Supporting Information

Urchin-like CoP_3/Cu_3P Heterostructured Nanorods Supported on 3D Porous Copper Foam for High-Performance Non-Enzymatic Electrochemical Dopamine Sensors

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Chemical reagents

Cobalt(III) sulfate heptahydrate ($CoSO_4.7H_2O$), copper(II) sulfate pentahydrate ($CuSO_4.5H_2O$), sodium hypophosphite monohydrate ($NaH_2PO_2.H_2O$), potassium hydroxide (KOH), urea ($(NH_2)_2CO$), and ethanol (C_2H_5OH) were purchased from Sigma-Aldrich.

Material Characterization

We obtained scanning electron microscopy images and energy-dispersive X-ray spectroscopy spectra on JEOL JSM-5300LV scanning electron microscope instrument. Transmission electron microscope, high-resolution TEM, and EDS elemental mapping images were achieved on a JEOL JEM-1230 transmission electron microscope instrument. The powder X-ray diffraction pattern was acquired on a Bruker D8 ADVANCE X-ray powder diffractometer.

Synthesis of CoP_3 NRs/CF

Initially, 0.79 g of $CoSO_4.7H_2O$ and 0.789 g of urea were added to 37 mL of distilled water under stirring. Next, the mixture solution was poured in to 50 mL Teflon lined stainless steel autoclave with copper foam and maintained at 85 ^oC for 2 h. After the hydrothermal reaction have finished, the product was washed and dried at 60 ^oC overnight prior to annealing at 300 ^oC for 2 h in air. Finally, the obtained oxide sample was heated with $NaH_2PO_2.H_2O$ at 300 ^oC for 2 h to form CoP_3 NRs/CF.

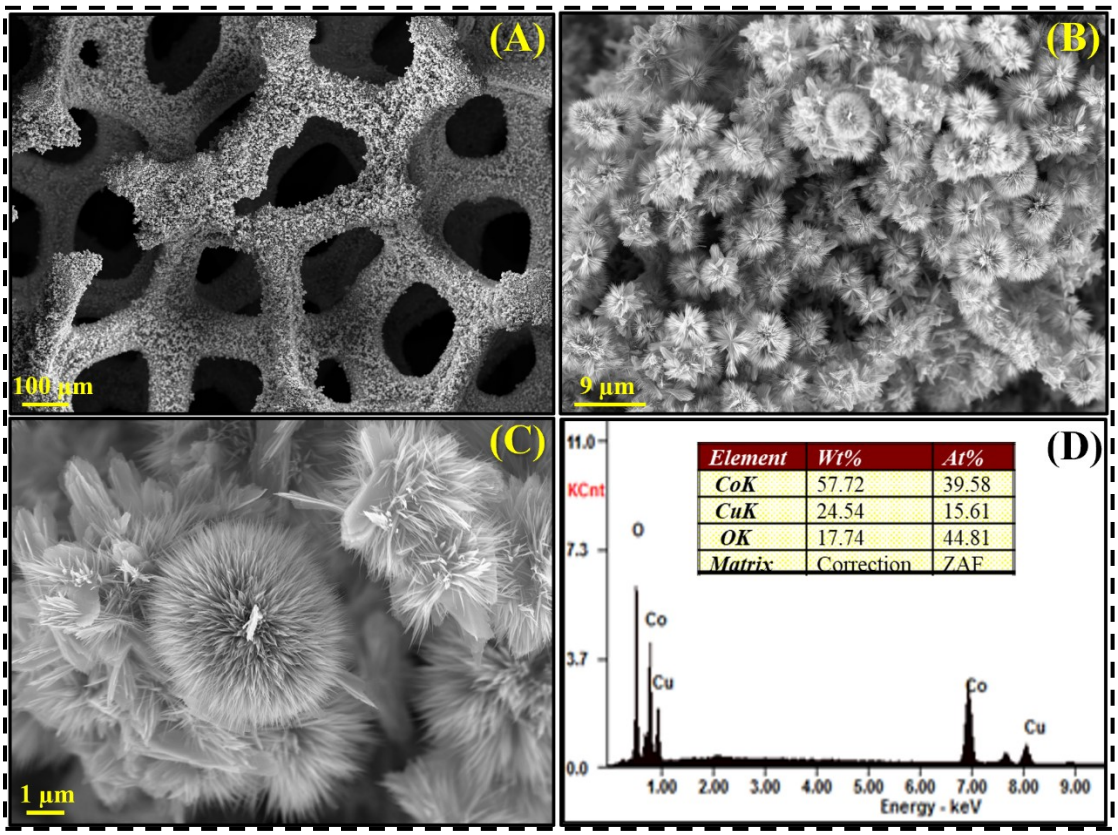

Figure S1. SEM images (A, B, and C) and EDS spectrum (D) of Co-Cu-O NRs/CF.

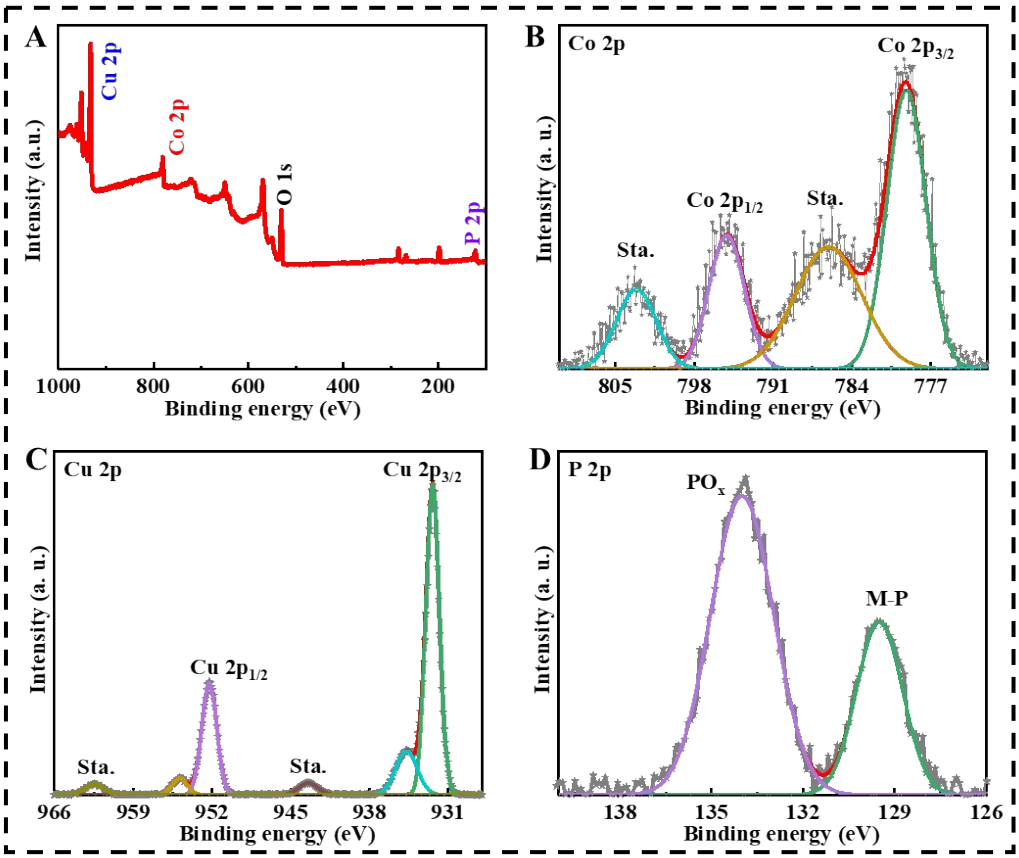

Figure S2. (A) XPS survey spectrum of the CoP_3/Cu_3P NRs/CF, and high-resolution XPS spectra of (B) Co 2p, (C) Cu 2p, and (D) P 2p in the CoP_3/Cu_3P NRs/CF.

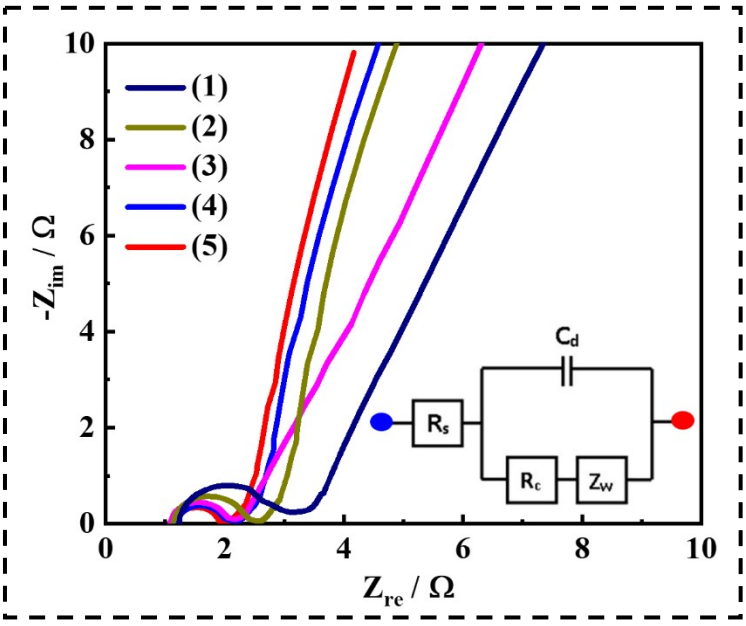

Figure S3. Nyquist plots for various samples. ((1): 3D copper substrate, (2) CoP_3 NRs/CF, (3) Co-Cu-OH NRs/CF, (4) Co-Cu-O NRs/CF, and (5) CoP_3/Cu_3P NRs/CF) (inset: an equivalent circuit to simulate the Nyquist plots).

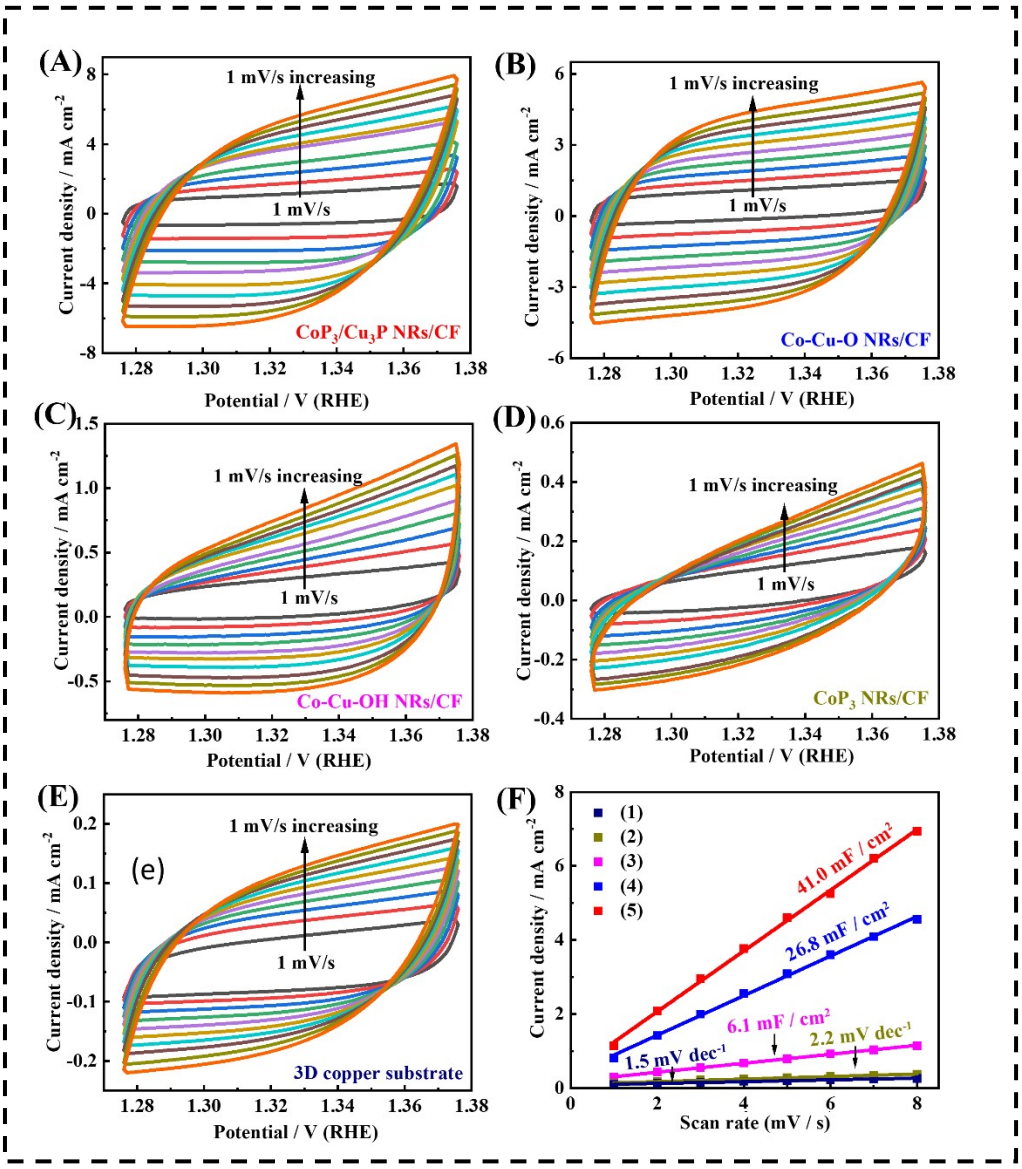

Figure S4. CV curves for (A) CoP_3/Cu_3P NRs/CF, (B) Co-Cu-O NRs/CF, (C) Co-Cu-OH NRs/CF, (D) CoP_3 NRs/CF, and (E) 3D copper substrate at various scan rates. (F) The C_{dl} values are determined using the current density as a function of scan rates (1) 3D copper substrate, (2) CoP_3 NRs/CF, (3) Co-Cu-OH NRs/CF, (4) Co-Cu-O NRs/CF, and (5) CoP_3/Cu_3P NRs/CF.

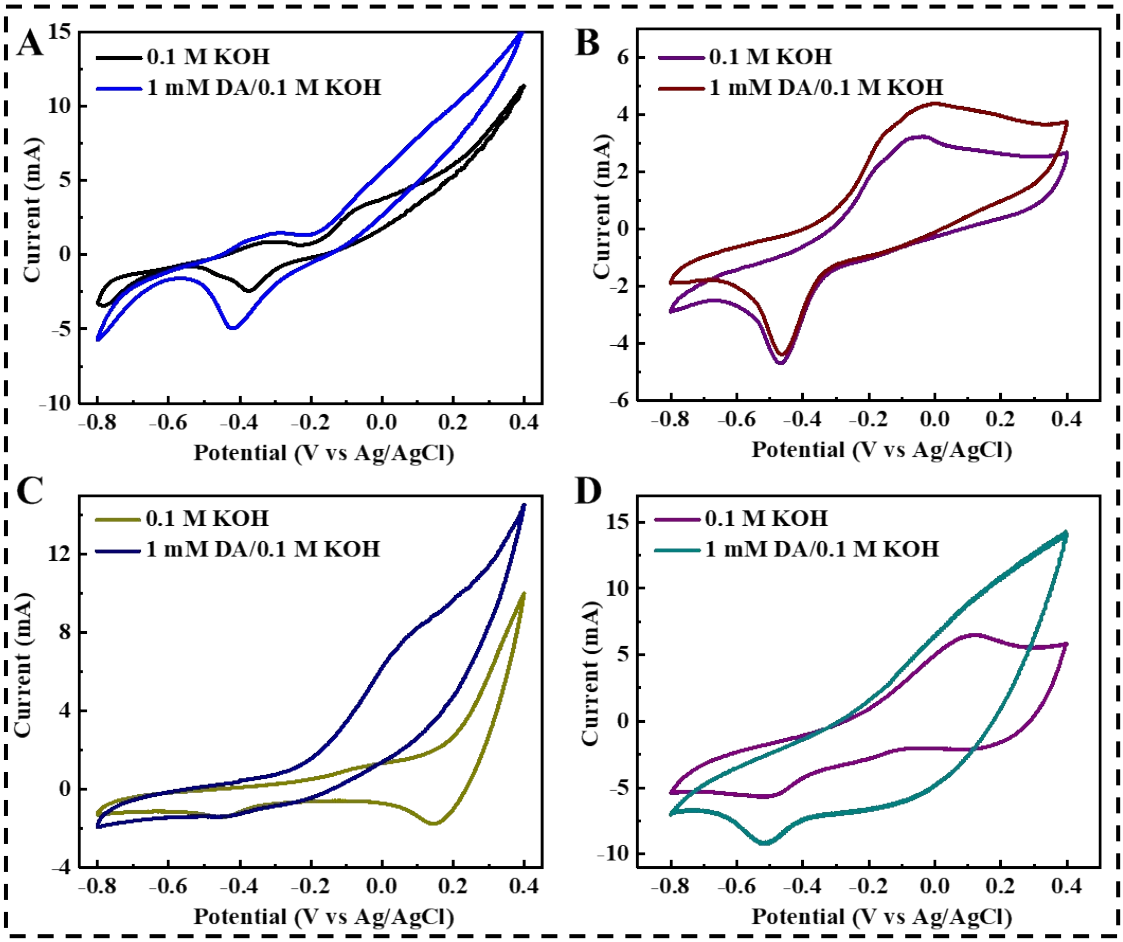

Figure S5. CV curves in 0.1 M KOH and 0.1 M KOH + 1 mM dopamine mediums at scan rate of 10 mV s^{-1} of (A) copper foam, (B) Co-Cu-OH NRs/CF, (C) Cu-Cu-O NRs/CF, and (D) CoP_3 NRs/CF.

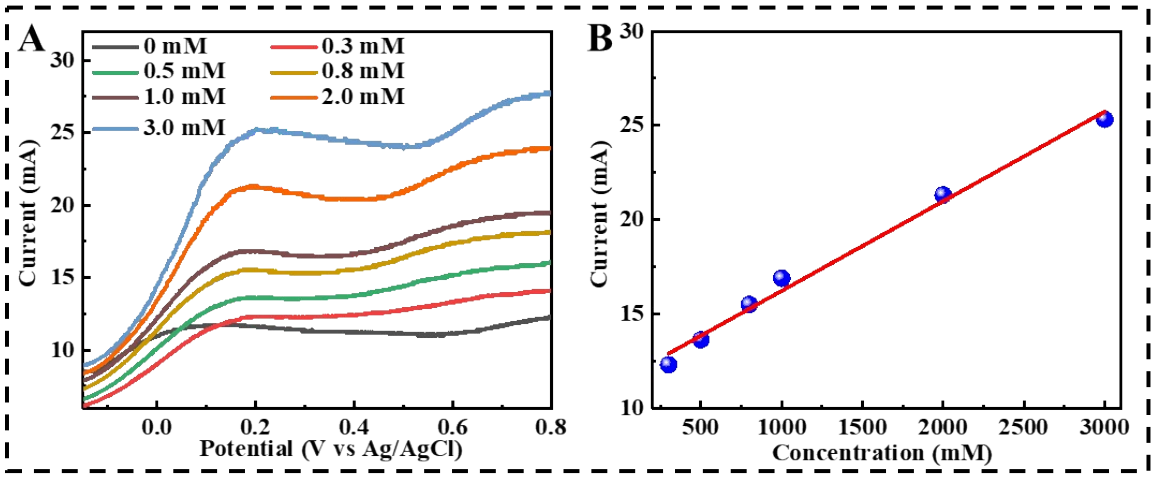

Figure S6. (A) Differential pulse voltammetry (DPV) current responses of the CoP_3/Cu_3P NRs/CF electrode obtained for various concentration of dopamine in 0.1 M KOH and (B) corresponding calibration plots of DPV responses *versus* dopamine concentrations.

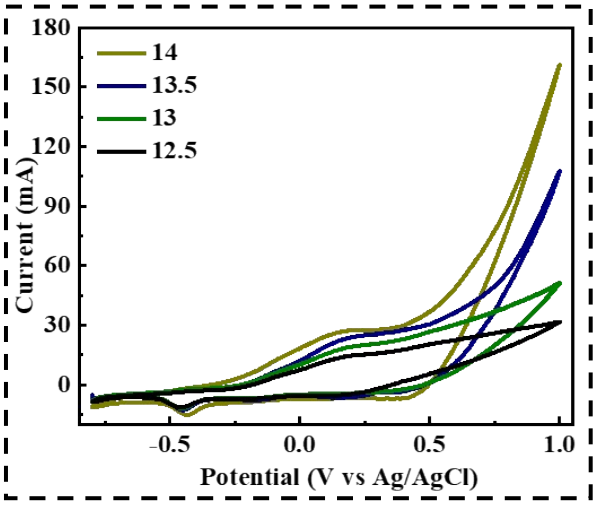

Figure S7. CV curves of the CoP_3/Cu_3P NRs/CF electrode at scan rate of 10 mV s^{-1} in different pH levels of 12.5, 13.0, 13.5, and 14.

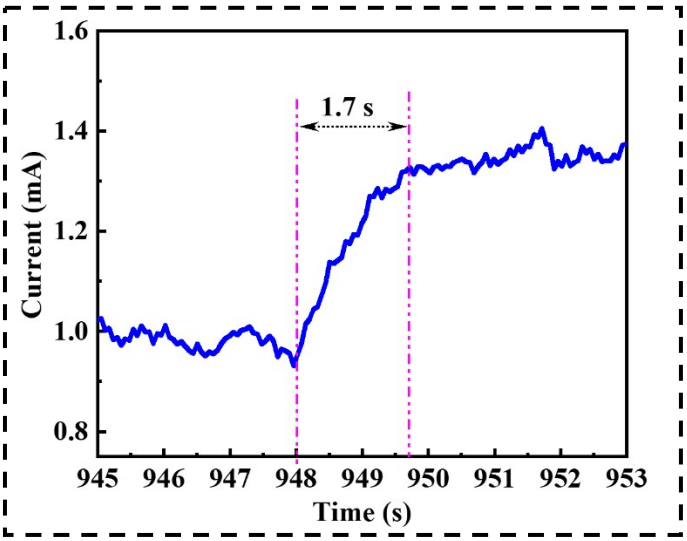

Figure S8. Plot of response time of the non-enzymatic electrochemical dopamine sensor based on the CoP_3/Cu_3P NRs/CF.

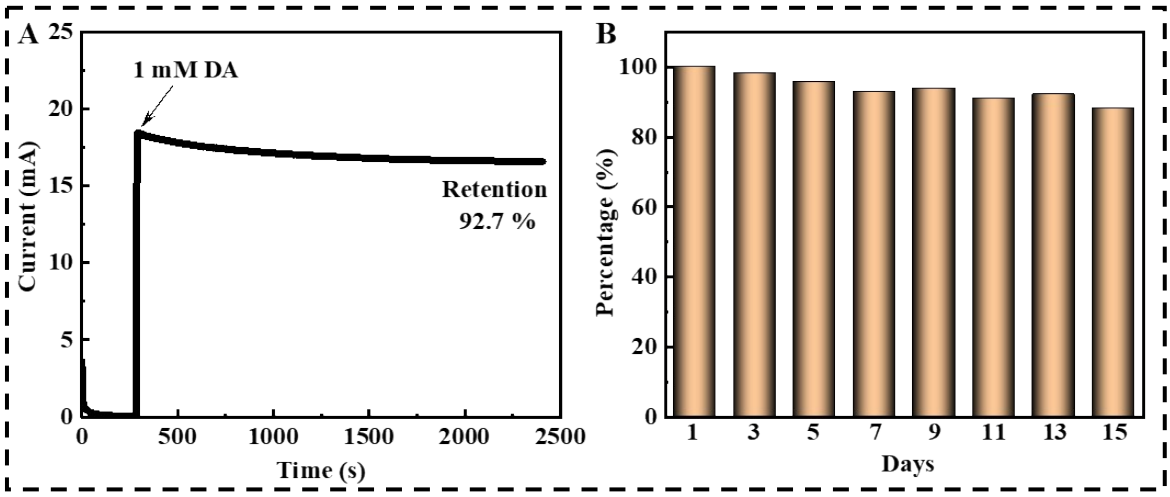

Figure S9. (A) Amperometric I-t response of the sensor based on the CoP_3/Cu_3P NRs/CF to 1 mM dopamine over 2,500 s. (B) The stability of the sensor based on the CoP_3/Cu_3P NRs/CF to dopamine tested every two days by amperometric measurement.

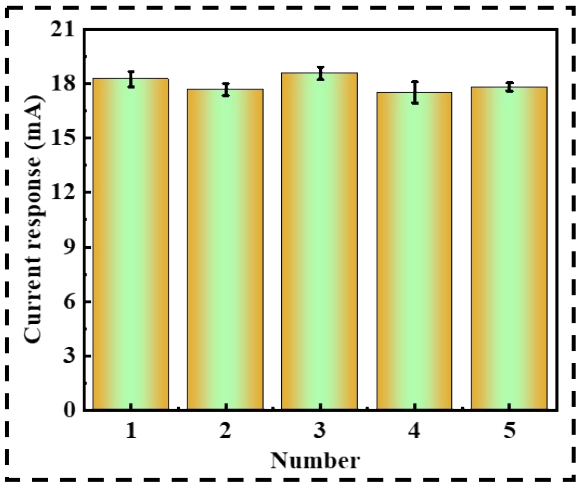

Figure S10. The response currents of five runs of CoP_3/Cu_3P NRs/CF towards 1 mM dopamine.

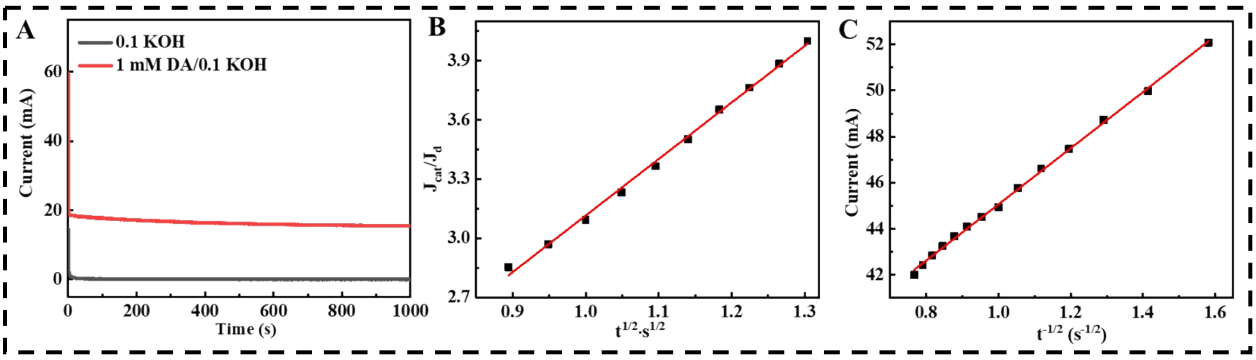

Figure S11. (A) Chronoamperometric curves of the CoP_3/Cu_3P NRs/CF electrode in 0.1 M KOH solution with and without the addition of 1 mM dopamine. (B) Calibration curves of J_{cat}/J_d versus $t^{1/2}$. (C) Calibration curves of J versus $t^{-1/2}$ derived from the data of chronoamperometric curves.

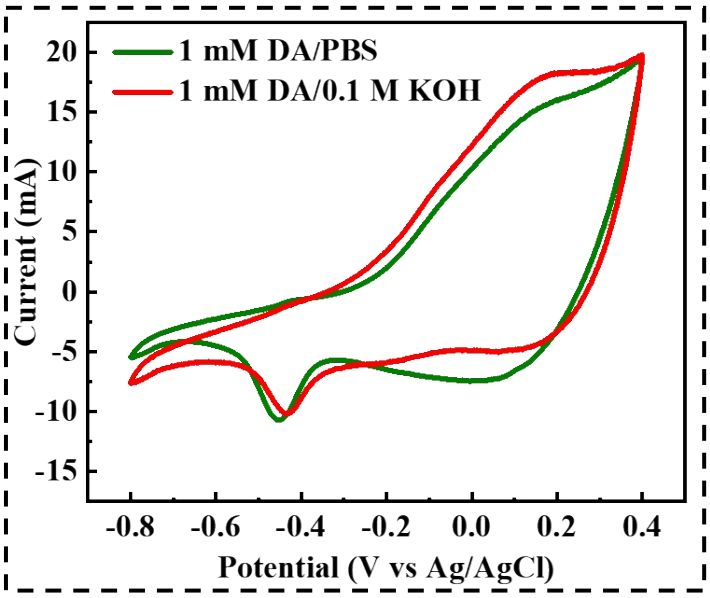

Figure S12. CV curves of the CoP_3/Cu_3P NRs/CF under alkaline conditions (0.1 M KOH + 1 mM dopamine) and neutral conditions (0.1 M PBS + 1 mM dopamine) at room temperature.

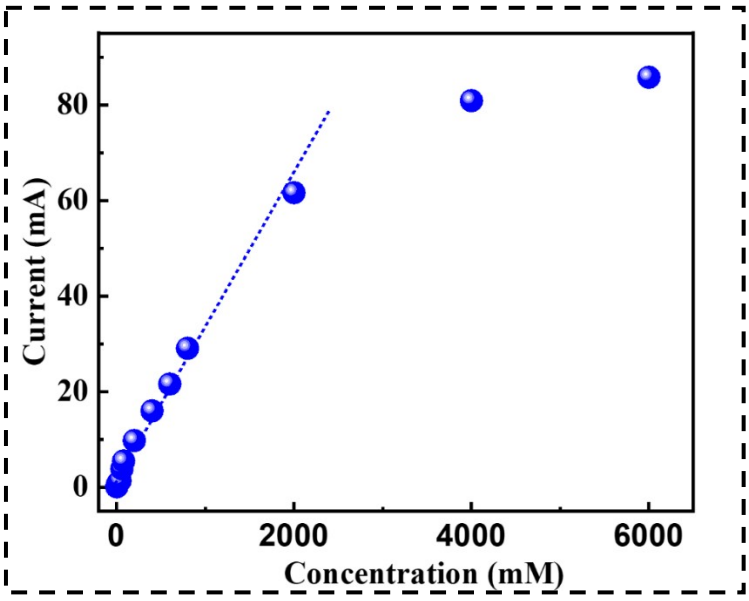

Figure S13. Calibration curve for the current response to dopamine concentration of the CoP_3/Cu_3P NRs/CF in neutral conditions with physiological pH of 7.25 and at temperature of 36.6 °C.

Table S1. Comparison of detection range and limit detection between the CoP_3/Cu_3P NRs/CF sensor and other non-enzymatic electrochemical dopamine sensors based on transition metals and their compounds reported elsewhere.

Electrode materials	LOD (μM)	Linear range (μM)	Reference
ITO/pGO–GNP–pGO	1.28	0.1 - 30	Sensors 2017, 17(4), 861
PA-MNPs	14.1	10 - 1000	Mater. Sci. Eng. B 2012, 177, 17, 1531-1537
rGO-WS2@Fe_3O_4	2.74	---	Mater. Chem. Phys. 2022, 287, 126283
Au-Cu_2O/rGO	---	10 – 90	
CoP_3/Cu_3P NRs/CF	0.51	0.2 to 2000	Present work

Table S2. Results of dopamine detection in human urine sample using the CoP_3/Cu_3P NRs/CF sensor.

Sample	Added (10^{-5} mol L^{-1})	Detected (10^{-5} mol L^{-1})
1	0	86.42
2	0.04	90.19
3	0.05	93.98
4	0.1	101.54
5	0.15	109.28
6	0.15	107.31
7	0.3	117.83
8	0.8	160.73
9	2.0	280.24
10	4.0	481.67