Supplementary Information

Heterometallic MIL-125(Ti-Al) frameworks for electrochemical determination of ascorbic acid, dopamine and uric acid

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S1. Materials and instruments

All the used chemical agents were analytical grade and used without further purification, except for aluminum nitrate nonahydrate ($Al(NO_3)_3·9H_2O$) and methanol (CH_3OH). $Al(NO_3)_3$ was obtained by treating $Al(NO_3)_3·9H_2O$ with decrystallized water, and methanol were put into the follow-up experiment after spinning distillation. Phosphate buffered solution (PBS, 0.1 M) was prepared by mixing the standard stock solution of 0.1 M of NaH_2PO_4 and hydrochloric acid. All the chemicals used were of analytical grades and aqueous solutions were prepared with deionized water. High purity nitrogen was used for deaeration.

Powder X-ray diffraction (PXRD) patterns were monitored on a SmartLab diffractometer using a Bruker D8-Focus Bragg-Brentano X-ray Powder Diffractometer with a Cu-Kα radiation. The patterns were recorded in the 2θ angular range of 5 − 50° with a scan rate of 10 $°·min^{-1}$. Scanning electron microscopy (SEM) images were obtained with a Hitachi SU8010 microscope. Energy-dispersive X-ray spectroscopy (EDS) of MIL-125(Ti-Al)-$x$$NH_2$ was performed with a Hitachi microscope (SU8010, x = 0% and 25%, and SU5000, x = 50%, 75% and 100%). UV-Vis spectroscopy was recorded using a U-3900 spectrophotometer. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was carried out on a Prodigy.

S2. Solvothermal synthesis of MIL-125(Ti-Al)-$x$$NH_2$ series

A mixture of titanium isopropoxide (0.2 mL, 0.67 mmol) and aluminum nitrate (16 mg, 0.075 mmol) as the metal sources, and 1,4-benzenedicarboxylic acid (H_2BDC) and 2-aminoterephthalic acid (NH_2-H_2BDC) in different proportions (1.5 mmol, 4:0, 3:1, 2:2, 1:3, 0:4) as the organic linkers was stirred ultrasonically in DMF (4 mL) and CH_3OH (1 mL) for 0.5 h. Then the resultant solution was placed in a Teflon vessel in a steel autoclave, heated at 160 °C for 48 h, then cooled to room temperature. The products were recovered by filtration, washed three times with DMF to remove the unreacted organic ligand, and then washed with methanol. Finally, the obtained crystalline products (MIL-125(Ti-Al)-$x$$NH_2$ (x = 0%, 25%, 50%, 75%, and 100%)) were dried under vacuum for subsequent experiments.

S3. Electrochemical studies

All electrochemical operations were conducted using CHI-760D (Chenhua, Shanghai) electrochemical station. A traditional three-electrode system was employed for all purposes, where a modified glassy carbon electrode (GCE) (3.0 mm diameter, 0.0706 cm^2 geometric area) was used as the working electrode, Ag/AgCl as the reference electrode, and a Pt wire as the counter electrode. The GCE was respectively polished with 0.3 and 0.05 μm alumina slurry followed by rinsing thoroughly with double distilled water, and then ultrasonically cleaned in ethanol and double distilled water to obtain a mirror-like surface. The as-prepared MIL-125(Ti-Al)-$x$$NH_2$ (x = 0%, 25%, 50%, 75%, and 100%) were mixed with carbon black (Vulcan XC-72R) in different mass ratios and added with deionized water (950 μL) containing 0.5 wt% Nafion (50 μL) by ultrasonication for 30 min at least. Then, 7.5 μL of catalyst ink was dropped onto the well-polished bare GCE and then evaporated in air. The resultant modified electrode was denoted as MIL-125(Ti-Al)-$x$$NH_2$/GCE and used for the electrochemical separately and simultaneously detection of ascorbic acid (AA), dopamine (DA) and uric acid (UA). The whole procedure was performed in 0.1 M PBS. The PBS was deoxygenated before each electrochemical operation by purging with high-purity N_2 gas.

S4. Selectivity study

To estimate the selectivity, some interfering substances of MIL-125(Ti-Al)-$x$$NH_2$/GCE electrodes were investigated under the same experimental condition. 1 mM of citric acid (CA) and lactic acid (LA), 1.5 mM of glucose (Glu), 50 μM of L-phenylalanine (L-Phe), glycine (Gly), and L-cysteine(L-Cys) were added separately to the detection system. Meanwhile, inorganic salts such as NaCl, KCl, $MgSO_4$, $CaCl_2$, and Na_2CO_3 were introduced with a concentration of 1 M, respectively.

S5. Real sample analysis

To assess the validity and reliability of the proposed sensor in practice, the analytical determinations of UA, DA, and AA in commercially available vitamin C tablets, dopamine hydrochloride injection and sweat samples were selected as real samples for analysis by using the standard addition method. Firstly, 0.028 g of vitamin C tablets (122 mg/0.65 g) were crushed, weighted, and dissolved in 30 mL PBS (pH 7.10). Then 5 mL of solution were transferred into an electrochemical cell. Secondly, 8 μL of dopamine hydrochloride injection (20 mg/2 mL) was diluted into 20 mL PBS (pH 7.10) for individual detection of DA. Thirdly, prior to physical testing, each subject agreed to an informed consent form and human sweat samples were directly employed after purification. The above-mentioned diluted samples were spiked with certain amounts of AA, DA, and UA before monitored, to ascertain the correctness.

Human sweat samples were collected from healthy subject in compliance with all the ethical guidelines under a protocol (ID 202302017) that was approved by Northeast Normal University. Subject gave written informed consent before participation in the study.

S6. Supporting tables

Table S1. The ratios of Ti:Al in MIL-125(Ti-Al)-xNH$_2$ (x = 0%, 25%, 50%, 75%, and 100%) materials.

As-prepared Products	Feeding	ICP results
MIL-125(Ti-Al)-0%NH$_2$		5.34:2.35
MIL-125(Ti-Al)-25%NH$_2$		5.65:2.35
MIL-125(Ti-Al)-50%NH$_2$	9:1	5.54:2.46
MIL-125(Ti-Al)-75%NH$_2$		5.88:2.12
MIL-125(Ti-Al)-100%NH$_2$		5.51:2.49

Table S2. Comparison of the electrochemical performance for the determination of AA, DA and UA.

Electrode	Method	Substance	Linear range (μM)	ΔE$_p$ (mV)	LOD (μM)	Ref.
MIL-125(Ti-Al)-75%NH$_2$/GCE	**DPV (simultaneous)**	**AA**	**1000 − 3500**	**220**	**224**	**This Work**
		DA	**5 − 90**	**140**	**0.056**	
		UA	**5 − 90**		**0.558**	
	DPV (individual)	**AA**	**1000 − 6500**	**—**	**215**	
		DA	**5 − 100**		**0.086**	
		UA	**5 − 120**		**0.876**	
Mn-BDC@MWCNT/GCE	DPV (simultaneous)	AA	1 − 600	184	0.25	1
		DA	0.5 − 660	145	0.024	
		UA	0.05 − 1400		0.023	
	DPV (individual)	AA	0.1 − 1150	—	0.01	
		DA	0.01 − 500		0.002	
		UA	0.02 − 1100		0.005	
UIO-66-NO$_2$@XC-72/GCE	DPV (simultaneous)	AA	0.2 − 3.5	215	0.12	2
		DA	0.03 − 2.0	150	0.005	
		UA	0.75 − 22		0.03	
L-Co-MOF/CC	DPV	DA	0.0075 − 10	140	0.001	3

	(simultaneous)		10 − 50		8	
		UA	0021 − 70		0.007	
	DPV (individual)	DA	0.0056 – 10 10 − 70	—	0.002 5	
		UA	0.021 – 150 150 − 350		0.007	
GO-ZIF-67/GCE	DPV (simultaneous)	DA	0.2 − 80	140	0.05	4
		UA	0.8 − 200		0.1	
NiCo-MOF/Ti_3C_2/CCE	DPV (simultaneous)	DA	0.01 − 300	128	0.004	5
		UA	0.01 − 350		0.006	
ITO/g-C_3N_4/NC@GC/h-ATS	DPV (simultaneous)	AA	0.1 − 200	236 204	0.02	6
		DA	2.5 − 100		0.01	
		UA	2.5 − 625		0.06	
3DGLCFs/GCE	DPV (simultaneous)	AA	12.5 – 400	230 130	2	7
		DA	0.05 – 10		0.01	
		UA	0.05 – 15		0.01	
PAYR/GCE	CV (simultaneous)	AA	80 – 2000	178 115	8.3	8
		DA	2.3 – 17.5		0.42	
		UA	33 – 330		4.3	
PMo_{12}@MIL-100(Fe)@PVP	DPV (simultaneous)	DA	1 − 247	146	0.586	9
		UA	5 − 406		0.372	
Co_3O_4/Fe_3O_4/mC@g-C_3N_4-150/GCE	DPV (simultaneous)	AA	500 − 8000	180 140	12.55	10
		DA	1.0 − 70		0.21	
		UA	5.0 − 100		0.18	
MOF-235/GCE	DPV	DA	10 − 90	133	3.33	11
		UA	10 − 90		3.27	
Ni-MOF/GCE	DPV	DA	0.2 − 100	—	0.06	12
β-CD/Ni-MOF/GCE	DPV	DA	0.7 − 310.2	—	0.227	13
HKUST-1/ITO	DPV	AA	10 – 25000 25000 – 265000	—	3	14
ZIF-65@CNTs/GCE	DPV (individual)	AA	200 − 2267	—	1030	15

S7. Supporting figures

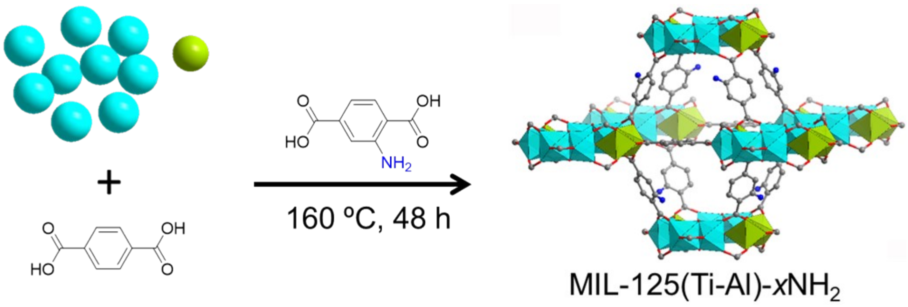

Fig. S1 The schematic syntheses of MIL-125(Ti-Al)-xNH$_2$ series. Color codes: Ti, cyan; Al, yellow.

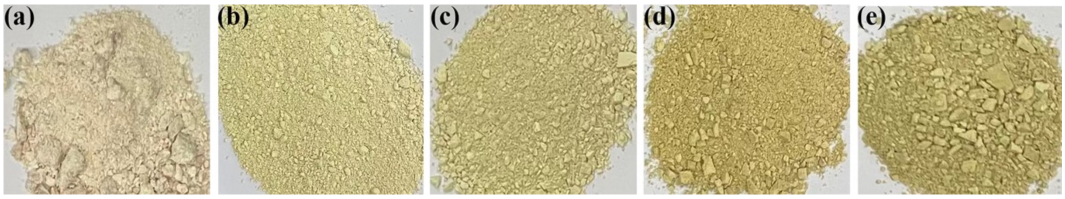

Fig. S2 The optical photos of MIL-125(Ti-Al)-xNH$_2$ (x = 0%, 25%, 50%, 75%, and 100%, from left to right), respectively.

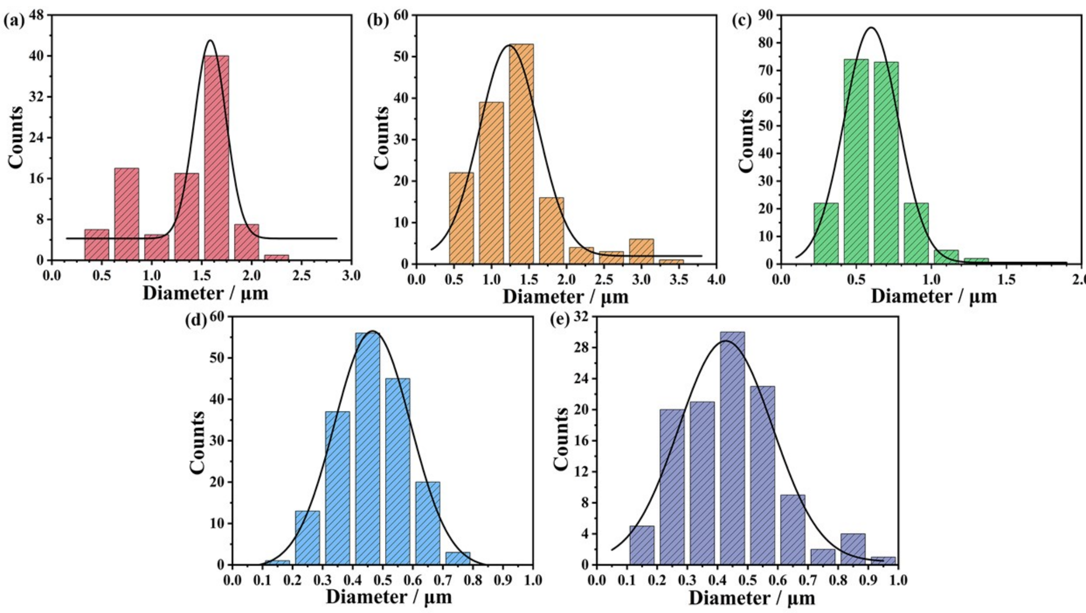

Fig. S3 The size distribution histograms of MIL-125(Ti-Al)-xNH$_2$ (a-e, x = 0%, 25%, 50%, 75%, and 100%), respectively.

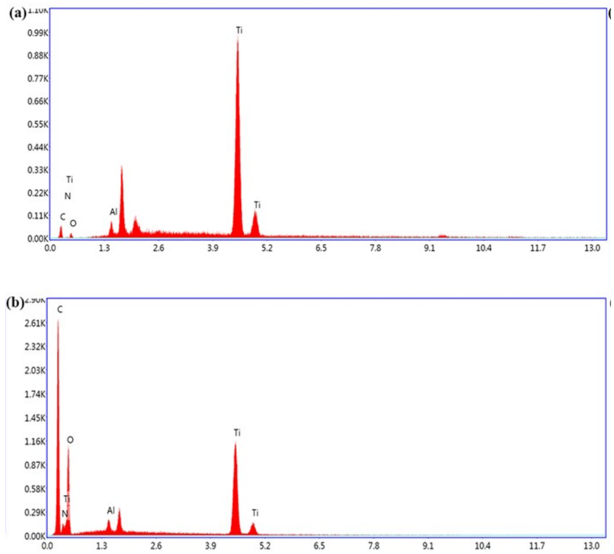

Fig. S4 The EDS spectra of (a) MIL-125(Ti-Al)-0%NH_2 and (b) MIL-125(Ti-Al)-25%NH_2.

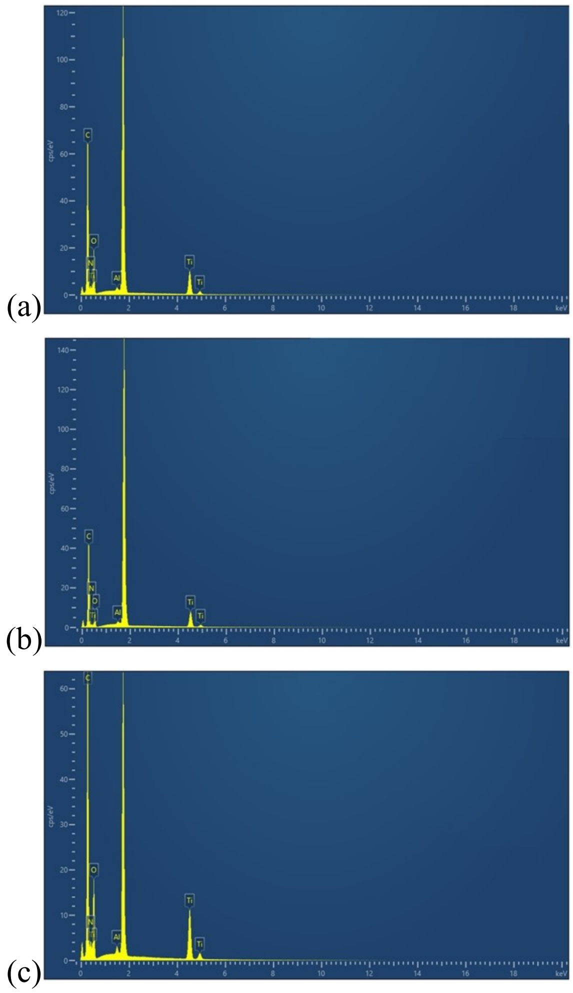

Fig. S5 The EDS spectra of (a) MIL-125(Ti-Al)-50%NH_2, (b) MIL-125(Ti-Al)-75%NH_2 and (c) MIL-125(Ti-Al)-100%NH_2.

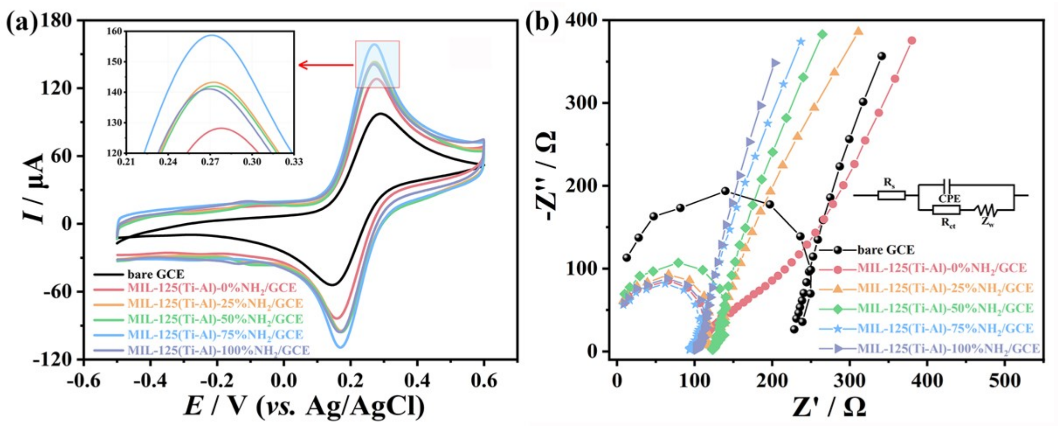

Fig. S6 (a) CV curves and (b) Nyquist plots of bare GCE and MIL-125(Ti-Al)-$x$$NH_2$ (x = 0%, 25%, 50%, 75%, and 100%)/GCE in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$ (1:1). Scan rate: 50 mV s^{-1}; frequency range, 0.1 Hz–500 kHz. (Inset of b: an approximate Randles' equivalent circuit model: R_s, CPE, R_{ct}, and Z_w represent the solution resistance, constant phase element, charge transfer resistance, and Warburg element, respectively).

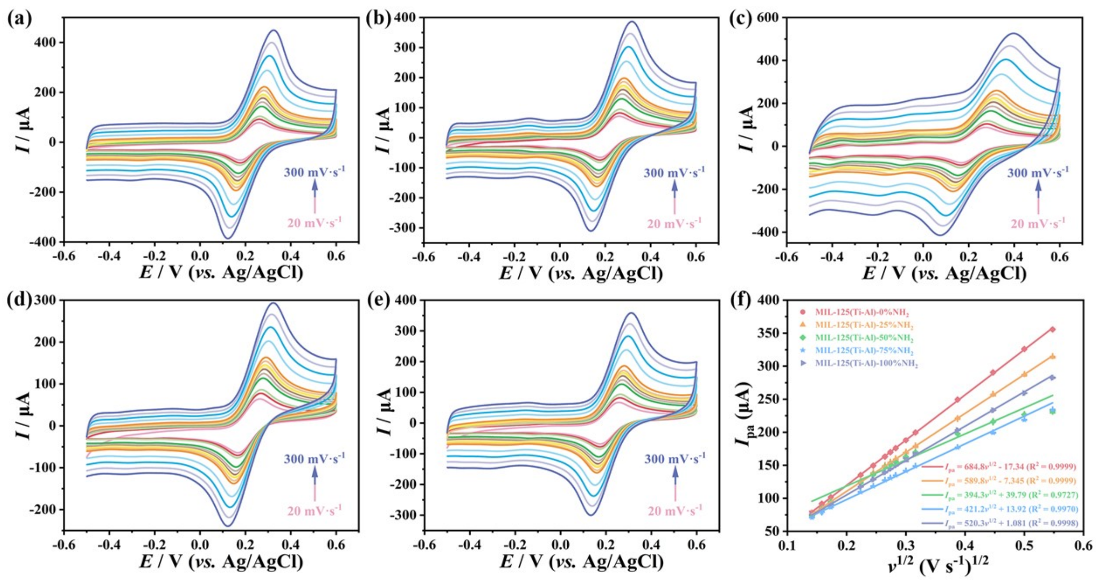

Fig. S7 CV curves of MIL-125(Ti-Al)-$x$$NH_2$ (a-e, x = 0%, 25%, 50%, 75%, and 100%) modified electrodes with various scan rates (25, 30, 50, 60, 75, 80, 100, 150, 200 mV·s^{-1}) in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$ (1:1), and (f) linear fitting curves corresponding to the peak current (I_{pa}) and the square root of the scanning rate ($v^{1/2}$) of modified electrodes.

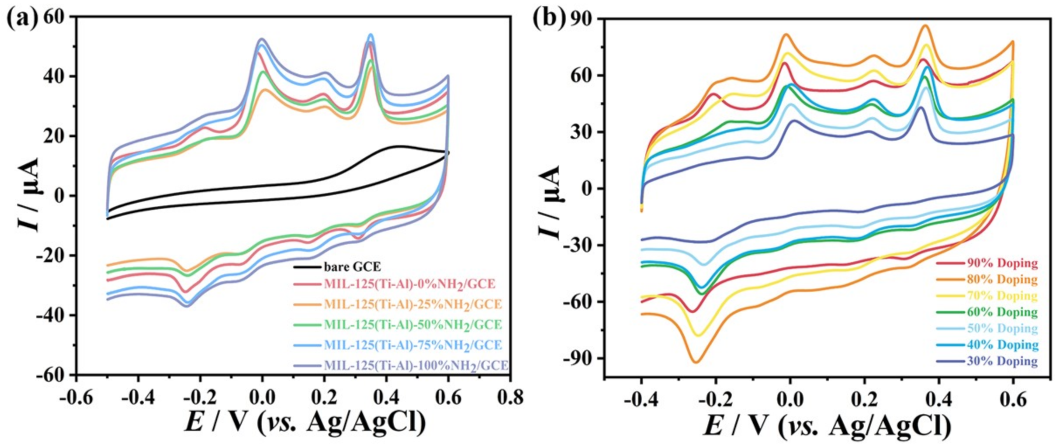

Fig. S8 (a) Bare GCE and MIL-125(Ti-Al)-$x$$NH_2$/GCE with 50% XC-72R doping ratio at pH = 7.10, and (b) MIL-125(Ti-Al)-75%NH_2/GCE materials mixed with different XC-72R doping ratios in 0.1 M PBS (pH 7.10) containing [AA]: 1 mM, [DA]: 30 μM, and [UA]: 50 μM. Scan rate: 100 mV·s^{-1}.

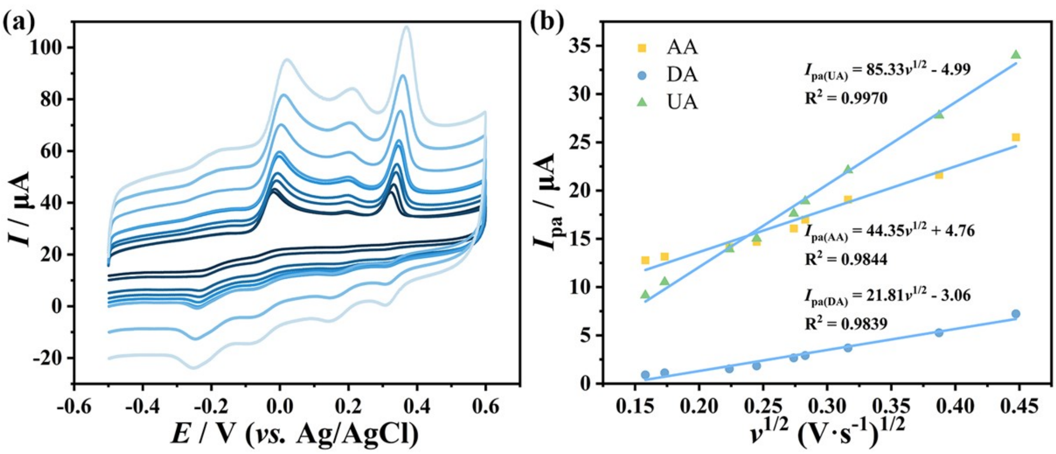

Fig. S9 (a) CV curves of MIL-125(Ti-Al)-75%NH_2 modified electrodes with different scan rates (25, 30, 50, 60, 75, 80, 100, 150, 200 mV·s^{-1}) in 0.1 M PBS solution containing [AA]: 1 mM, [DA]: 30 μM, and [UA]: 50 μM. And (b) linear fitting curves corresponding to the peak current (I_{pa}) and the square root of the scanning rate ($v^{1/2}$).

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