, with peak current varying based on the AA concentration in the analyte solution. At higher concentrations, the analyte adsorbs onto the MIL-PdMNQDs-SPE₁ surface, interacting with the active sites on the working WE and also with the platinum CE.²⁰ This adsorption generates a high oxidation peak current in a lower current range (Figure 5d). In contrast, at lower concentrations (10–100 nM), all analytes are directed to the WE, resulting in an oxidation peak current in a higher current range but with lower peak intensity (Figure 5b). Additionally, the AA converts to Acs-, forming a nonconductive, irreversible layer that hinders further sensing and reduces peak

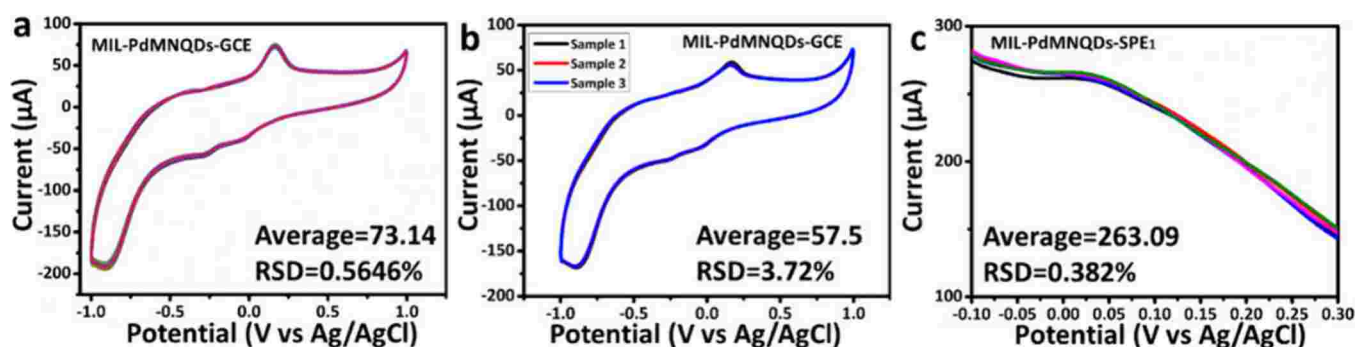


Figure 7. (a) Stability assessment of MIL-PdMNQDs-GCE in 1 mM PBS at 100 nM AA, (b) reproducibility assessment of MIL-PdMNQDs-GCE in 1 mM PBS at 20 nM AA, and (c) storage stability assessment of MIL-PdMNQDs-SPE₁ at 100 nM AA.

current. The formation of a black-colored layer on the counter surface indicates electrode fouling and further decreases the current intensity at higher concentrations. This confirms that the Metrohm-based MIL-PdMNQDs-SPE₁ is single-use for AA sensing.

We utilized Shenzhen More-Suns Electronics SPE₂ to evaluate the interference response of AA toward other analogs in PBS. The Shenzhen SPE₂ featured carbon as both the WE and CE, with Ag as the RE. For the interference study, we chose glucose (GL), dopamine (DA), lactic acid (LA), uric acid (UA), and citric acid (CA) as the chemicals that may interfere with the analysis. Each interferant was sequentially added at a concentration of 4 mM to the modified SPE, resulting in an unresponsive potential–current plot from the MIL-PdMNQDs-SPE₂ (Figure 6a). However, upon adding 100 μ M AA to the interferant-containing solution, MIL-PdMNQDs-SPE₂ demonstrated a response with a peak at 0.24 V and 233.19 μ A (Figure 6b). The excellent conductivity and selectivity of the composite are attributed to the abundant electrons near the Fermi level provided by MNQDs. The slight positive shift in AA sensing observed between Figures 6b and 6c is attributed to differences in the pH of the buffers used in the SPE₂-based analyses for the sensing and interference experiments. In Figure 6b, a basic pH PBS buffer was used for the interference study of AA and UA, to ensure complete dissolution of UA. In contrast, for Figure 6c, artificial sweat was used as the solvent for AA analysis. In both cases, Pd's superior oxidation activity compared to gold and platinum enhances electrical and sensing performance. The Fe-based MIL supports the PdMNQDs, while the conductive properties of both Fe and MIL-53 enhance overall charge transfer.

The average concentration of UA in human blood ranges from 240 to 600 μ M. We examined UA interference in a slightly alkaline PBS solution by adding 2 mg of NaOH to achieve complete dissolution of UA. Introducing 200 μ M UA onto the MIL-PdMNQDs-SPE₂ produced a small DPV peak at 0.05 V with a current of 18.3 μ A. Adding 200 μ M AA resulted in a more pronounced peak with a current of 28.6 μ A (Figure 6b). Repeating the experiment with an additional 200 μ M UA produced a peak of 27.5 μ A, demonstrating that the MIL-PdMNQDs-SPE₂ is more sensitive to AA than UA. The slight shift in the DPV peak toward 0.05 V compared to Figure 6a is due to the alkaline nature of the PBS.

We performed a sensing experiment using MIL-PdMNQDs-SPE₂ in an artificial sweat solution. The solution consisted of NaCl (85 mM), KCl (13 mM), urea (16 mM), and LA (17 mM) in 0.1 M PBS with a pH of 6.5 (Figure 6c). The probe detected AA concentrations ranging from 100 to 1000 μ M, with current responses between 11.132 and 64.83 μ A. The peak current position shifted to 0.25 V compared to Figure 6a, due to the presence of dissolved salts, urea, and the slightly acidic pH. Additionally, the peak shift during high concentration (Figure 6c) is partially attributed to electrode fouling caused by the adsorption of Asc^{•−} on the electrode surface which blocks the active sites of MIL-PdMNQDs-SPE₂. The linearity plot with an R^2 value of 0.9903 indicates the probe's selective sensing capability for AA in the artificial sweat solution (Figure S21b).

Chronoamperometry (CA), a technique that applies a constant potential to the electrode, is well-suited for analyte analysis and continuous monitoring due to its high sensitivity and real-time responsiveness.⁴² In our study, we conducted CA measurements under stirred electrolyte conditions using a MIL-PdMNQDs-GCE system at a fixed potential of 0.041 V (Figure S21d). For AA concentrations between 100 and 500 μ M, peak currents ranged from 0.485 to 5.85 μ A. Additionally, interference tests were performed with DA, GL, and UA. The findings illustrate that DA and GL caused negligible interference with the MIL-PdMNQDs-GCE probe, while UA introduced slight interference with the modified GCE (Figure S21e). Figure S21d demonstrates that peak stability decreases at higher concentrations over time due to surface fouling, which diminishes the active surface area and reduces current responses. AA oxidation products, such as DHA, adsorb onto the MIL-PdMNQDs-GCE and block active sites, impeding further continuous monitoring.

We investigated the response of AA sensing across a pH range from 7.4 to 3.7 (Figure 6d). The pH experiments were conducted at 500 nM using MIL-PdMNQDs-GCE in PBS. Thirty μ L of 1 mM sulfuric acid was added to the PBS to lower the pH from 7.4 to an acidic condition.^{43,44} The peak current increases from primary conditions to pH 5 due to the oxidation of AA to DHA. Between pH 5 and 4.2, the anodic current stabilizes, and below pH 4.2, the peak current decreases (Figure 6d & S21c). This decline is caused by an excess of protons that hinder the oxidation of AA.^{54,55} For the cathodic current, the peak becomes more prominent as the conditions shift from basic to acidic, and it stabilizes between pH 5 and 4.2. The reduction peak current decreases below pH 4.2 due to excess proton in PBS which impedes the reduction of DHA to AA.

Stability and Reproducibility Studies of MIL-PdMNQDs-GCE and SPE. The stability of an electrode greatly influences the cost-effectiveness of producing an electrochemical probe. We examined the stability of 100 nM AA with the modified GCE over ten cycles, resulting in a highly stable CV peak (Figure 7a & S22a). The stability experiment yielded an average value of 73.14 μ A and a root mean squared (RSD) value of 0.5646%, confirming the high stability of our probe. For the reproducibility studies, we prepared the MIL-PdMNQDs for three times. In each cycle, the prepared MIL-PdMNQDs-GCE give a stable peak and average of 57.5 A and RSD of 3.72% for the AA concentration of 20 nM (Figure 7b & S22b). Using the MIL-PdMNQDs-SPE₁, we performed a storage stability test via DPV over 25 days, with measurements taken every 5 days for 100 nM AA (Figure 7c & S22c). The DPV results validate a consistent plot, averaging 263.03 μ A with an RSD of 0.382%. These findings demonstrate that the MIL-PdMNQDs-based probe exhibits excellent stability, reproducibility, and cost-effectiveness. We compared our MIL-PdMNQDs-based probe, which exhibits superior sensitivity and selectivity, to other reported materials (Table 1).

Following ten CV cycles, we conducted SEM and EDX analyses on MIL-PdMNQD-GCE to evaluate the stability of the synthesized material (Figure S23). Using 100 nM AA, we ran 10 cycles and collected the dried sample from the GCE surface for SEM analysis. The SEM results confirmed that MIL-PdMNQDs maintained their

Table 1. Comparison of MIL-PdMNQDs-GCE towards Various Modified GCEs

Composite	Method	Linear range (μM)	LOD (μM)	ref
NH ₂ -MIL-101(Fe)	SWV	50–300	2	44
PAnI	CV	2–24	5.1	45
α -Bi ₂ O ₃	CV	1–5	1	46
Pt SA/CsPbBr ₃	CV	1–50	0.0369	47
CuxO/NPC@Co ₃ O ₄ /NPC-10-7	Amperometry	0.5–23.334	0.24	48
PCN-333 (Al)-KB	DPV	14100–5500	4.6	49
GQDs/IL-SPCE	DPV	25–400	6.64	50
PPF/GNS	CV	400–600	120	23
Cu ₃ (HHTP) ₂ /SPE	DPV	25–1645	2.4	51
PTh/SWCNT	CV	20–200	13	52
PdNPs/rGO	DPV	500–3500	79	53
Ti–C–T _x	DPV	100–1000	4.64	20
MIL-PdMNQDs	CV	0.01–0.1	0.004705	This work

structural stability and octahedral morphology. The elemental composition, with C, N, O, Ti, Fe, and Pd at 0.44%, 0.65%, 0.27%, 0.07%, 0.19%, and 0.34%, respectively, aligns with previous SEM-EDX data, validating the chemical stability of MIL-PdMNQDs after ten CV cycles (Figure S7 and S23). Additionally, SEM-EDX findings demonstrate the lack of surface fouling at low concentrations, as the EDX data matches the earlier studies. However, CV and CA analyses at higher concentrations indicate surface fouling (Figure 6c and S21d), likely due to the adsorption of ascorbate ions on the MIL-PdMNQDs-GCE surface.

CONCLUSIONS

In precision medicine, the essential step is to deliver the right amount of medicine or nutrients specifically suited to each person. It is vital to use advanced, portable sensors to measure the exact levels of nutrients, vitamins, and neurotransmitters. Vitamin C is an essential nutrient that must be provided in the accurate amount, as a deficiency can cause scurvy and excessive levels can lead to gastric upset. Our group prepared carbon-doped MXene quantum dots (MNQDs) by reacting CA with EDA. We then modified the MNQDs with Pd and incorporated them into MIL-53 to prepare MIL-PdMNQDs. We specifically used MIL-PdMNQDs-GCE and SPE for CV and DPV tests in PBS, human serum, and artificial sweat to detect AA. MIL-PdMNQDs-GCE and SPE₁ was employed to measure AA concentrations in PBS, ranging from 10 to 100 nM, using the CV and DPV techniques. The experiment demonstrated a linear anodic peak current from 52.05 to 82.44 μA , with an R^2 value of 0.9885. To study AA's redox response in human serum mixed with PBS, we prepared a 5 mL human serum solution in 95 mL PBS. Using MIL-PdMNQDs-SPE₁, we detected AA concentrations from 10 to 50 μM , illustrated a DPV redox peak currents from 124.39 to 152.54 μA , with an R^2 value of 0.9901, aligning with normal AA levels. In artificial sweat, MIL-PdMNQDs-SPE₂ detected AA concentrations from 100 to 1000 μM , with readings from 11.132 to 64.83 μA and an R^2 value of 0.9903, confirming the probe's selective sensing capability. Ultimately, the MIL-PdMNQDs-SPE₁ proved highly effective for AA sensing, the SPE₁ provided portability and compatibility with biological systems, illustrating a linear detection range of 10–100 nM and a detection

limit (LOD) of 7.53 nM. The experiments demonstrate that the MIL-PdMNQDs-based sensor is highly stable and excels in selectively detecting AA, effectively distinguishing it from other chemical analogues and interferences.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.4c05225>.

Experimental data processing; Instruments and methods, spectroscopic plots from XRD, XPS, Raman, TEM, and SEM; electrochemical plots from CV, DPV, and chronoamperometric studies (PDF)

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Author Contributions

Jose Paul: Conceptualization, investigation, formal analysis, writing original draft, editing, and review. Jongsung Kim: Validation, investigation, supervision, funding acquisition, formal analysis, and software.

Notes

The authors declare no competing financial interest.

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