

Supporting Information

**Polyoxometalate adsorbed in a metal–organic framework for
electrocatalytic dopamine oxidation**

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S1. Experimental section

1. Chemicals

Zirconium(IV) oxychloride octahydrate (Sigma-Aldrich, 98%), *p*-anisic acid (ACROS, 98%), meso-tetra(4-carboxyphenyl)porphine (TCPP, Frontier Scientific, United States, 98%), dimethylformamide (DMF, ECHO Chemical Co, Ltd., Taiwan, $\geq 99.8\%$), hydrochloric acid (HCl, J. T. Baker, 36.5-38.0%), acetone (ECHO Chemical Co, Ltd., Taiwan, $\geq 99.0\%$), nitric acid (HNO₃, Honeywell Fluka, $\geq 65\%$), sulfuric acid (H₂SO₄, Honeywell Fluka, 95.0-98.0%), hydrogen peroxide solution (H₂O₂, Honeywell Fluka, 30-31%), 3-(N-morpholino)propanesulfonic acid (MOPS, Sigma-Aldrich, $\geq 99.5\%$), sodium hydroxide (NaOH, Fluka, $\geq 98\%$), HCl (used for the synthesis of V₁₀O₂₈, Honeywell Fluka, 37%), sodium metavanadate (NaVO₃, Sigma-Aldrich, 99.9%), and dopamine hydrobromide (DA, ACROS, 99%) were purchased and used as received. Deionized water was used as the water source throughout the work.

2. Synthesis of V₁₀O₂₈

The V₁₀O₂₈ aqueous solution was prepared according to the method described in our previous publication.^{1, 2} First, 3 g of sodium metavanadate (NaVO₃) was dissolved in 100 mL of deionized water. After filtering the solution, the pH value was reduced to 4.5 by adding 4 M HCl (aq), and an orange-colored V₁₀O₂₈ aqueous solution with a concentration of 0.024 M was obtained. For preparing dry V₁₀O₂₈ powder for nitrogen adsorption-desorption measurements, the obtained V₁₀O₂₈ aqueous solution was dried by directly evaporating water. The obtained orange-colored powder was further dried in a vacuum oven at 80 °C for 24 h.

3. Synthesis of V₁₀O₂₈@NU-902

NU-902 was synthesized by following the recipe reported in a recent study which utilized *p*-anisic acid as the modulator.³ NU-902 was activated by heating around 75 mg of the obtained solid in the mixture of 0.5 mL of 8 M HCl (aq) and 10 mL of DMF at 100 °C

for 24 h, followed by successive washing with DMF, solvent exchange with acetone, and drying; the same activation process to remove ligated modulators can be found in a previous study in details.⁴

To synthesize $V_{10}O_{28}@NU-902$, 0.7 mL of the $V_{10}O_{28}$ aqueous solution (0.024 M) was first diluted with 2.8 mL of an aqueous solution of HCl with an adjusted pH value of 4.5; the HCl solution with a pH value of 4.5 was prepared by adding 2 μ L of HCl (36.5-38.0%) into 230 mL of deionized water. Thereafter, 20 mg of activated NU-902 and the obtained $V_{10}O_{28}$ aqueous solution (0.0168 mmol of $V_{10}O_{28}$; two equivalents to the total amount of hexazirconium nodes in NU-902) were added into a scintillation vial, and the mixture was sonicated for 10 min. Thereafter, the mixture was kept for three days at room temperature. After the impregnation step, the obtained solid was washed with 5 mL of the fresh HCl aqueous solution (pH = 4.5) for two times by centrifugation. After the removal of the supernatant, another 5 mL of the fresh HCl aqueous solution (pH = 4.5) was added into the centrifuge tube, and the mixture was kept for overnight to ensure the complete removal of excess POM from the MOF solid. The acidic solution was thereafter removed by centrifugation, and the solid was washed with 5 mL of acetone for three times by centrifugation, with the immersing periods of 2 h, overnight, and 2 h in between to ensure the complete solvent exchange. The resulting solid was then dried in a vacuum oven at 80 °C for overnight, and the $V_{10}O_{28}@NU-902$ was obtained.

4. Preparation of thin films

For electrochemical measurements, the NU-902 and $V_{10}O_{28}@NU-902$ were deposited on fluorine doped tin oxide (FTO) conducting glass substrates as thin films by drop casting.⁵ A FTO substrate (7 Ω /sq.) was washed by sonicating in soapy water, ethanol, and acetone for 5 min, sequentially. After drying the substrate with nitrogen flow, an insulating polyamide tape was used to obtain an exposed FTO area of 0.25 cm² (0.5 cm $\times$ 0.5 cm). For preparing thin films of NU-902 and $V_{10}O_{28}@NU-902$, 6 mg of the solid was dispersed in 0.5 mL of

acetone by sonicating for 10 min, and 6 μL of the obtained suspension was drop-casted on the exposed FTO area.

5. Instrumentations

Scanning electron microscopic (SEM) images and energy-dispersive X-ray spectroscopic (EDS) data were collected by using SEM SU-8010 (Hitachi). Samples were sputtered with Pt before all SEM and EDS measurements. Powder X-ray diffraction (PXRD) patterns were collected by an Ultima IV powder diffractometer (Rigaku). Nitrogen adsorption-desorption isotherms were measured by an ASAP 2020 (Micromeritics). Inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements were conducted on a JY 2000-2 ICP-OES spectrometer (Horiba Scientific). For preparing ICP-OES samples, around 1 mg of $\text{V}_{10}\text{O}_{28}@\text{NU-902}$ was mixed with 0.75 mL of concentrated H_2SO_4 and 0.25 mL of 30% H_2O_2 aqueous solution in a microwave vial (2-5 mL, Biotage). The vial was then crimped and heated in an oil bath at 100 $^\circ\text{C}$ for 24 h. The resulting homogeneous solution was diluted with 40 mL of 3 wt% HNO_3 aqueous solution before the ICP-OES measurements. The ^{51}V nuclear magnetic resonance (NMR) spectra of $\text{V}_{10}\text{O}_{28}$ solutions were recorded on a 500 MHz BRUKER AVANCE 500 NMR instrument. A Heraeus™ Megafuge™ 16 centrifuge (Thermo Fisher Scientific) along with a Fiberlite™ F15-6x100y fixed-angle rotor was used throughout all the washing and solvent exchange steps, with a rotating speed of 12,300 rpm. The synchrotron-based radiation PXRD measurement was carried out at the beamline BL02B2 at the SPring-8 in Japan, by using X-ray with the energy of 15.498 eV. The sample was activated and then sealed in a borosilicate capillary ($\phi = 0.4$ mm) prior to the measurement.

All electrochemical measurements were performed on a CHI6273E electrochemical workstation (CH Instruments Inc.) at the temperature of 25 $^\circ\text{C}$. A three-electrode cell was used, with a platinum wire and a $\text{Ag}/\text{AgCl}/\text{NaCl}$ (3 M) (BASi°) as the counter electrode and reference electrode, respectively. The bare FTO substrate or the FTO substrate modified with each thin film with an area of 0.25 cm^2 was used as the working electrode. 20 mL of aqueous

solution prepared by titrating 0.05 M of MOPS aqueous solution with 0.05 M of NaOH (aq) to achieve a pH value of 4.5 was used as the electrolyte for all electrochemical experiments. Amperometric sensing experiments were conducted with a stirring speed of 450 rpm.

S2. NMR spectrum of the $V_{10}O_{28}$ solution

Figure S1 shows the ^{51}V NMR spectrum of the $V_{10}O_{28}$ aqueous solution. It reveals characteristic signals at -516 ppm, -500 ppm, and -423 ppm which represent the three different environments of V atoms in $[V_{10}O_{28}]^{6-}$ polyanions.^{1, 2} This result confirms the successful synthesis of $V_{10}O_{28}$.

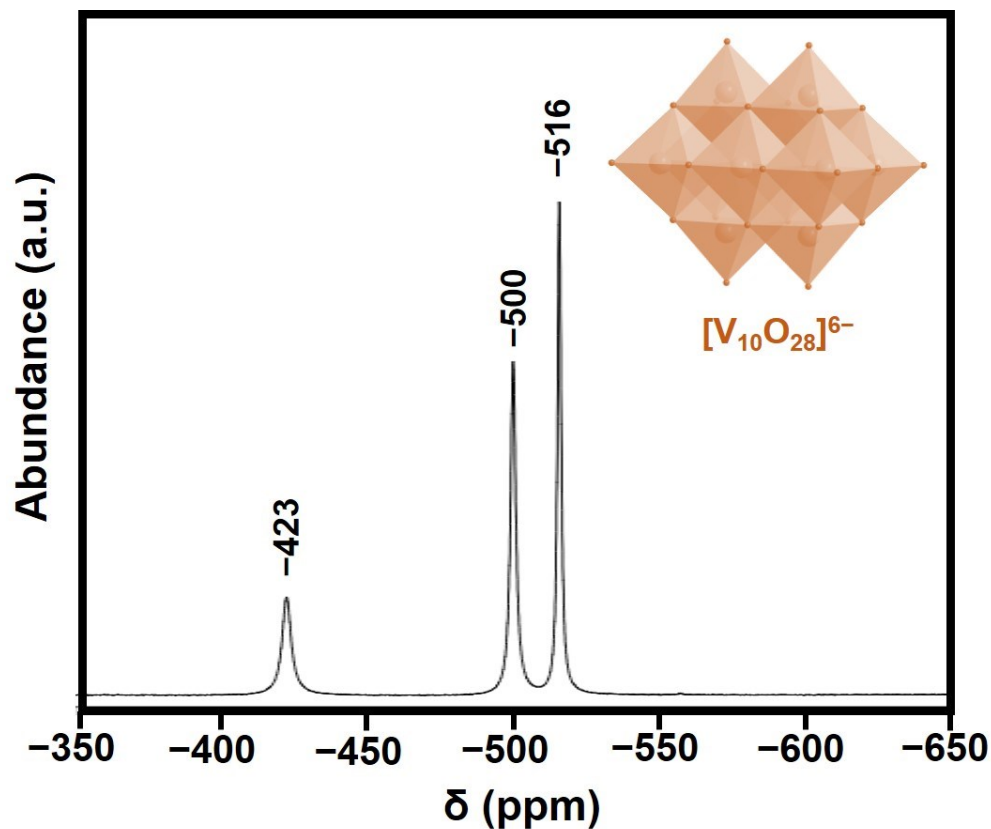


Figure S1. ^{51}V NMR spectrum of the $V_{10}O_{28}$ aqueous solution. Inset is the molecular structure of $[V_{10}O_{28}]^{6-}$ polyanion.

S3. SEM images and EDS spectrum

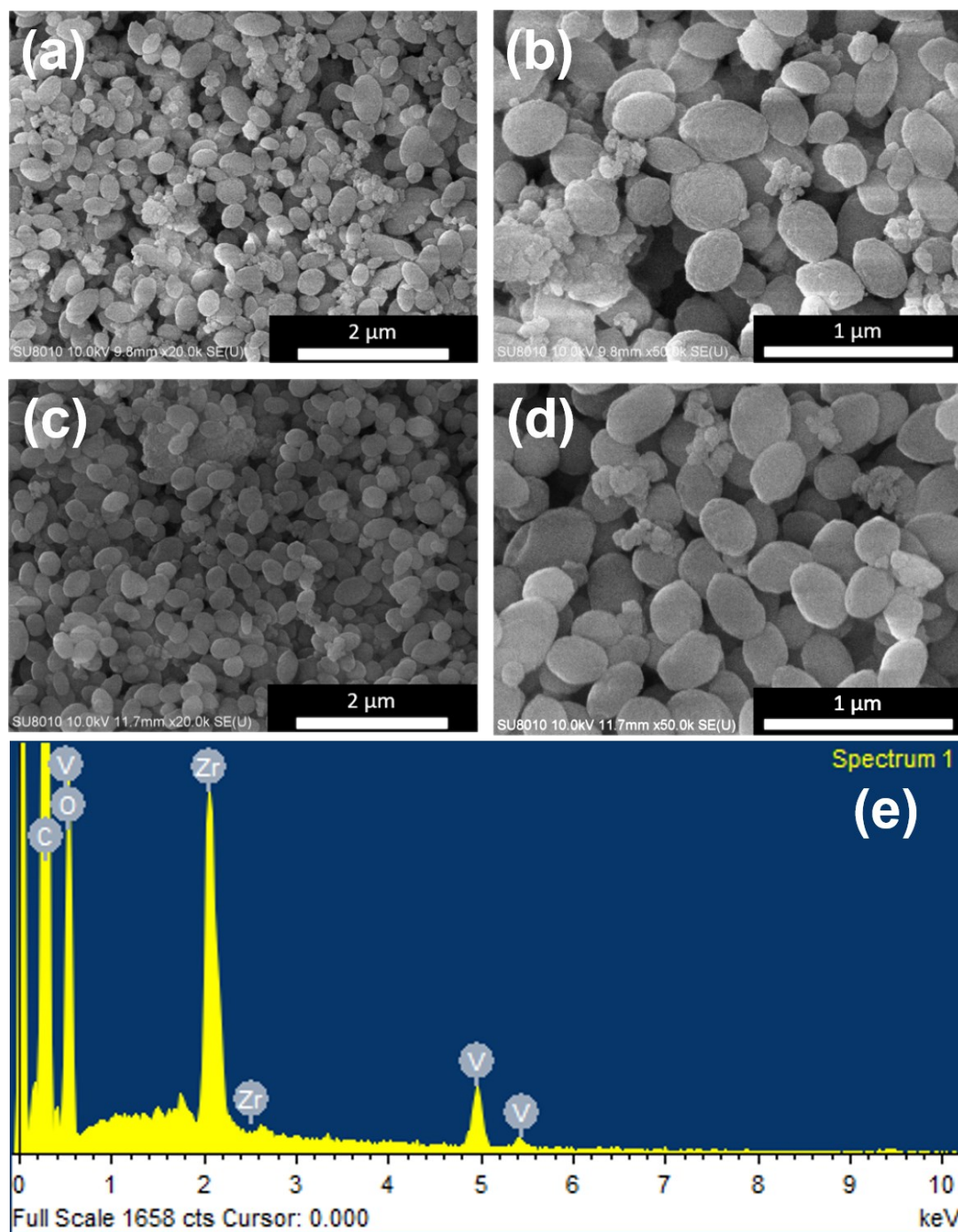


Figure S2. SEM images of (a-b) NU-902 and (c-d) $\text{V}_{10}\text{O}_{28}@NU-902$. (e) A representative EDS spectrum of $\text{V}_{10}\text{O}_{28}@NU-902$.

S4. Synchrotron-based radiation PXRD analysis

The synchrotron-based PXRD diffraction pattern of $V_{10}O_{28}@NU-902$ (Figure S3(a)) was first analyzed by Le Bail method using Topas3 software (Bruker AXS) to obtain the unit cell parameters of $V_{10}O_{28}@NU-902$. For the referencing point of the fitting, the parameters of the reported modeled structure of NU-902 (Triclinic $P1$; $a = 20.932 \text{ \AA}$, $b = 20.932 \text{ \AA}$, $c = 17.122 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 60^\circ$) was used;⁴ see the modeled electron density map of the pristine NU-902 shown in Figure S3(b). For the experimental pattern of $V_{10}O_{28}@NU-902$, the fitting gave the slightly shrunk cell of $a = 20.879 \text{ \AA}$, $b = 21.013 \text{ \AA}$, and $c = 17.029 \text{ \AA}$ with $R_{\text{exp}} = 0.87$, $R_p = 2.22$, and $R_{\text{wp}} = 3.35$. We attempted to obtain the structural information by the Rietveld analysis with the reported structural model but the analysis was not successful, probably due to the inaccurate space group of this initial structure (Triclinic $P1$) and the disorder of the accommodated $V_{10}O_{28}$. Thus, we tried to calculate the electron density maps from the diffraction data using charge flipping method⁶ using the Superflip program equipped in the RIETAN software,⁷ based on the Le Bail analysis using a partial structure. As revealed in the resulting electron density map of $V_{10}O_{28}@NU-902$ shown in Figure S3(c), cluster-shape extra electron densities can be observed near the four corners of the diamond-shape 1D channels, which indicates the immobilization of $V_{10}O_{28}$ into NU-902 by the electrostatic interaction between the hexa-zirconium nodes and POMs. As such extra electron densities of installed POMs were obtained from the PXRD pattern of bulk powder, the finding here also implies that the $V_{10}O_{28}$ clusters have been installed uniformly within the pores of the entire MOF crystals rather than being adsorbed solely on the crystal surface. It should be noted that the low resolution of the electron density originated from POM shown in Figure S3(c) may be attributed to the disordered distribution and low loading of $V_{10}O_{28}$ in NU-902, *i.e.*, around 0.36 POM in each diamond-shape cavity based on the ICP-OES data.

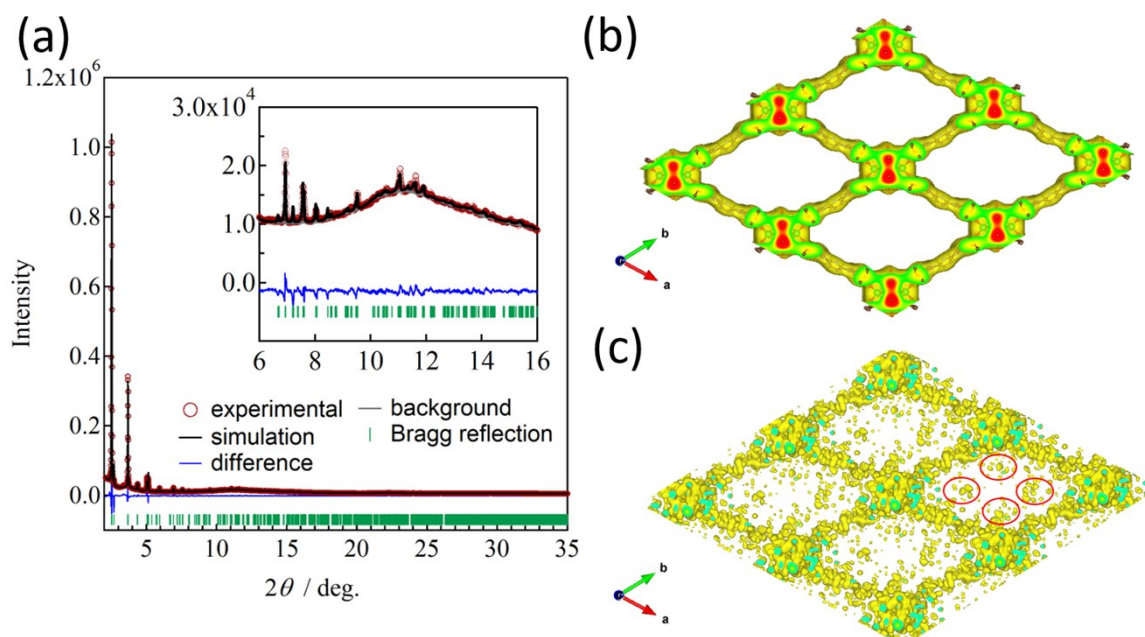


Figure S3. (a) Synchrotron-based radiation PXRD pattern (wavelength = 0.8000 Å) and its Le Bail fitting profile of V₁₀O₂₈@NU-902. (b) The modeled electron density map from the empty structural model calculated by VESTA software. (c) The experimental electron density map produced by charge flipping methods (resolution = 0.1 Å; isosurface level = 0.9 eÅ⁻³). Some additional electron densities (as circled in red) were observed near the four corners of the diamond-shape 1D channels in the framework, implying the installation of disordered V₁₀O₂₈ species with a low occupancy.

S5. Chemical stability of NU-902

To test the chemical stability of NU-902 in the aqueous solution containing 0.05 M MOPS and NaOH with a pH value of 4.5, 20 mg of NU-902 was immersed in 10 mL of the aforementioned solution and kept for 24 h at room temperature. Then the solid was washed with 10 mL of water for three times and transferred into 10 mL of acetone. Solvent exchange was then performed by washing with 10 mL of acetone for three times with the immersing periods of 2 h, overnight, and 2 h, respectively. The resulting solid was dried under vacuum and subjected to PXRD measurements. As shown in Figure S4, the NU-902 after one day of immersion in the MOPS/NaOH aqueous electrolyte (pH = 4.5) is still well crystalline, confirming the good chemical stability of the Zr-MOF in such an aqueous solution.

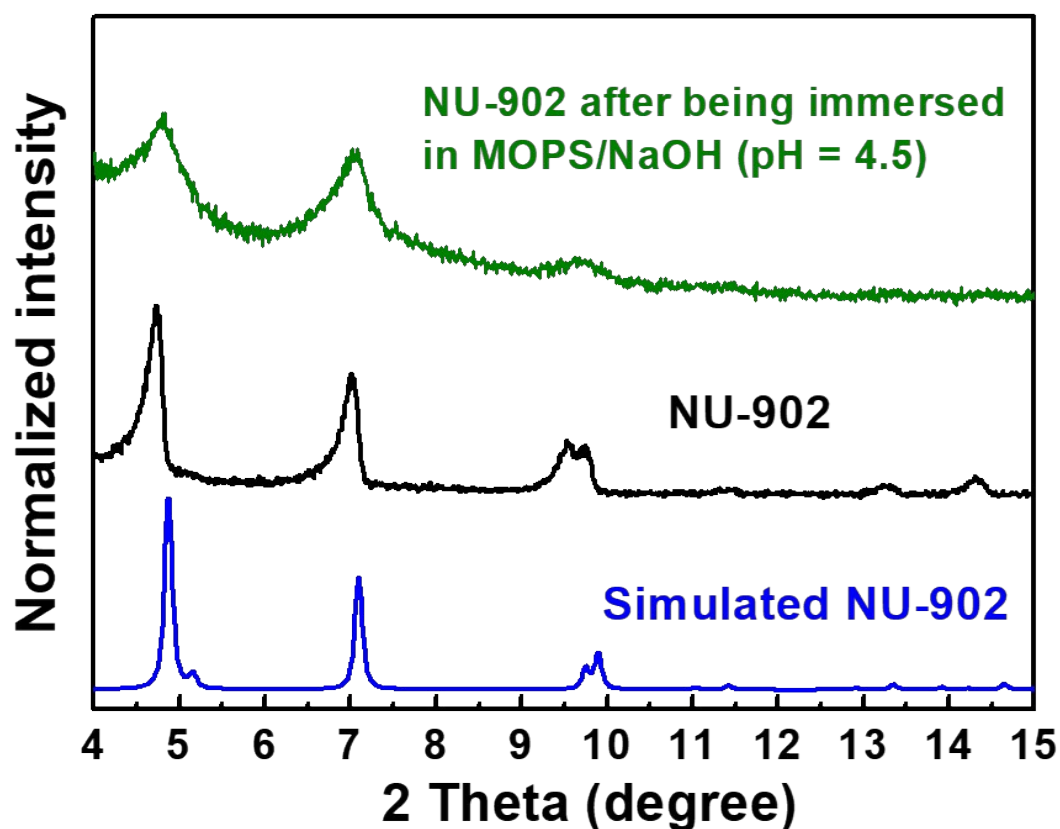


Figure S4. PXRD patterns of fresh NU-902 and the NU-902 after being immersed in the MOPS/NaOH aqueous solution (pH = 4.5) for 24 h. The simulated pattern is also shown.

S6. Electrochemical behavior of the V₁₀O₂₈@NU-902 thin films

CV curves of the V₁₀O₂₈@NU-902 thin film measured in the 0.05 M MOPS/NaOH aqueous solution (pH = 4.5) at different scan rates are shown in Figure S5(a). Thereafter, the values of anodic peak current density (J_{pa}) extracted from Figure S5(a) were plotted with the square root of scan rate ($\nu^{0.5}$) and scan rate (ν), as shown in Figure S5(b) and Figure S5(c), respectively. It can be observed that the values of J_{pa} show a slightly better linearity to $\nu^{0.5}$ compared to the linearity to ν , which implies that a diffusion-like charge-transport behavior does occur within the V₁₀O₂₈@NU-902 thin film during the electrochemical reaction.⁸⁻¹³ It should be noted that the values of J_{pa} also show a good linearity to ν , which suggests that such a charge-transport behavior, solely occurring between the electrochemically addressable V₁₀O₂₈ sites within the thin film, is considerably fast over the time scale of the CV experiments.

As the diffusion-like behavior does occur within the V₁₀O₂₈@NU-902 thin film during the electrochemical reaction, the apparent diffusivity (D_{app})^{12, 13} for the redox hopping between those adsorbed V₁₀O₂₈ sites can be estimated by Randle-Sevcik equation,¹⁰

$$J_{pa} = (2.69 \times 10^5) n^{1.5} D_{app}^{0.5} C \nu^{0.5} \quad (1)$$

where J_{pa} is the anodic peak current density in A/cm², n is the number of electron involved in the reaction, which is assumed as 10 for V₁₀O₂₈, ν is the scan rate in V/s, and C is the concentration of redox-active V₁₀O₂₈ sites presented within the MOF thin film in mol/cm³. From the crystal structure of NU-902 and the V₁₀O₂₈ loading estimated by ICP-OES (*i.e.*, 0.36 V₁₀O₂₈ per node), the value of C was calculated to be 9.2×10^{-5} mol/cm³. Thereafter, the value of D_{app} was calculated to be 4.3×10^{-15} cm²/s.

According to the total mass loading of the drop-casted V₁₀O₂₈@NU-902 thin film and the molecular weight of the V₁₀O₂₈@NU-902 sample loaded with 0.36 Na₆V₁₀O₂₈ per node, the total loading of POM within the V₁₀O₂₈@NU-902 thin film was calculated as 3.7×10^{-8} mol

$\text{V}_{10}\text{O}_{28}/\text{cm}^2$. Amperometric experiments were then carried out to switch the applied potential from +0.1 V to +0.6 V vs. Ag/AgCl/NaCl (3 M) in order to estimate the electrochemically active amount of $\text{V}_{10}\text{O}_{28}$ within the entire $\text{V}_{10}\text{O}_{28}@\text{NU-902}$ thin film. From the integrated charge density shown in Figure S6, the electrochemically active amount of $\text{V}_{10}\text{O}_{28}$ in the thin film was found to be $1.5 \times 10^{-10} \text{ mol}/\text{cm}^2$, which suggests that the electrochemically addressable fraction of POM within the entire $\text{V}_{10}\text{O}_{28}@\text{NU-902}$ thin film is 0.4%; this value is in general similar to those of some reported Zr-MOFs relying on redox hopping to transport charge in aqueous electrolytes.^{14, 15} It should be noted that according to the cross-sectional SEM images of the $\text{V}_{10}\text{O}_{28}@\text{NU-902}$ thin films (Figure S7), the thickness of the drop-casted thin films is in the range of 7-8 μm , which means that 0.4% of the thin film, *c.a.*, 30 nm in thickness, is electrochemically addressable. As the distances between two adjacent hexa-zirconium nodes in the structure of NU-902 range between 1.3 nm and 3.1 nm depending on the direction of charge transport, the result here suggests that the redox hopping between the immobilized POM units in $\text{V}_{10}\text{O}_{28}@\text{NU-902}$ thin films can occur within around 10-25 layers of unit cells in the MOF structure on average.

The $\text{V}_{10}\text{O}_{28}@\text{NU-902}$ thin film was subjected to 20 cycles of CV measurement in the 0.05 M MOPS/NaOH aqueous solution (pH = 4.5) at a scan rate of 50 mV/s. As shown in Figure S8(a), the electrochemical activity of the thin film is stable during the scan. After the electrochemical test, the $\text{V}_{10}\text{O}_{28}@\text{NU-902}$ thin film was rinsed with water for two times and placed in 10 mL of acetone. After immersing in acetone for 2 h, the thin film was transferred into 10 mL of fresh acetone and kept for overnight to allow complete solvent exchange. After drying the sample, the resulting thin film after the electrochemical test was examined by SEM. As revealed in Figures S8(b) and S8(c), the $\text{V}_{10}\text{O}_{28}@\text{NU-902}$ thin film still shows the same morphology, and the $\text{V}_{10}\text{O}_{28}$ immobilized in the Zr-MOF can still be observed by EDS, which suggests the stability of the material during the electrochemical test in the MOPS-based electrolytes.

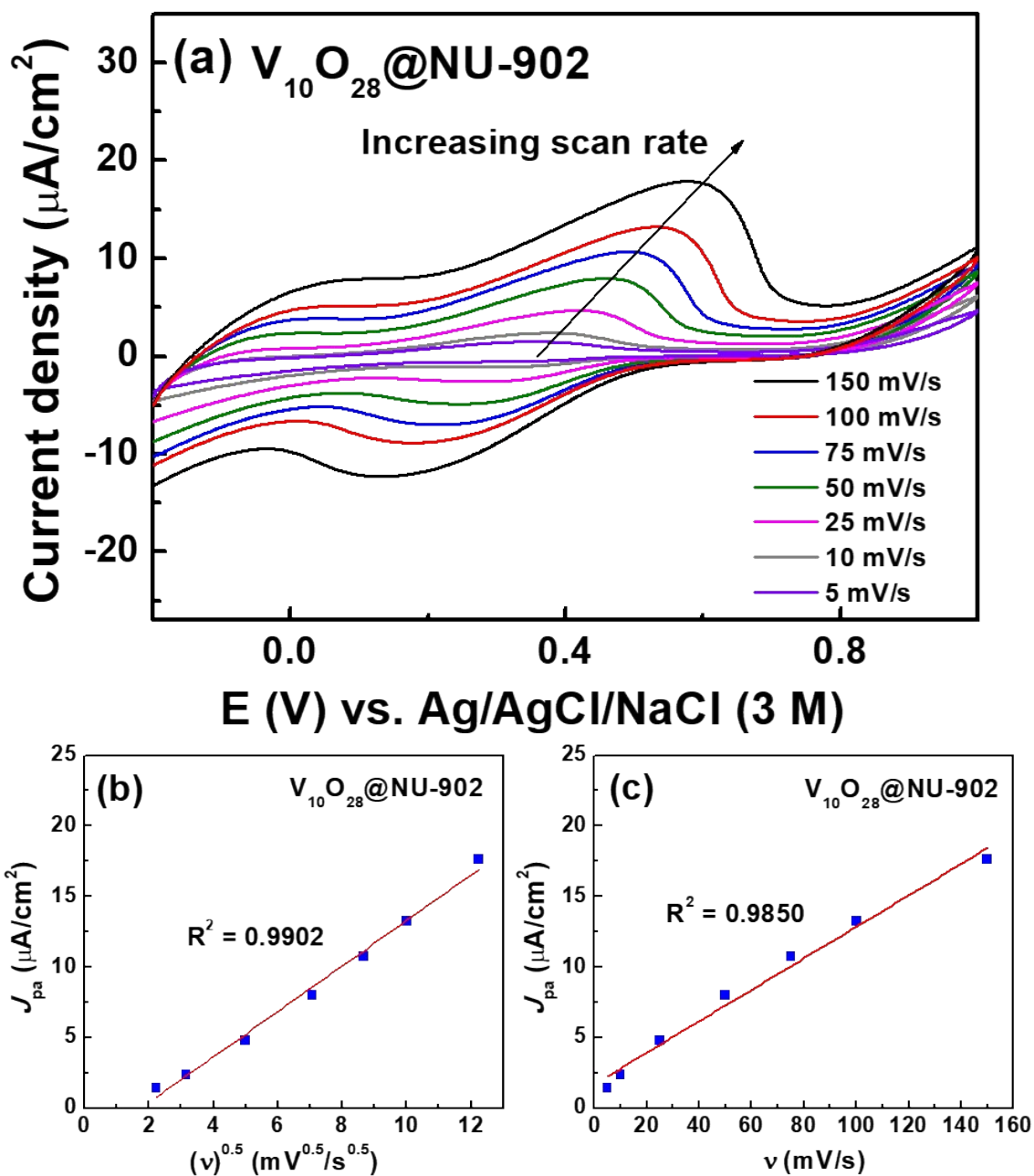


Figure S5. (a) CV curves of the $V_{10}O_{28}@NU-902$ thin film measured in the 0.05 M MOPS/NaOH aqueous solution (pH = 4.5) at different scan rates. Relationships between J_{pa} and (b) $v^{0.5}$, and (c) v .

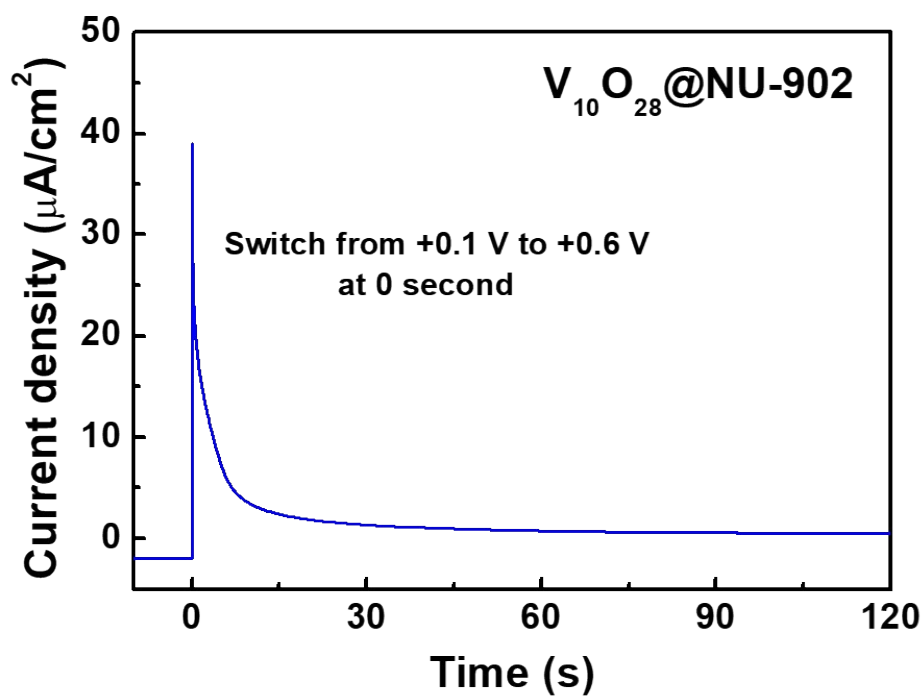


Figure S6. Amperometric curve of the $V_{10}O_{28}@NU-902$ thin film recorded during the switch of applied potential from +0.1 V to +0.6 V (vs. Ag/AgCl/NaCl (3 M)) at 0 s. The curve was measured in the 0.05 M MOPS/NaOH aqueous solution (pH = 4.5).

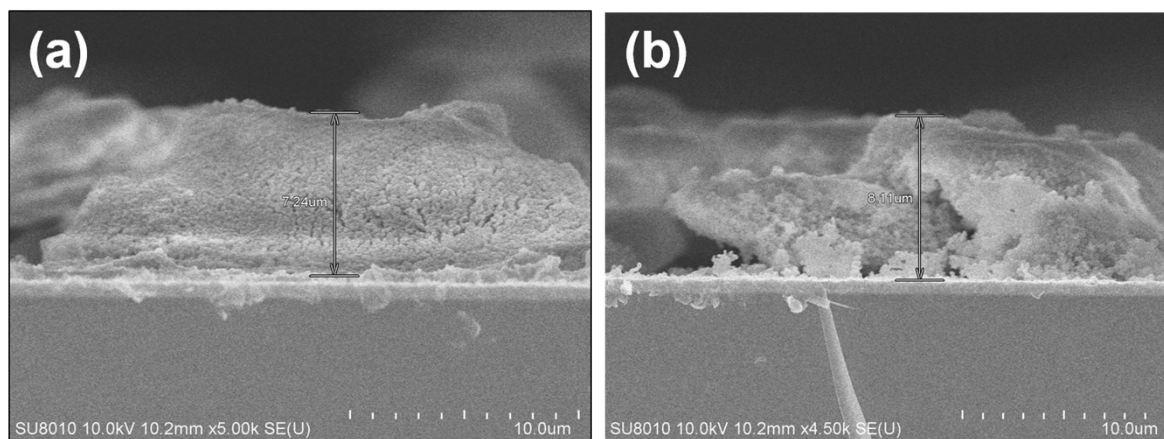


Figure S7. Representative cross-sectional SEM images of the $V_{10}O_{28}@NU-902$ thin films.

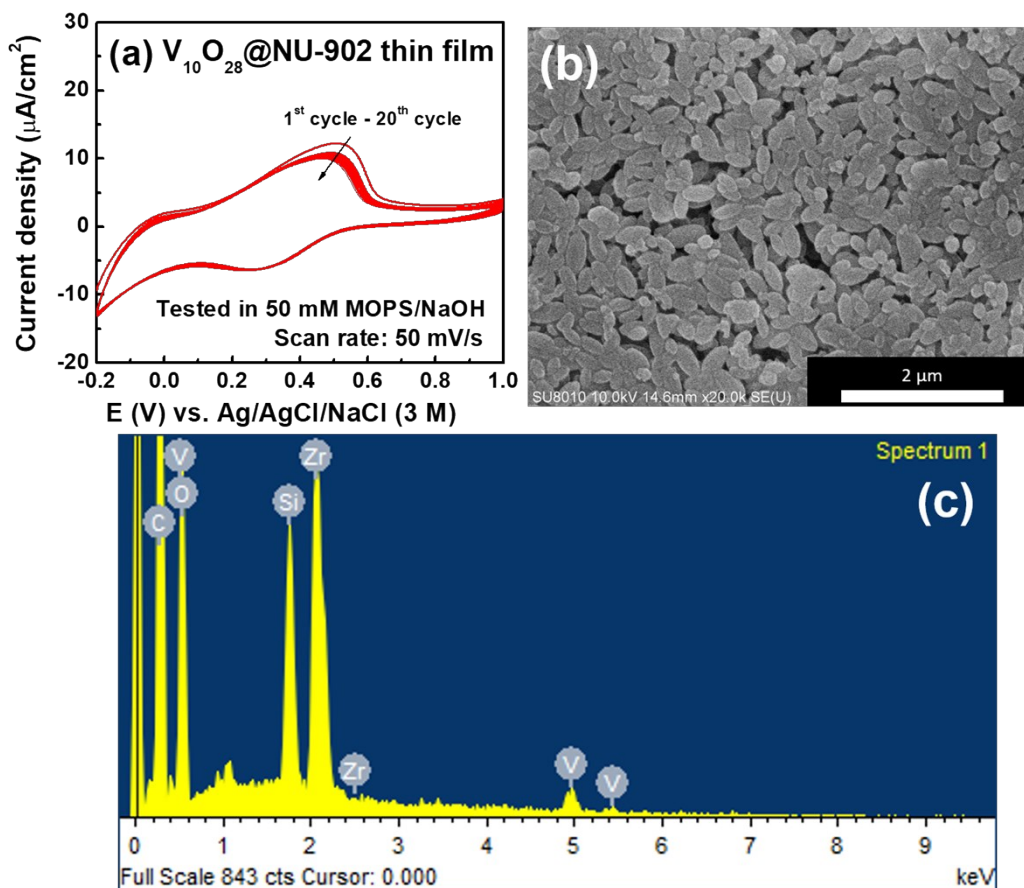


Figure S8. (a) 20-cycle CV curve of the $\text{V}_{10}\text{O}_{28}@NU-902$ thin film measured in the 0.05 M MOPS/NaOH aqueous solution ($\text{pH} = 4.5$) at a scan rate of 50 mV/s. (b) SEM image and (c) EDS spectrum of the $\text{V}_{10}\text{O}_{28}@NU-902$ thin film after the electrochemical test shown in (a).

S7. Homogeneous electrocatalytic oxidation of DA with dissolved $\text{V}_{10}\text{O}_{28}$

CV curves of the bare FTO substrate were measured in the 0.05 M MOPS/NaOH aqueous solutions ($\text{pH} = 4.5$) containing various concentrations of DA. As shown in Figure S9(a), the anodic peaks for the oxidation of DA with the current signal increasing with increasing concentration of DA can be observed at around +0.8 V vs. $\text{Ag}/\text{AgCl}/\text{NaCl}$ (3 M). In order to test the catalytic activity of $\text{V}_{10}\text{O}_{28}$ as a homogeneous electrocatalyst, the aqueous solution of $\text{V}_{10}\text{O}_{28}$ was added into the electrolyte to prepare the 0.05 M MOPS/NaOH aqueous solutions ($\text{pH} = 4.5$) containing 0.1 mM of $\text{V}_{10}\text{O}_{28}$. With such solutions as the

electrolytes, the resulting CV curves of the bare FTO substrate are shown in Figure S9(b). The anodic peaks for the oxidation of DA shift to around +0.5 V vs. Ag/AgCl/NaCl (3 M), with a much higher current density with increasing concentration of DA compared to that shown in Figure S9(a). CV curves of the bare FTO electrode measured in the solution containing 0.1 mM of $V_{10}O_{28}$ at various scan rates (Figure S10) also reveal a much better linearity between J_{pa} and $v^{0.5}$ compared to that between J_{pa} and v , indicating that the electrochemical reactions belong to a diffusion-controlled process. This observation verifies that the dissolved $V_{10}O_{28}$ ions diffused through the electrolyte during the electrochemical process rather than adsorbing on the FTO surface to generate a layer of heterogeneous electrocatalyst. All the findings here suggest that the $V_{10}O_{28}$ dissolved in the electrolyte can be served as a homogeneous electrocatalyst to catalyze the oxidation of DA.

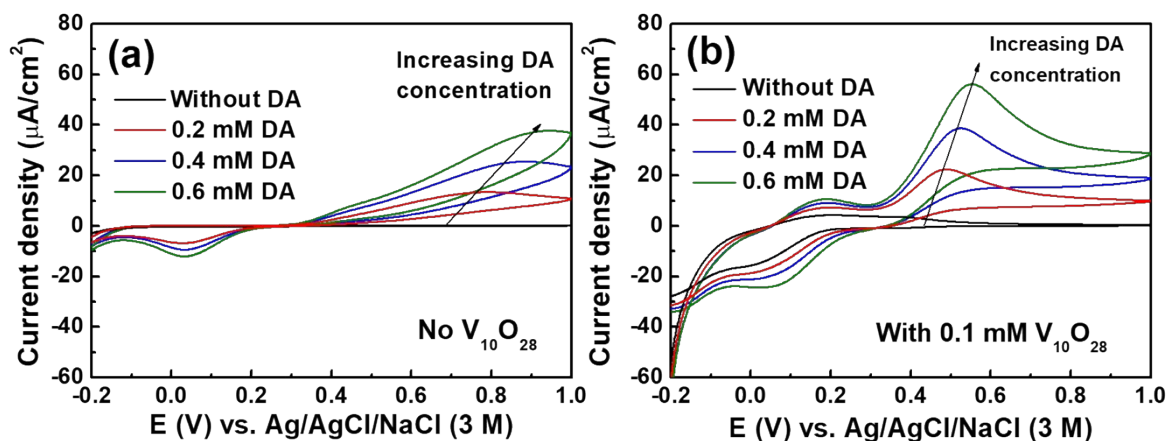


Figure S9. CV curves of the bare FTO substrates measured in 0.05 M MOPS/NaOH aqueous solutions (pH = 4.5) containing various concentrations of DA (a) in the absence of and (b) in the presence of 0.1 mM $V_{10}O_{28}$. Scan rate: 10 mV/s.

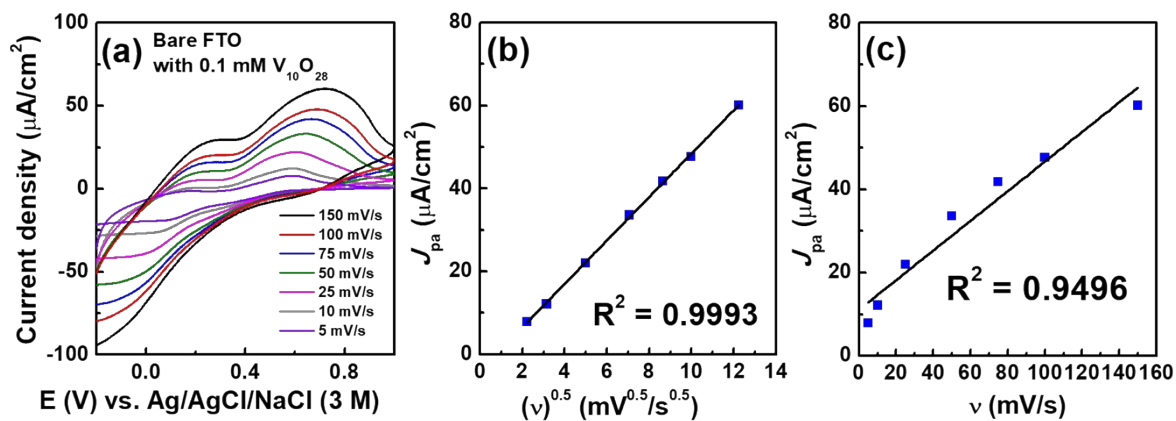


Figure S10. (a) CV curves of the bare FTO substrate measured in the 0.05 M MOPS/NaOH aqueous solution (pH = 4.5) at various scan rates in the presence of 0.1 mM $V_{10}O_{28}$. The relationship between J_{pa} extracted from (a) and (b) $v^{0.5}$ and (c) v .

S8. Mechanism for the electrocatalytic oxidation of DA on $V_{10}O_{28}@NU-902$

CV curves of the $V_{10}O_{28}@NU-902$ thin film were measured at various scan rates in the electrolyte containing 0.4 mM of DA (Figure S11(a)), and the normalized current density ($J_{pa}/\nu^{0.5}$) was plotted with scan rate to obtain Figure S11(b). It can be observed that the normalized current density is close to a constant value at relatively faster scan rates, and increases remarkably when the scan rate decreases. This feature agrees well with the typical characteristic of an EC_{cat} process.^{10, 11, 16}

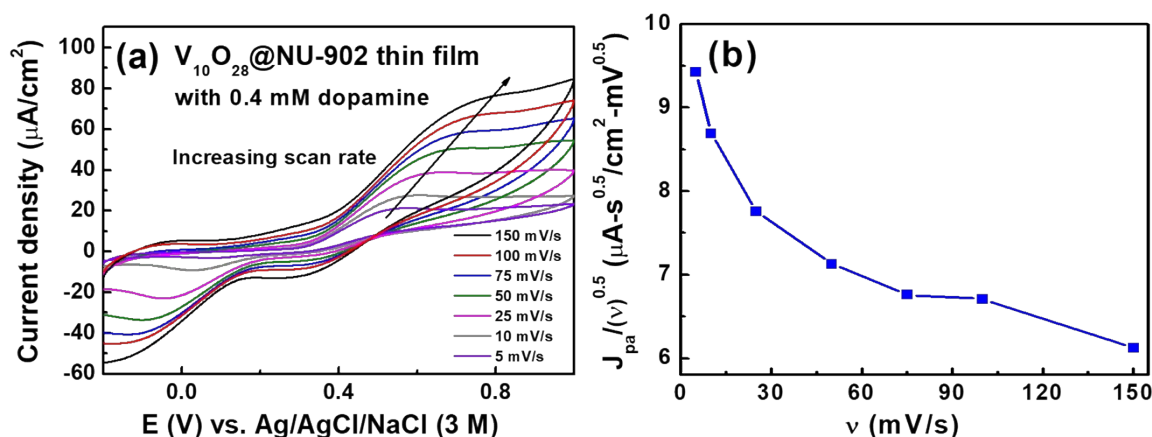


Figure S11. (a) CV curves of the $V_{10}O_{28}@NU-902$ thin film measured in the 0.05 M MOPS/NaOH aqueous solution (pH = 4.5) at various scan rates in the presence of 0.4 mM DA. (b) The relationship between the normalized current density ($J_{pa}/\nu^{0.5}$) extracted from (a) and ν .

S9. Amperometric DA sensor with $V_{10}O_{28}@NU-902$ thin films

Linear sweep voltammetric (LSV) curves of the $V_{10}O_{28}@NU-902$ thin film were first measured in the presence and in the absence of DA at a slow scan rate of 0.2 mV/s in order to find the proper applied potential for amperometric detection of DA. As revealed in Figure S12, the net current response shows a clear plateau at around +0.7 V vs. Ag/AgCl/NaCl (3 M), which suggests that such an applied potential is within the diffusion-controlled range for

the electrocatalytic oxidation of DA. Amperometric sensing experiments were then performed with $V_{10}O_{28}@NU-902$ thin films at an applied potential of +0.7 V vs. Ag/AgCl/NaCl (3 M) in 0.05 M MOPS/NaOH aqueous solutions (pH = 4.5), as shown in Figure S13(a). The current response was recorded at 30 s for each amperometric curve, and the plot of current response versus the concentration of DA is shown in Figure S13(b). The sensitivity of the sensor can be estimated from the slope of Figure S13(b), and the linear range of the sensor can also be gauged from Figure S13(b). A limit of detection (LOD), based on the signal-to-noise ratio of 3, was estimated by the following equation,

$$LOD = \frac{3 \times N}{Sensitivity} \quad (2)$$

where N is the noise in current density collected from the amperometric curve before adding DA. For $V_{10}O_{28}@NU-902$ thin films, the LOD, linear range, and sensitivity were estimated as 2.1 μM , 25-400 μM , and 85 $\mu A/mM\cdot cm^2$, respectively.

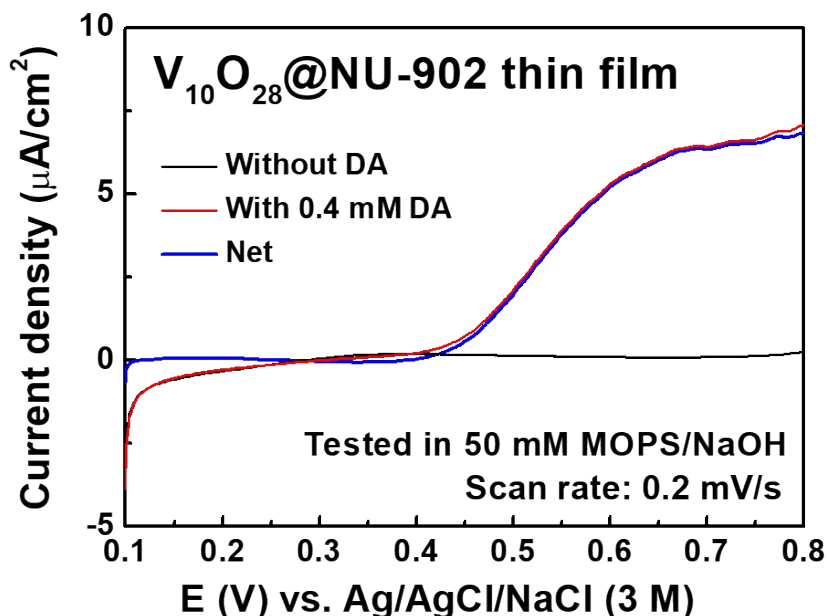


Figure S12. LSV curves of the $V_{10}O_{28}@NU-902$ thin film measured in 0.05 M MOPS/NaOH aqueous solutions (pH = 4.5) with and without 0.4 mM of DA. The net response between two LSV curves is also shown.

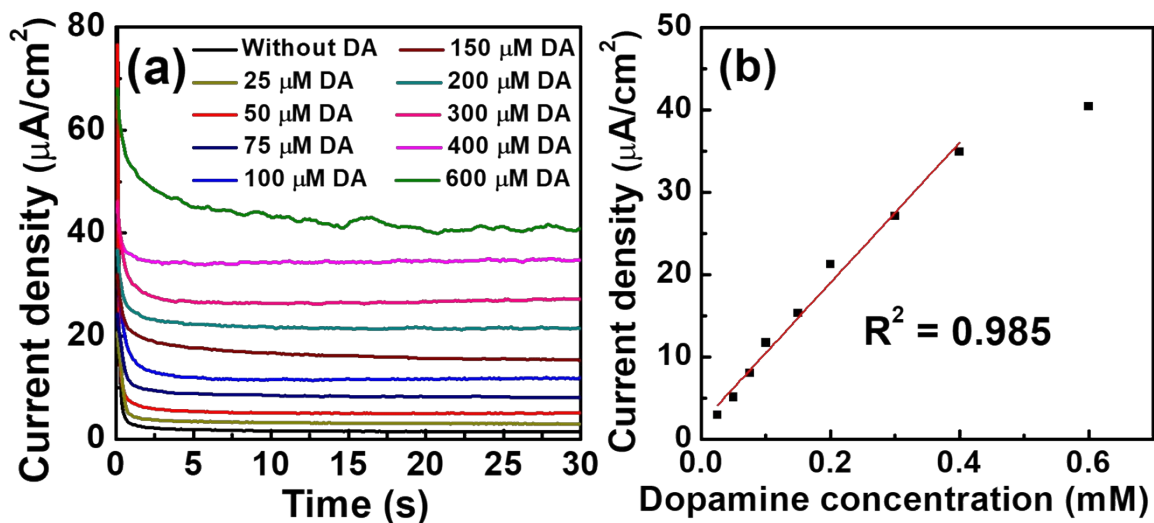


Figure S13. (a) Amperometric curves of $\text{V}_{10}\text{O}_{28}@NU-902$ thin films at an applied potential of +0.7 V vs. Ag/AgCl/NaCl (3 M) measured in 0.05 M MOPS/NaOH aqueous solutions (pH = 4.5) with various concentrations of DA. (b) Plot of current response versus the concentration of DA.

For comparison, the bare FTO substrate was subjected to the same amperometric sensing experiments for DA at +0.7 V vs. Ag/AgCl/NaCl (3 M), and the results are shown in Figures S14(a) and S14(b). The LOD, linear range, and sensitivity were estimated as 4.0 μM , up to 1,600 μM , and 16 $\mu\text{A}/\text{mM}\cdot\text{cm}^2$, respectively. It can be seen that the $\text{V}_{10}\text{O}_{28}@NU-902$ thin film shows a much higher sensitivity and thus a lower LOD for sensing DA compared to the bare substrate. The same amperometric experiments for DA sensing were also performed with the dissolved 0.1 mM $\text{V}_{10}\text{O}_{28}$ homogeneous electrocatalyst, as shown in Figures S14(c) and S14(d). The LOD, linear range, and sensitivity were estimated as 0.3 μM , up to 600 μM , and 125 $\mu\text{A}/\text{mM}\cdot\text{cm}^2$, respectively. The sensing performances of the homogeneous electrocatalytic system are in general better than those of the $\text{V}_{10}\text{O}_{28}@NU-902$ -based heterogeneous system, which is consistent with the CV results shown in Figures S9 and S10. However, the homogeneous system requires a much higher amount of $\text{V}_{10}\text{O}_{28}$ to be dissolved

in the entire liquid samples and shows more difficulty in the reuse of the dissolved electrocatalyst compared to the thin-film electroanalytical system.

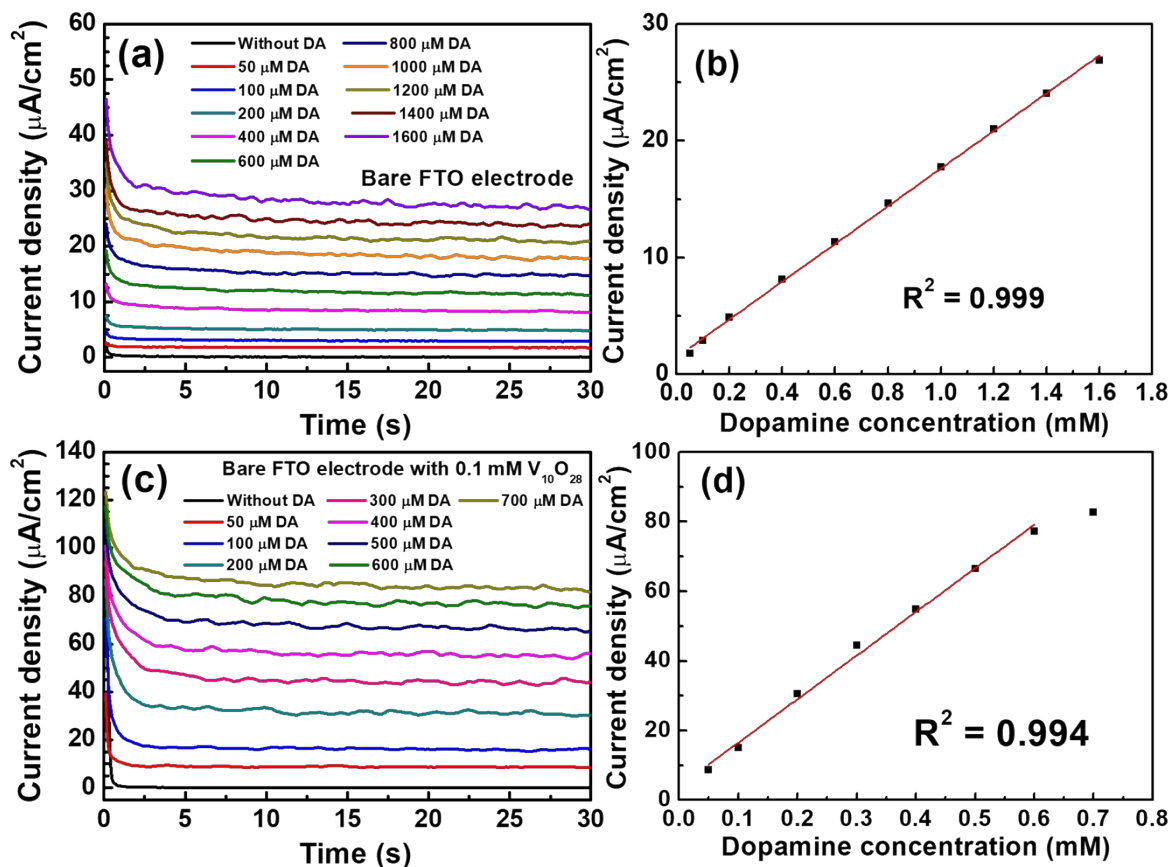


Figure S14. Amperometric curves of the bare FTO substrate at an applied potential of +0.7 V vs. Ag/AgCl/NaCl (3 M) with various concentrations of DA, measured in (a) 0.05 M MOPS/NaOH aqueous solutions (pH = 4.5) and (c) 0.05 M MOPS/NaOH aqueous solutions (pH = 4.5) in the presence of 0.1 mM dissolved $\text{V}_{10}\text{O}_{28}$ homogeneous electrocatalyst. Figure (b) and (d) show the plots of current response versus the concentration of DA extracted from (a) and (c), respectively.

Table S1. Comparison between the sensing performances of some reported electrochmical DA sensors and those of the V₁₀O₂₈@NU-902-based DA sensor.

Material	Method	Linear range (μM)	LOD (μM)	Reference
Au/PPy/Ag ^a	AMP ^f	100–5000	50	[17]
N-doped Cu-based MOF	AMP ^f	0.0005–46.81 46.81–1780	0.00015	[18]
Graphene-ZIF-8	AMP ^f	3–1000	1	[19]
V ₁₀ O ₂₈ @NU-902	AMP ^f	25–400	2.1	This work
PyC ^b	DPV ^g	18–270	2.3	[20]
MOF-525-PEDOT NTs ^c	DPV ^g	2–270	0.04	[21]
Ni ₃ (HHTP) ₂ ^d	DPV ^g	0.063–200	0.063	[22]
TiO ₂ -graphene	DPV ^g	5–200	2	[23]
PXa/Au/Cu-TCPP ^e	DPV ^g	5–125	1	[24]
Graphene	DPV ^g	4–100	2.64	[25]
HKUST-1	DPV ^g	0.5–100	0.11	[26]
Au@ZIF-8	DPV ^g	0.1–50	0.01	[27]

^aPPy: polypyrrole; ^bPyC: pyrolytic carbon; ^cPEDOT NTs: poly(3,4-ethylenedioxythiophene) nanotubes; ^dHHTP: 2,3,6,7,10,11-hexahydroxytriphenylene; ^ePXa: polyxanthurenic acid, TCPP: tetrakis(4-carboxyphenyl)porphyrin; ^fAMP: amperometry; ^gDPV: differential pulse voltammetry.

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