Supplementary Information (SI) for RSC Advances.

Supporting information for

2D assembled ZnO/$ZnCo_2O_4$ heterostructures as an efficient electrocatalyst for electrochemical detection of ofloxacin in water: Experimental and DFT study

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Content

Supplemental water and eye drops samples preparation

The water samples were obtained from tap water from Nanomaterials for environmental and biomedical applications (NEB) laboratory at Phenikaa University and lake water from Duong Noi, Hanoi, Vietnam. It is worth emphasizing that the water samples were analyzed without a pretreatment step.

Pharmaceutical samples (commercial eye drops) chosen for the real sample were collected from pharmaceutical shop. Two commercial eye drop samples were diluted by distilled water and PBS solution (pH 4.0) to obtain the samples containing OFL concentration of 10 µM for real sample tests.

Supplemental Results and Discussions

Table S1. The obtained Rietveld refinement parameters of $ZnO/ZnCo_2O_4$ samples with two phases of ZnO and $ZnCo_2O_4$.

Phase	R_{wp} / R_{exp} (%)	χ^2	Lattice parameter (Å)	Quality percentages (%)	Atom site (Occupancy)		
ZnO	6.66 / 5.58	1.42	a=b=3.26; c=5.24	*38.5*	Zn (1.0)		O(1.0)
$ZnCo_2O_4$			a=b=c=8.15	*61.5*	Zn_{tet}(1.0)	Co_{oh}(2.0)	O(4.0)

Table S2. Atomic percentage of $ZnO/ZnCo_2O_4$ samples obtained from EDX analysis

Element	**Weght (%)**	**Atom (%)**
O	27.27	59.64
Co	24.45	14.52
Zn	48.28	25.84

Electrochemical characterizations

Figure S2 represents the CV curves of bare-SPE, ZCO/SPE and ZnO/ZCO/SPE in 0.1 M KCl solution containing 2.5 mM $K_3[Fe(CN)_6]$ and 2.5 mM $K_4[Fe(CN)_6]$with scan rate in the range of 10-60 $mV.s^{-1}$. The electroactive surface area (EASA) could to be calculated from the Randles–Sevcik equation as follows:

$$I_p = 2.69 \text{ x} 10^5 n^{3/2} D^{1/2} A C v^{1/2} \quad (1)$$

Where I_p is the peak current, $D = 7.6 \times 10^{-6} cm^2 s^{-1}$ is the diffusion coefficient values of the $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$, n is the number of electrons transferred, A is the electroactive surface area of modified electrodes, C is the concentration of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$, and v is scan rate. According to equation (1), the EASA values of bare-SPE, ZCO/SPE, and ZnO/ZCO/SPE were calculated to be 0.045 cm^2, 0.130 cm^2, and 0.116 cm^2, respectively. There is no significant difference in EASA value of ZCO/SPE and ZnO/ZCO/SPE.

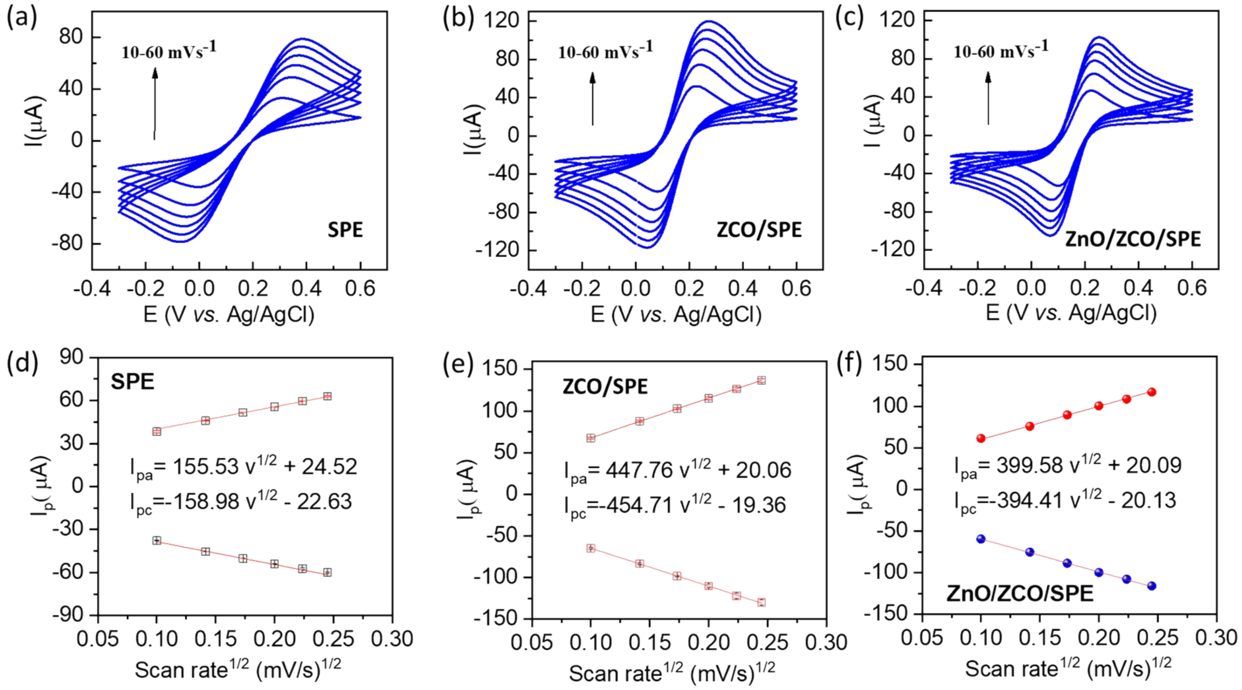

Fig. S1 CV curves of (a) SPE, (b) ZCO/SPE and (c) ZnO/ZCO/SPE in 0.1 M KCl solution containing 5 mM $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ with scan rates of 10-60 mVs^{-1}, (d, e, f) corresponding calibration plots of peak current response vs. square root of scan rate with error bars.

Fig. S2a represents the Nyquist diagrams of bare-SPE, ZCO/SPE, and ZnO/ZCO/SPE electrodes at a frequency range from 0.01 Hz to 50 kHz. The EIS patterns exhibit a straight line in the low-frequency region and a semicircle in the high-frequency. The straight line at low-frequency region is attributed to the semi-infinite linear transport of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ ions. The semicircle at high-frequency region corresponds to the charge-transfer process through the electrolyte/electrode interface. The EIS patterns are fitted with the equivalent circuits using Zview softwave. The Randles equivalent circuit model (inset of Fig. S2 b, c, d) was used in EIS analysis to evaluate the charge-transfer ability of the modified electrodes. In this model, R_1 is the solution resistance; R_2 is the charge-transfer resistance (R_{ct}) across the electrode-electrolyte interface, W_1 is the Warburg impedance arising from mass-transfer limitations and C_1 is the double-layer capacitance related to the charging and background current. The obtained parameters were summarized in Table S2.

Table S3. Solution resistance (R_s), charge-transfer resistance (R_{ct}), double layer capacitance (C_{dl}), diffuse layer capacitance (Z_W) evaluated from EIS patterns

Electrode	**R_s**	**R_{ct} (Ω)**	**C_{dl} (μF)**	**Z_W (kσ)**
SPE	125.0	3150.0	1.95	0.299
ZCO/SPE	117.5	593.7	12.0	1.253
ZnO/ZCO/SPE	114.0	269.3	29.0	0.287

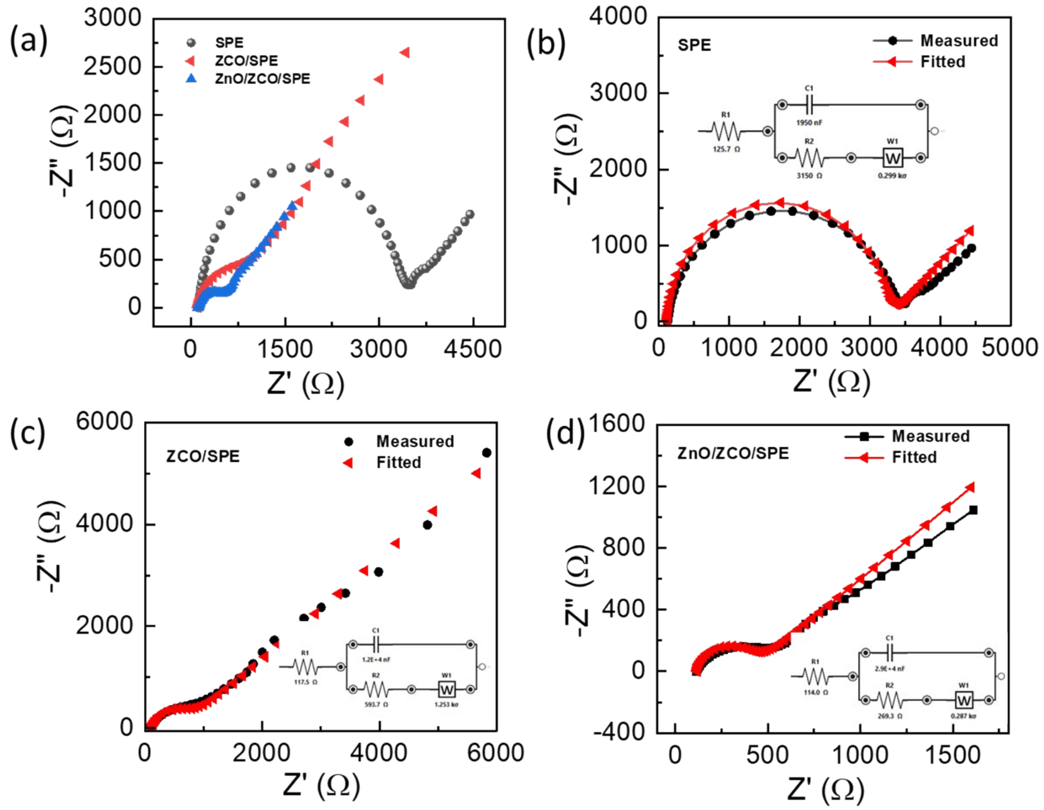

Fig. S2 (a) Nyquist diagram for SPE (black), ZCO/SPE (red) and ZnO/ZCO/SPE (blue) in 0.1 M KCl solution with 2.5 mM $K_3[Fe(CN)_6]$ and 2.5 mM $K_4[Fe(CN)_6]$, and the fitting of the experimental data for SPE (b), ZCO/SPE (c) and ZnO/ZCO/SPE (d). (inset: their equivalent circuit used for fitting the data).

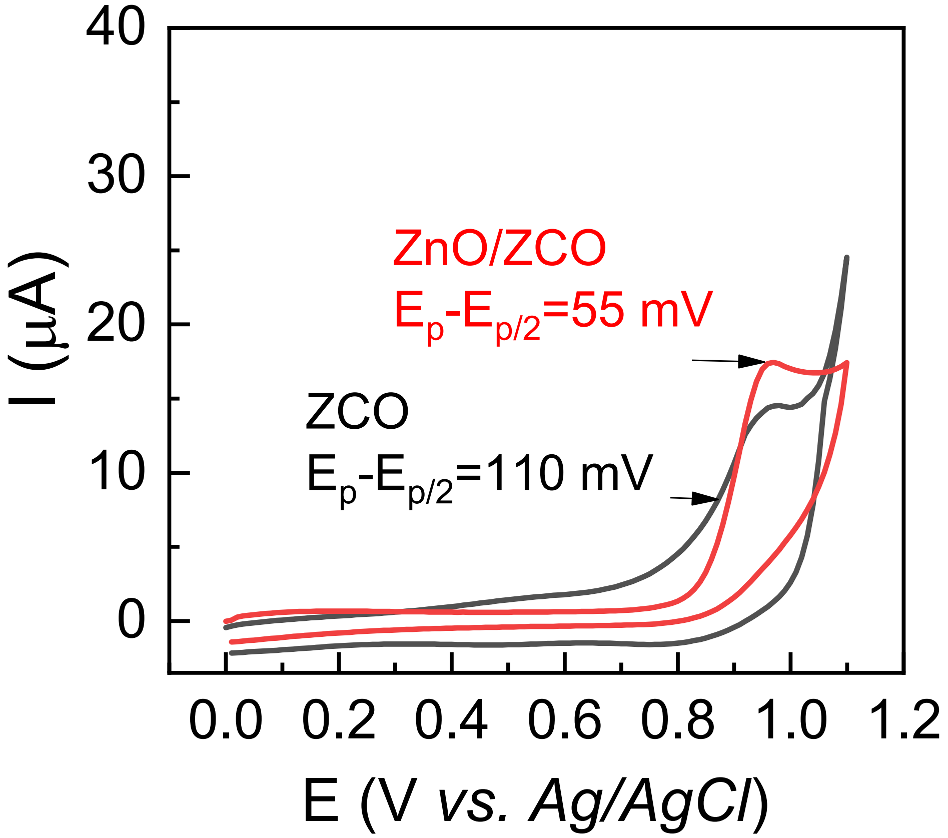

Fig. S3. CV curves for ZCO/SPE and ZnO/ZCO/SPE at 100 μM OFL in 0.1 M BPS buffer solution.

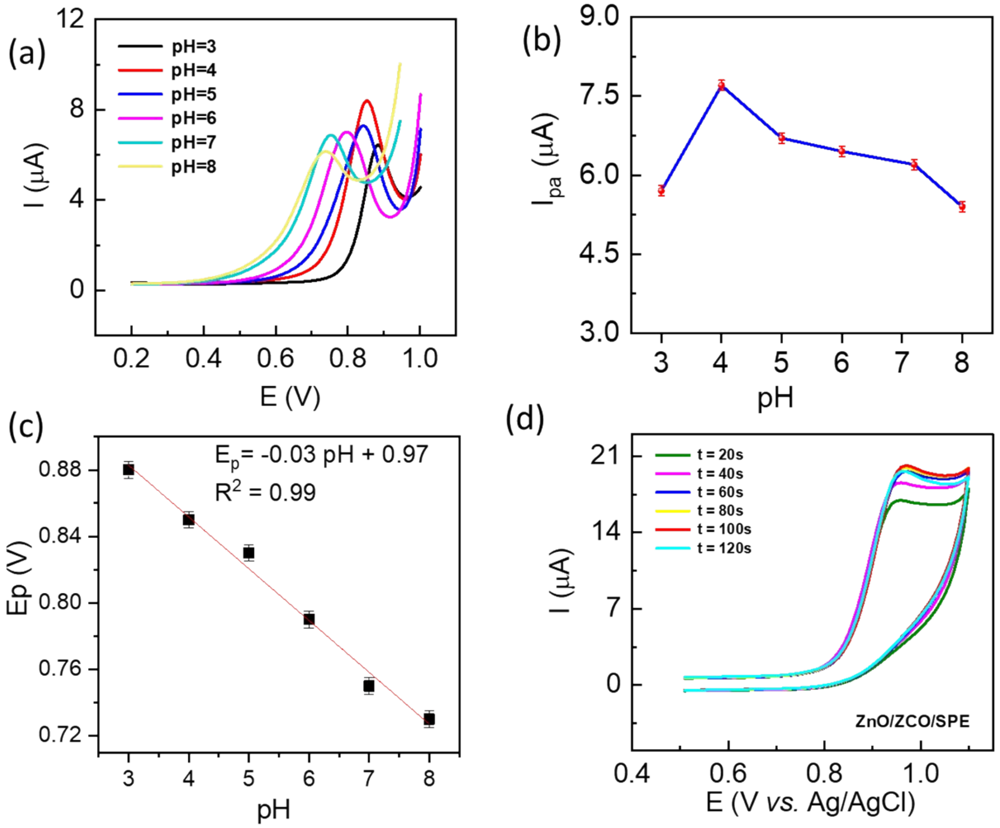

Fig. S4. (a) DPV curve for different pH study at ZnO/ZCO/SPE in 0.1 M BPS buffer solution containing 100 μM OFL, (b, c) dependence of peak current and potential on pH.

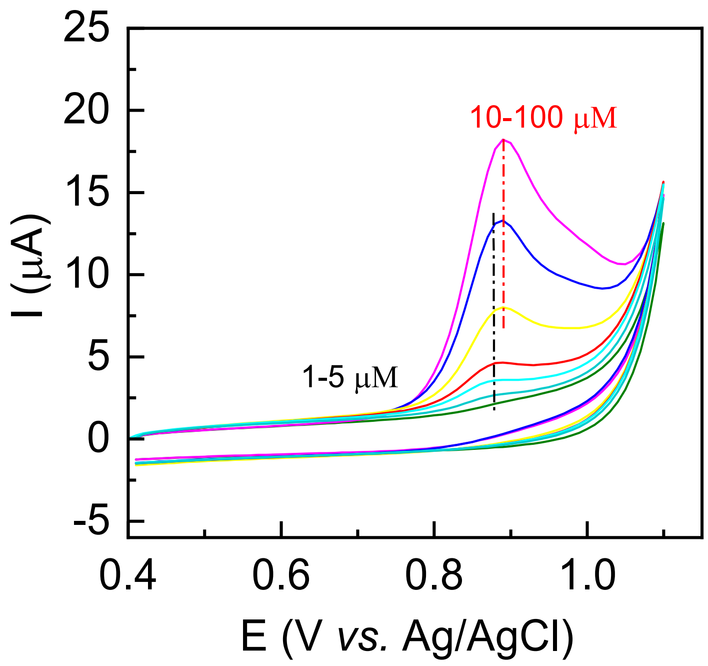

Fig. S5. CV curves of OFL with various concentrations of 1-100 μM in PBS solution (pH=7.4) on the ZnO/ZCO/SPE

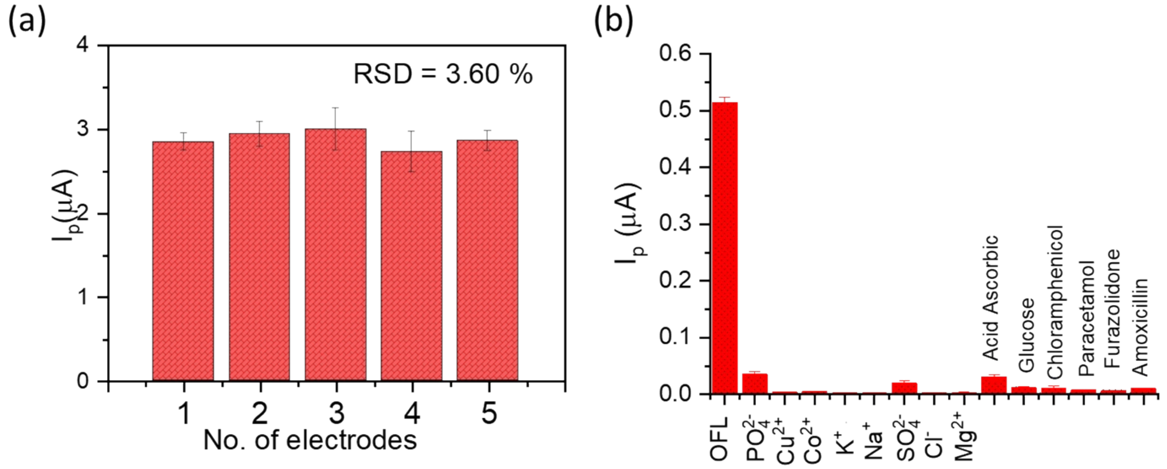

Fig. S6. (a)The reproducibility of ZnO/ZCO/SPE. DPV tests were recorded in PBS solution (pH=4.0) in the presence of 25 μM OFL. (b) Effects of the addition of different kinds of ions, organic substances, and antibiotics on the peak current of OFL oxidation (5 μM).

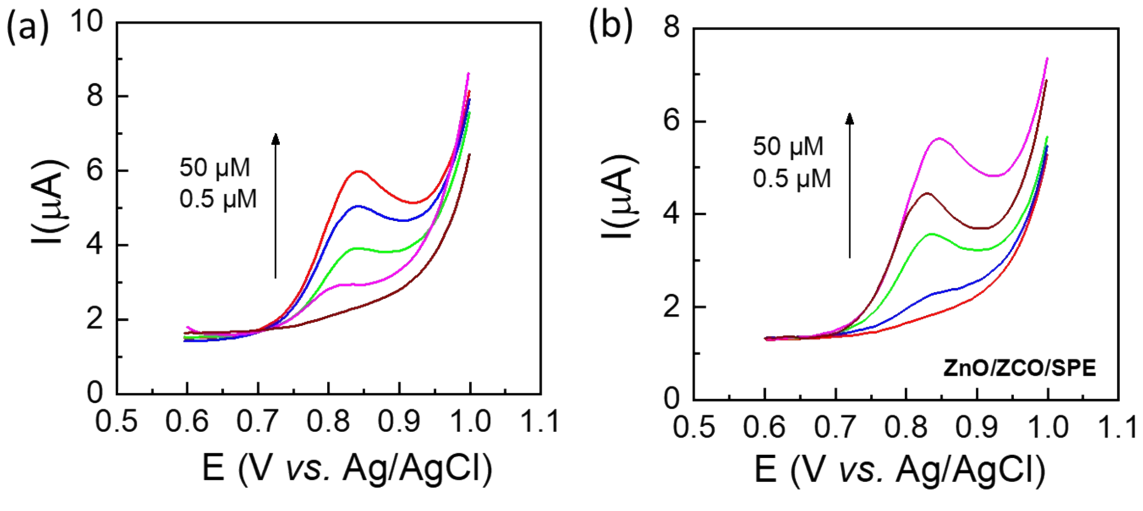

Fig. S7 DPV probe for various OFL addition (0, 0.5, 10, 25, 50 μM) in (a) lake water and (b) tap water sample test

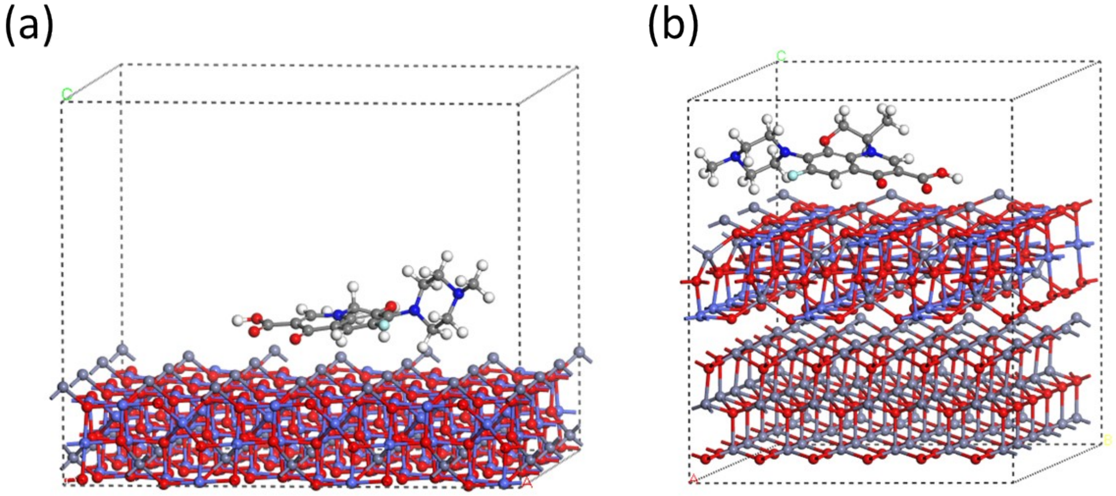

Fig. S8. Geometries of OFL adsorbed on ZCO (a) and ZnO/ZCO (b) with (001) crystal plane

Table S4. Adsorption energy E_a (kcal/mol), distance d (Å) between metal ion center and oxygen atom of electrocatalytic materials (ZCO and ZnO/ZCO) and atoms (O and H) of OFL.

System		E_a(kcal/mol)	d (Å)		
			O-H	Zn-O	Co-O
ZCO	OFL	-15.06	2.815	3.09	2.865
ZnO/ZCO	OFL	-20.51	2.841	2.752	3.519