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Supplementary Information

Rhombohedral type of $LaCoO_3$ with carbon nanofiber composite as an electrocatalyst enables for amperometry detection of vanillin in food samples

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No. of. Figures: S7

No. of. Tables: S2

S1. Chemicals and Reagents

The analytical grade chemicals are Lanthanum (III) nitrate hydrate (La $(NO_3)_3.6H_2O$), Cobalt (II) nitrate hexahydrate (Co $(NO_3)_2.6H_2O$), citric acid (HOC (CO_2H) $(CH_2CO_2H)_2$) precursors, carbon nanofiber (CNF). sodium phosphate monobasic (NaH_2PO_4) and sodium phosphate dibasic (Na_2HPO_4) are utilized to prepare 0.1 M PBS (phosphate buffer solution) as the supporting electrolyte. Potassium chloride (KCl), potassium ferricyanide (K_3[Fe $(CN)_6$]), sodium hydroxide (NaOH), vanillin (VNL), caffeic acid (CA), sucrose (Su), catechol (CA), glucose (Glu), potassium (K^+), ascorbic acid (AA), sodium chlorine (NaCl), dopamine (DPA) paracetamol (PA), catechol (CC) and all other chemicals are used without further refinement from Sigma-Aldrich, 98%.

S2. Materials characterization

As-synthesized $LaCoO_3$@CNF composite material was studied using phase identification was performed by using X-ray diffraction (XRD) using XRD, Rigaku D/maxB, DMX-2200. Raman spectroscopy (Horiba HR 800UV confocal Raman spectrophotometer). The surface morphology was used in Field Electron-Scanning Electron Microscopy (FE-SEM, Hitachi S4700) and energy dispersive X-ray (EDX, HORIBA EMAX XACT) spectroscopy. X-ray photoelectron spectroscopy (ESCA/Auger Laboratory). AC impedance spectroscopy was performed by Ω-metrohm autolab (AUT51770). CHI 6171D Electrocatalytic work station was functional to carry out the electrochemical measurements in three electrode cells, as well as amperometric (i-t) method. Here, the modified GCE saturated Ag/AgCl and Pt wire were active as working, reference and counter electrodes, respectively.

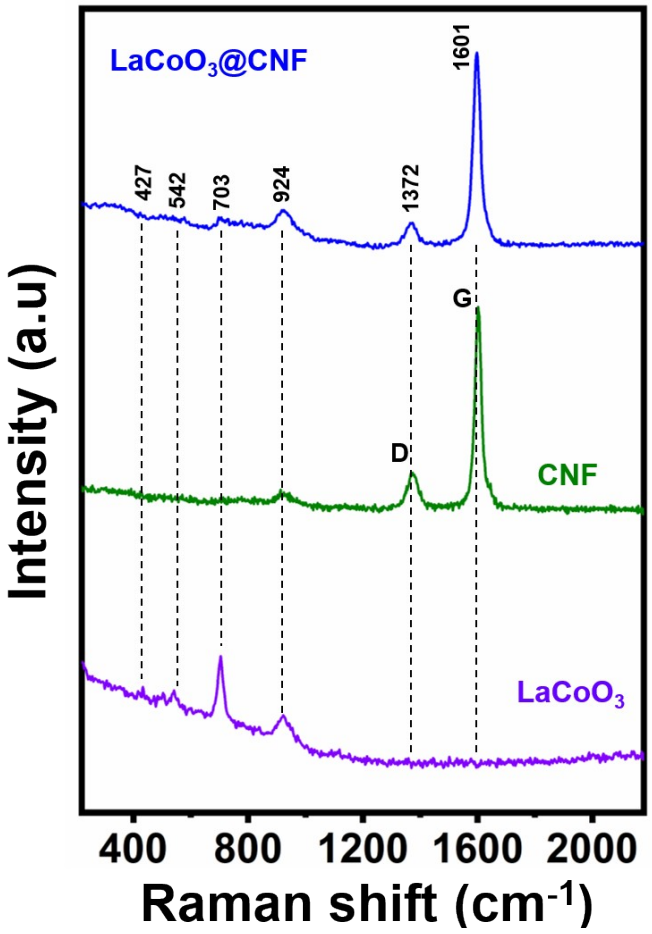

Fig.S1. Raman spectra of LCO, CNF and LCO@CNF composite.

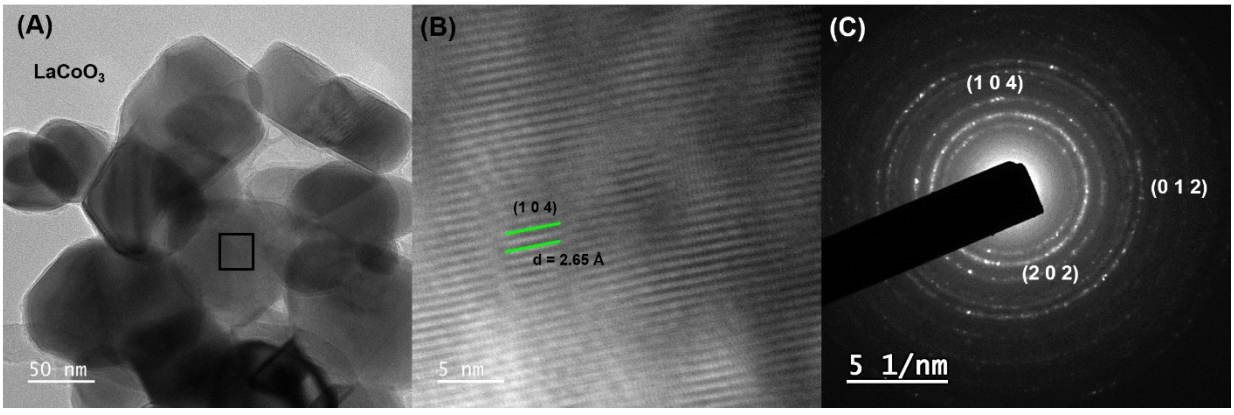

Fig.S2. (A) HRTEM image of material, (B-C) LCO images of corresponding lattice fringe and SAED pattern.

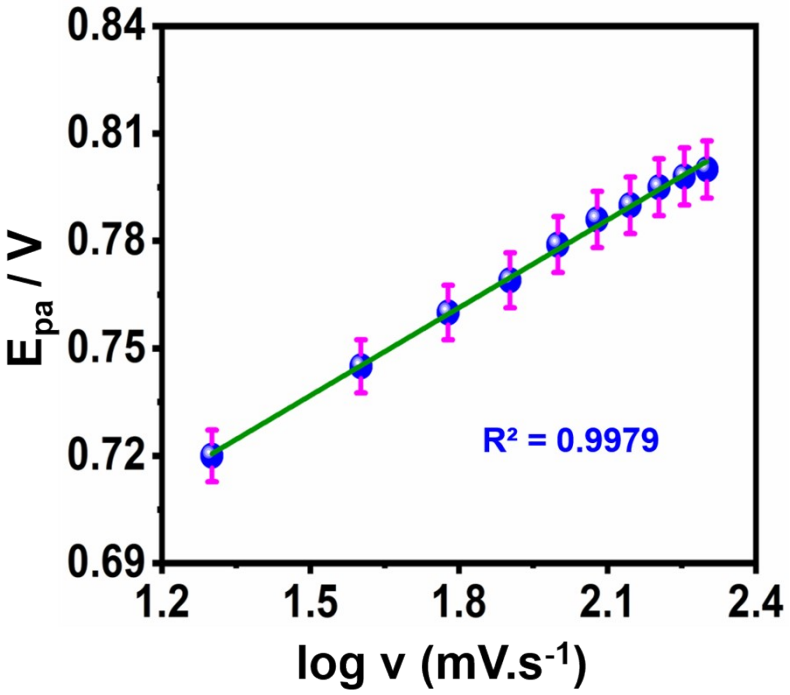

Fig.S3. The calibration plot of different scan rate on modified LCO@CNF composite.

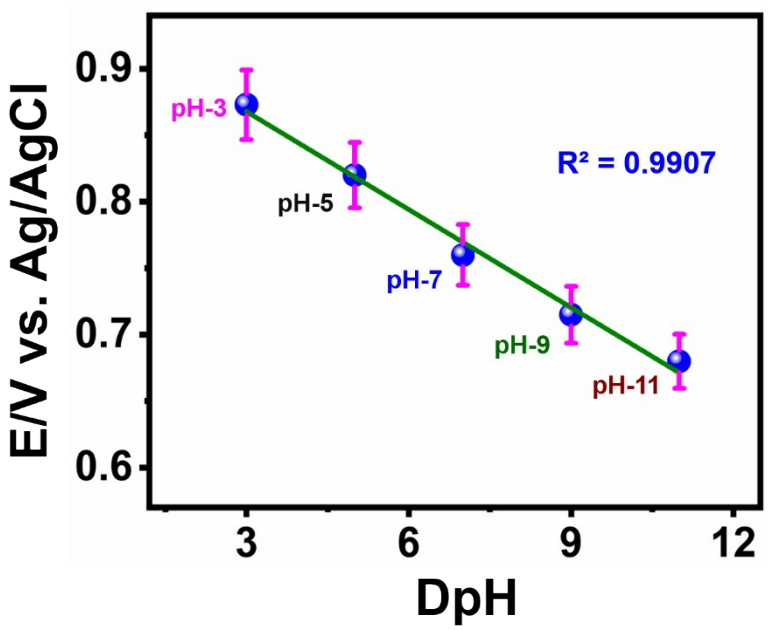

Fig.S4. Electrolyte studies of LCO@CNF composite towards VNL in DpH vs potentials.

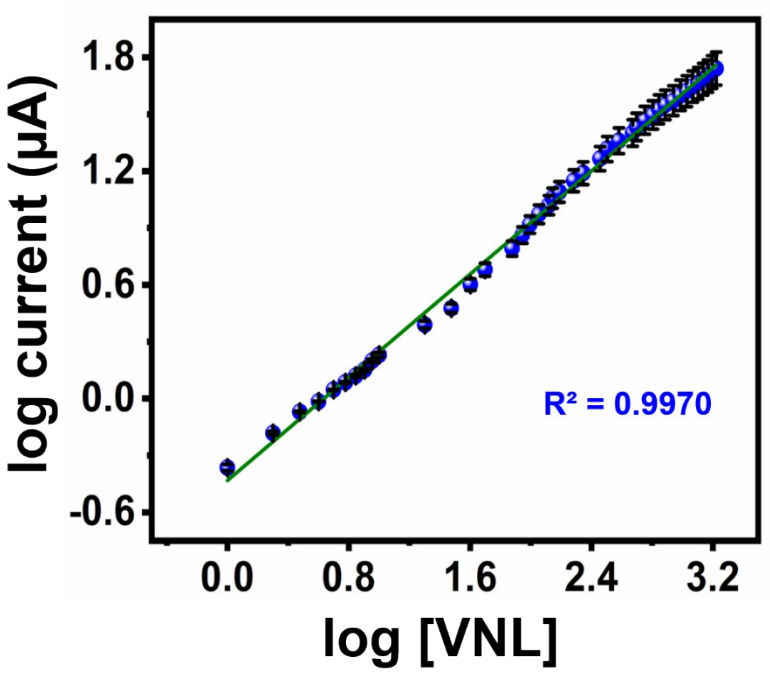

Fig.S5. The calibration plot of log current vs log VNL on modified LCO@CNF composite.

Table.S1. Comparison table of VNL detection in modified composite with the previous literature.

Electrode materials	**Method**	**LOD (nM)**	**Linear range (μM)**	**Real sample**	**Ref.**
[a]CuS-H	[j]DPV	53	0.1-46.5	Biscuits, Milk powder, Chocolate	40
[b]PTY/OL/CNPE	DPV	49	2.0-40.0	Biscuits	41
[c]PMOMGPE	DPV	73	10.0-35.0	Vanilla essence	42
[d]Poly(GA)/(MWCNTs-GT)CPS	DPV	199	0.50-13.0	Milkshake, Cream cake, Vanilla extract.	39
[e]Ag-Pd/GO	DPV	5	0.02-45	cookie, pastry, jelly and chocolate	43
[f]Arg-G	DPV	1000	2-70	ice cream, biscuit	44
[g]BDD electrode	[k]SWV	160	3.3-98	commercial pudding powder	45

[h]Ag NPs/GN	SWV	332	2-100	biscuit	46
CuO@SiO_2	DPV	53	0.05-111.2	Chocolate, biscuit	47
[i]poly(T3T)	DPV	40	0.1-11.3	Sugared vanilla, Coffee	48
Au–Ag alloy	[l]i-t	40	0.2-50	Vanilla tea, bean	49
Fe@Fe_3C-C	DPV	2.36	10-50	cooky, yogurt, jelly and chocolate	50
[m]AuNPs/Fc-KB/ZIF-8	SWV	3	0.01-200	white chocolate and nougat	51
LCO@CNF	**i-t**	**4.67**	**0.01-1670**	**Vanilla ice cream, Cocoa biscuit**	**Our work**

[a]CuS-H - Copper sulfide - hexagonal phase, [b]PTY/OL/CNPE - Poly (titan yellow) and octoxynol-9 modified carbon nanotube paste electrode, [c]PMOMGPE – Poly methyl orange modified graphene, [d]Poly(GA)/(MWCNTs-GT)CPS - Poly(glutamic acid)/(multi-walled carbon nanotubes-graphite) composite, [e]Ag-Pd/GO - Ag-Pd bimetallic nanoparticles-decorated graphene oxide, [f]Arg-G-Arginine-graphene, [g]BDD electrode - Boron-doped diamond electrode, [h]Ag NPs/GN - Silver nanoplates/graphene, [i]poly(T3T) - Poly(1H-1,2,4-triazole-3-thiol/Au, [j]DPV – different pulse voltammetry, [k]SWV - square wave voltammetry, [l]i-t – amperometry (i-t) method, [m]AuNPs/Fc-KB/ZIF-8- gold nanoparticles/ferrocene-Ketjen black/zeolite-like MOFs.

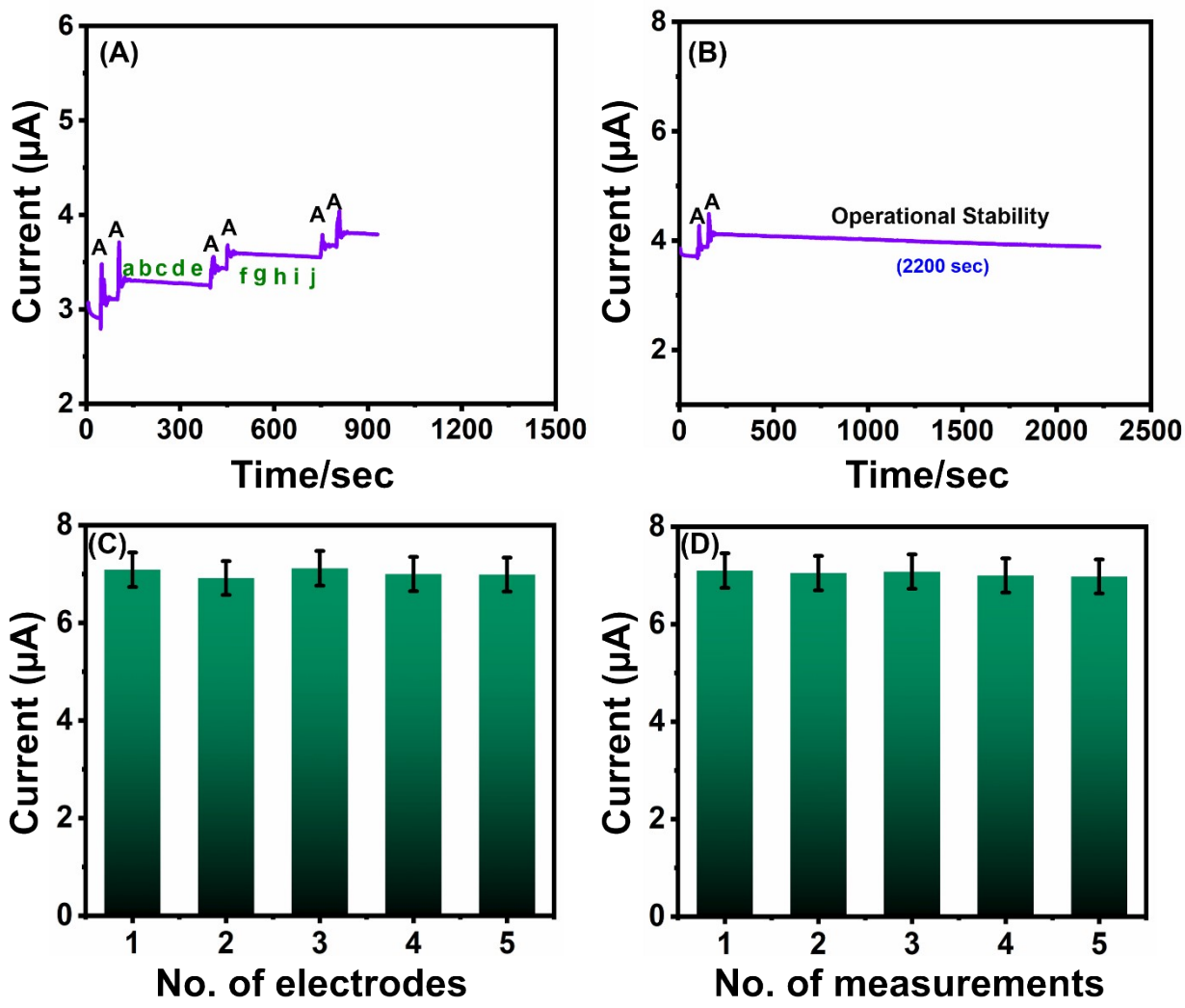

Fig.S6. (A) Anti-interfering analysis by (i-t) method (A: VNL, a: CA, b: Su, c: CC, d: Glu, e: K^+, f: AA, g: Cl^-, h: Na^+, i: DPA and j: PA), (B) The operational stability studies of modified electrode, (C-D) Bar diagrams of reproducibility and repeatability studies of LCO@CNF towards VNL.

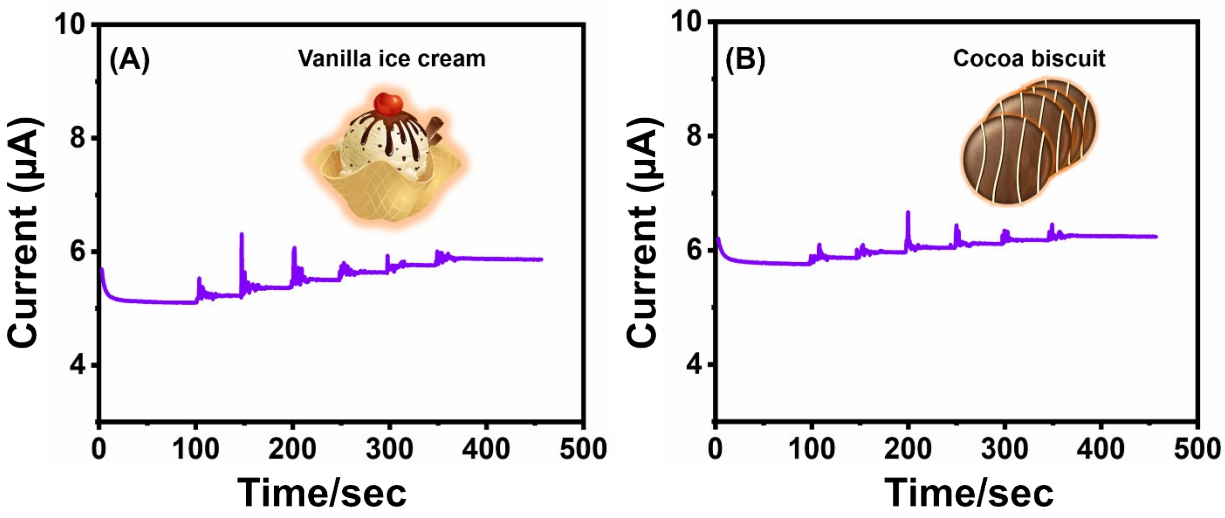

Fig.S7. (A-B) Real samples analysis of vanilla ice cream and cocoa biscuit.

Table.S2. Determination of VNL in food samples with modified composites.

Effluents	**Spiked (μM)**	**Found (μM)**	***RSD (%)**	**Recovery (%)**
Vanilla ice cream	0	0.21 ± 0.0038	1.80	-
	5	4.96 ± 0.071	1.43	100.80
	10	9.75 ± 0.24	2.46	102.56
	15	14.95 ± 0.44	2.94	100.30
	20	19.88 ± 0.689	3.46	99.60
	25	24.85 ± 0.907	3.64	99.40
	30	29.75 ± 1.175	3.94	99.16
Cocoa biscuit	0	0.13 ± 0.0017	1.30	-
	5	4.25 ± 0.11	2.58	100.30
	10	9.15 ± 0.30	3.27	100.92
	15	14.28 ± 0.49	3.43	99.20
	20	19.65 ± 0.72	3.66	98.25
	25	24.85 ± 0.96	3.86	99.40
	30	29.95 ± 1.17	3.90	99.83

**RSD = Relative standard deviation*

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