Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary document

3D Architectured Zinc- Chromium Layered Double Hydroxide with Nickel Cobalt Sulfide Composite for the Electrochemical Detection of Ronidazole

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Chemicals and reagents

Zinc nitrate hexahydrate ($Zn(NO_3)_2$.6H2O; 98.0%), chromium(III) nitrate nonahydrate ($Cr(NO_3)_3.9H_2O$; 99.0%), ammonium fluoride (NH_4F; ≥99.99%), urea ($CO(NH_2)_2$; ≥99.5%), Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2$. $6H_2O$, ≥97.0%), Cobalt (II) nitrate hexahydrate ($Ni(NO_3)_2$. $6H_2O$; ≥98.0%), glycerol ($C_3H_8O_3$; ≥99.0%), isopropanol (C_3H_8O; anhydrous; 99.5%), thioacetamide (C_2H_5NS; 98.0%), Ronidazole ($C_6H_8N_4O_4$; ≥95.0%), sodium phosphate dibasic anhydrous (NaH_2PO_4, ≥99.0%), sodium phosphate monobasic dihydrate ($NaH_2PO_4 \cdot 2H_2O$, <=100%) were purchased from Sigma- Aldrich (Taiwan). Sodium hydroxide (NaOH, ≥98%), potassium chloride (KCl, <=100%) hydrochloric acid (HCl, ≥37%) were purchased from Honeywell Fluka (Taiwan). Potassium ferricyanide ($K_3Fe(CN)_6$, >98%) and potassium ferrocyanide ($K_4Fe(CN)_6.3H_2O$, >99%) from Duksan (Taiwan). Alumina powder (0.05µm) and ethanol (C_2H_5OH, 95%) were bought from Struers (Taiwan) and Taiwan Sugar Corporation. De-ionized water (DI) was used for preparation and washings. All the chemicals were analytical grade and used without further purification.

Instrumentation

X-ray diffraction analysis (XRD) was done with an X-ray diffractometer (PANalytical B.V.) using the monochromatic Cu-Kα line with a PIXcel3D detector. Fourier-transform infrared (FT-IR) spectroscopy was performed using a JASCO FT/IR-6600 spectrophotometer. Transmission electron microscope (TEM) images were obtained from a JEOL-JEM-2100F equipped with selected area electron diffraction (SAED), energy-dispersive X-ray (EDX) spectrometer, and elemental mapping. High-resolution X-ray photoelectron spectroscopy (HR-XPS) was conducted with Thermo ESCALAB 250. Electrochemical Impedance Spectroscopy (EIS) was performed with Admiral Instruments Squidstat Plus Potentiostat (1709 CH1).

Electrochemical cell setup

In the three-electrode electrochemical cell setup, a Glassy carbon electrode (GCE), Ag/AgCl (saturated KCl) electrode, and platinum wire were taken as working, reference, and an auxiliary electrode. Cyclic voltammetry (CV) and Difference Pulse Voltammetry (DPV) measurements were carried out with CH Instrument electrochemical workstation CHI 611A and CHI 900. 0.1 M phosphate buffer (PB) solution was chosen as the working electrolyte in all experiments.

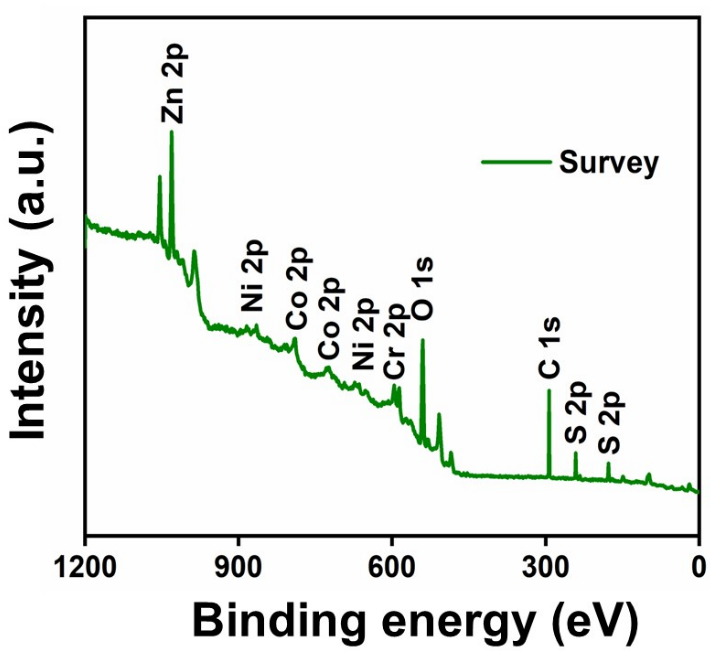

Fig. S1 Survey spectrum of ZC/NCS composite.

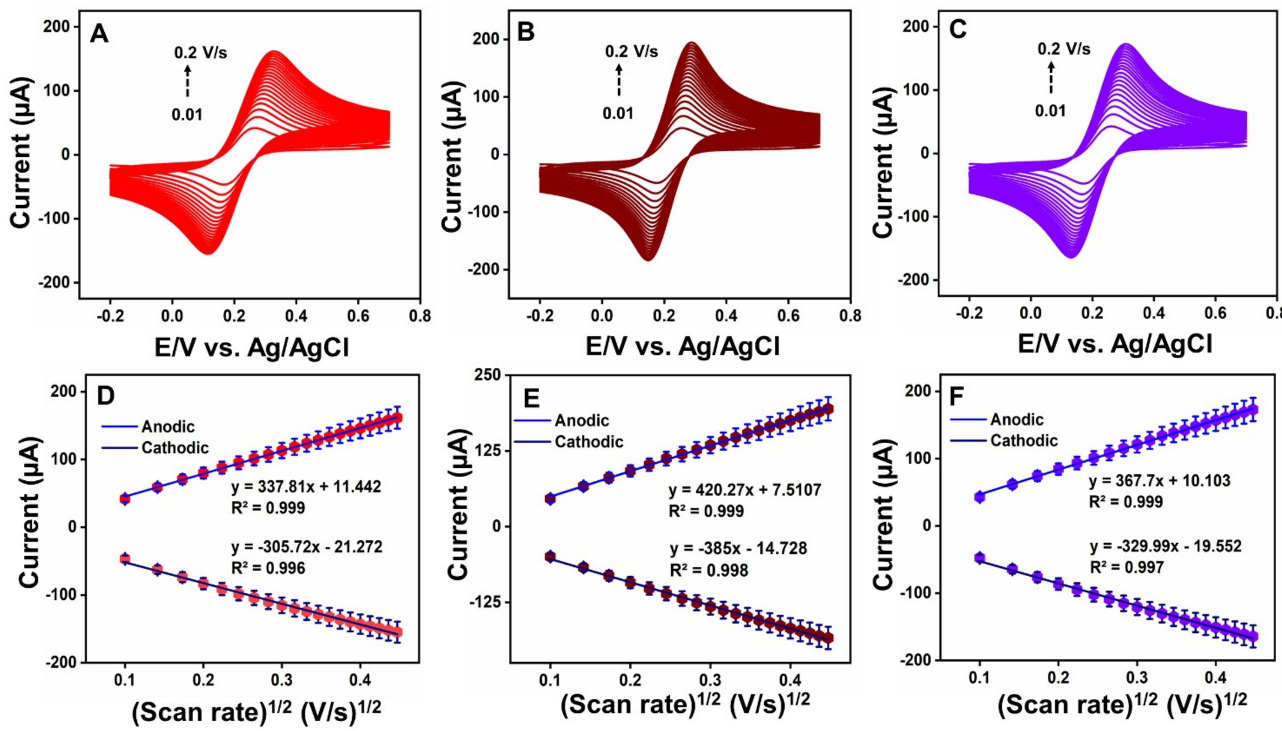

Fig. S2 CV curves of (A) bare GCE, (B) ZC/GCE, (C) NCS/GCE at various scan rates and their respective linear calibration plots of resultant current (D) bare GCE, (E) ZC/GCE, and (F) NCS GCE.

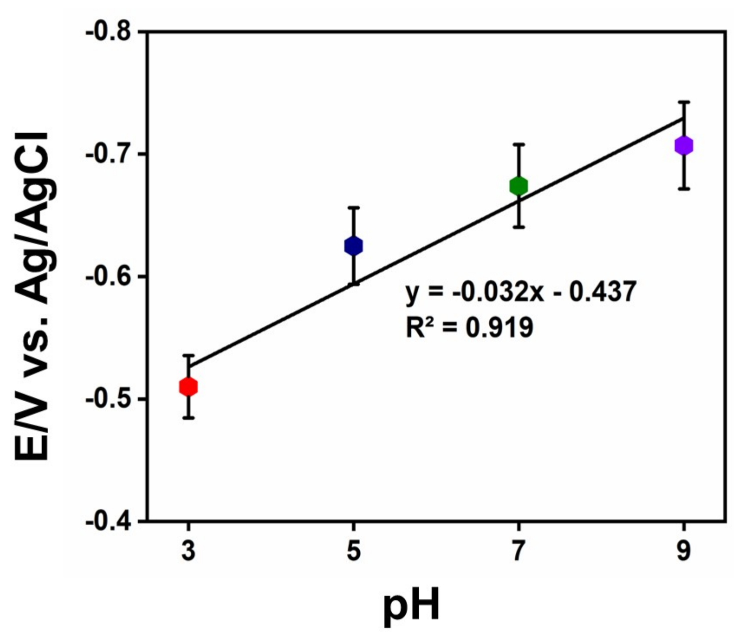

Fig. S3 A linear plot between the potential shift Vs. pH.

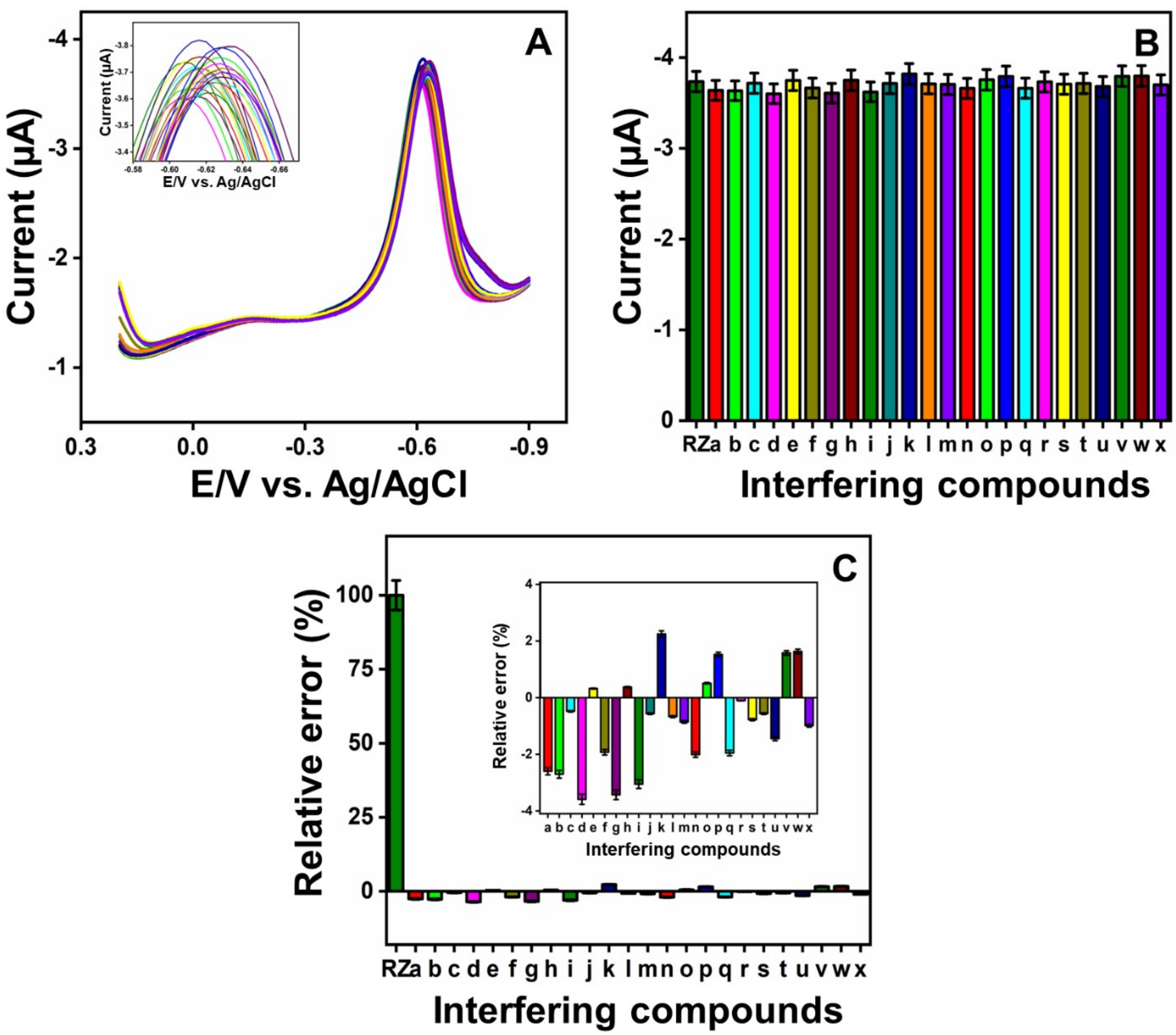

Fig. S4 DPV response of (A) multiple interfering compounds (*inset:* at high magnification), (B) its bar graph diagram, and (C) relative error bar diagram (*inset:* at high magnification) at ZC/NCS/GCE.

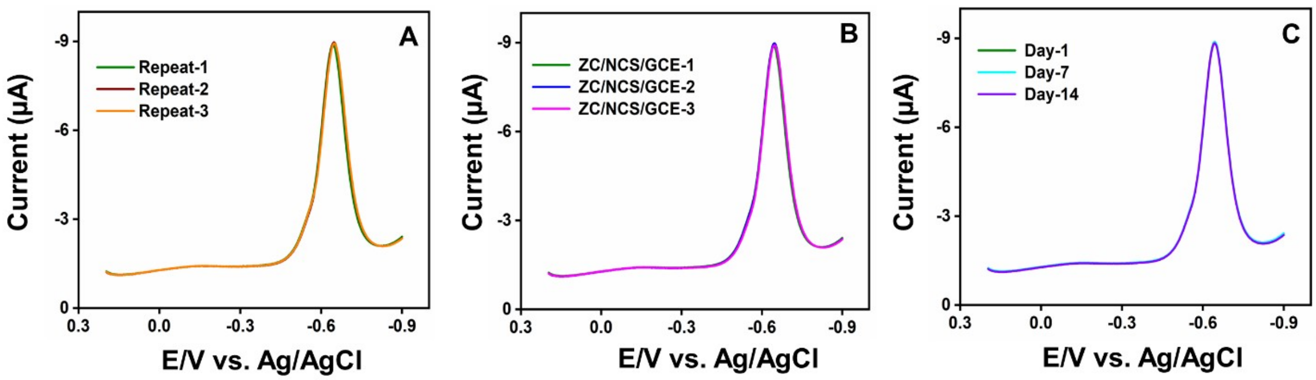

Fig. S5 Electroanalytical performance results (A) Repeatability, (B) Reproducibility, and (C) Stability tests of ZC/NCS/GCE.

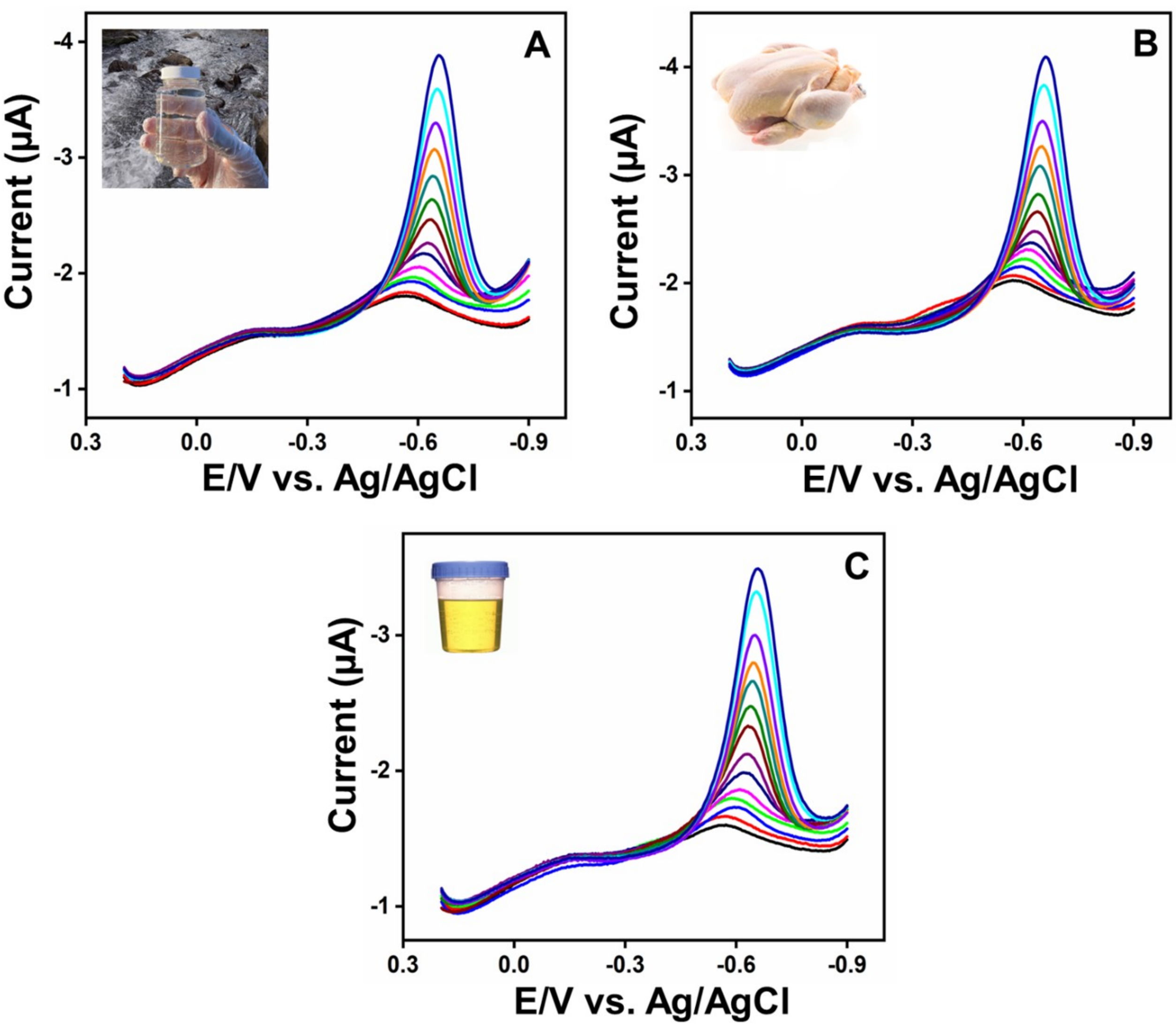

Fig. S6 Real sample analysis of ZC/NCS/GCE on (A) River water, (B) Chicken meat extract and (C) Human urine.

Table S1 Electrochemical detection of RZ in Real samples (n=3).

Real samples	Added (μM)	Found (μM)	Recovery (%)	Mean±RSD
	2.1	2.096	98.6	98.4±0.119
	18.1	18.098	99.6	99.4±0.003
River water	38.1	38.096	99.5	99.5±0.006
	39.1	39.098	99.8	99.6±0.006
	42.1	42.099	99.9	99.8±0.001
	2.1	2.105	101.8	100.4±0.013
	18.1	18.099	99.8	99.6±0.002
Chicken	38.1	38.094	99.2	99.4±0.002
	39.1	39.092	99.1	99.3±0.005
	42.1	42.097	99.7	99.8±0.002
	2.1	2.098	99.3	99.4±0.024
	18.1	18.097	99.4	102.3±0.047

Urine	38.1	38.096	99.6	100.6±0.018
	39.1	39.09	98.9	97.8±0.029
	42.1	42.099	99.9	99.3±0.009