Supporting Information

Design and Fabrication of La-based Perovskites Incorporated with Functionalized Carbon Nanofibers for Electrochemical Detection of Roxarsone in Water and Food Samples

Mariya Antony John Felix[a] , Santhiyagu Sahayaraj Rex Shanlee[a] , Shen-Ming Chen[a,*] , Ruspika Sundaresan[a] , Ramachandran Balaji[b*], Narendhar Chandrasekar[c], and Periyanayagam Arockia Doss[d]

[a]Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No.1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan

[b]Department of Electronics and Communication Engineering, Koneru Lakshmaiah Education Foundation, Andhra Pradesh 522302, India

[c]Department of BioNano Technology, Gachon University, Seongnam 13120, Gyeonggi, Republic of Korea

[d]Department of Chemistry, St. Joseph's College (Autonomous), (Affiliated to Bharathidasan University, Tiruchirappali 620024), Tiruchirappalli, Tamilnadu 620002, India

*Corresponding authors:

Prof. Dr. S. M. Chen, Email: smchen1957@gmail.com, smchen78@ms15.hinet.net, Tel: +886 2270 17147, Fax: +886 2270 25

Dr. Ramachandran Balaji, Email: balajiyashik@gmail.com, rbalaji@kluniversity.com

Experimental Section

Chemicals

Carbon nanofibers (conical, 98% carbon basis, D x L 100 nm x 20–200 μm), Lanthanum nitrate hexahydrate (La $(NO_3)_3$.$6H_2O$,99.9%), Manganese nitrate hexahydrate [Mn $(NO_3)_2$·6H2O, 99%], ethylene glycol ($(CH_2OH)_2$, ≥99%) Urea (NH_2CONH_2, 99.0), sodium phosphate dibasic (Na_2HPO_4), sodium phosphate monobasic (NaH_2PO_4), sodium hydroxide (NaOH, ≥ 98.0%), hydrochloric acid (HCl, 36.5–38.0%), nitric acid (HNO_3, 70%), potassium ferrocyanide ($K_3[Fe(CN)_6]$), potassium chloride (KCl, 99.0 – 100.5%), all the chemicals were purchased from Sigma-Aldrich used as received without further purification. 0.1 M of phosphate buffer (PB) was used as a supporting electrolyte through homogeneous Na_2HPO_4 and NaH_2PO_4 in DI water and their pH was adjusted by HCl and NaOH. Double distilled water (DI) and ethanol were used for the preparation of the required solutions. All the above chemicals used in these experiments were of standard analytical grade and electrochemical experiments were carried out in a nitrogen (N_2) gas-saturated atmosphere at room temperature.

Preparation of functionalized carbon nanofiber (*f*-CNF)

Carbon nanofiber attains solubility and high electrical conductivity by the processing of functionalization. In the standard experiment way, CNF was weighed about 1 g and it was added into the 40 mL of nitrating mixture. After that, the above solution mixture is placed in the unceasing magnetic stirring for 8h at the temperature of 50°C. Throughout this procedure, the defect site was introduced with the help of sulfuric acid and nitric acid generating the oxy-functional groups. The subsequent product was centrifuged and washed with DI water until it reached a pH of 7. Lastly, the *f*-CNF was dried in the vacuum oven overnight.

Fabrication of electrode

For the LMO/*f*-CNF modified glassy carbon electrode (GCE) firstly, the surface of the bare glassy carbon electrode (GCE) was polished with 0.05 μm alumina powder to obtain mirror-like surfaces followed by thorough cleansing using DI water and ethanol, finally kept for drying in an oven. After that, LMO/*f*-CNF dispersion at a concentration of 3.0 mg in 3 mL of DI H_2O and ultrasonicated for 30 minutes. The homogeneously dispersed mixture was coated on the surface of GCE with the amount of 4 μL by using the drop-casting technique and dried in a hot air oven at 60 °C.

Real sample preparation

The tap water was collected and with the 0.1 M of PB solution was used to prepare the water sample in a ratio of 1:9. The mixture was centrifuged several times. The egg was purchased from a local shop in New Taipei City, Taiwan. The white egg was separated from the egg and it was made up by using 0.1 M of PB solution in the ratio of 1:9 and centrifuge several times.
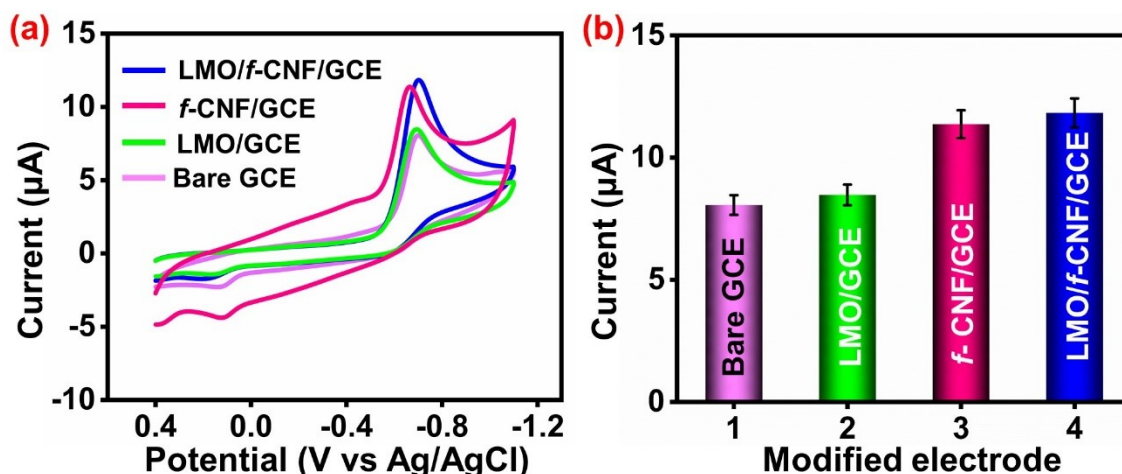

Figure S1. (a) The CV curve of bare GCE, LMO/GCE, *f*-CNF/GCE, LMO/ *f*-CNF/GCE in the presence of 100 μM RSN **(b)** the bar diagram of the modified electrodes.
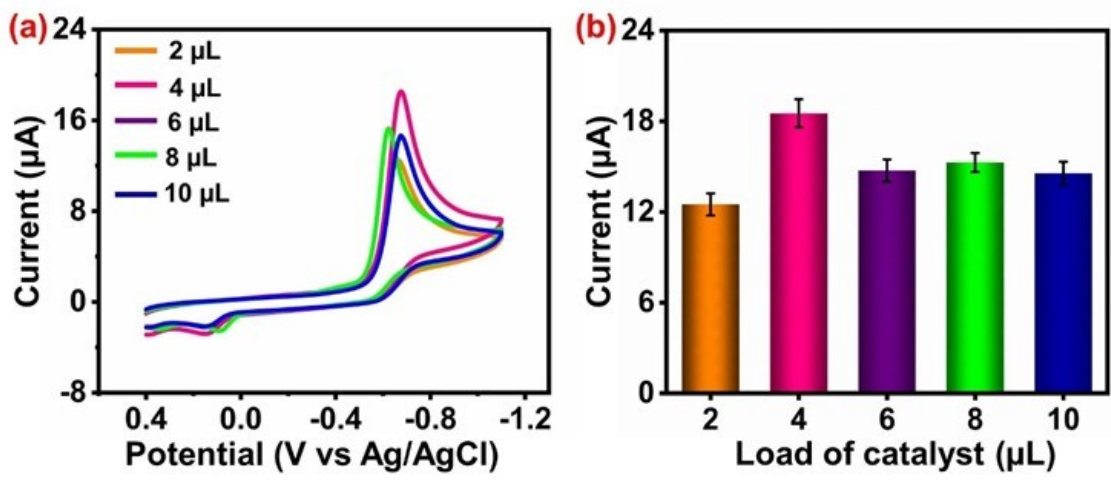
Figure S2. (a) The CV curves of different loading of LMO/*f*-CNF/GCE in the presence of 100 µL of RSN, **(b)** corresponding bar diagram of different load catalysts of LMO/*f*-CNF/GCE.
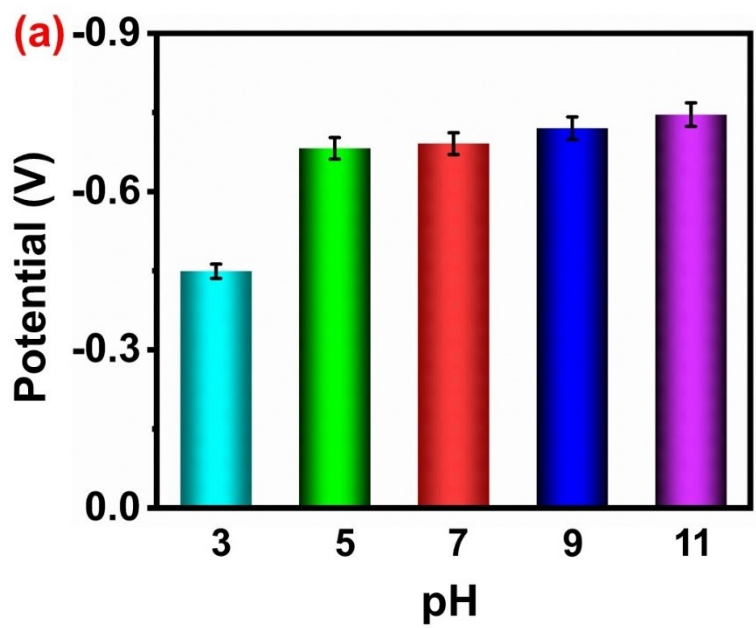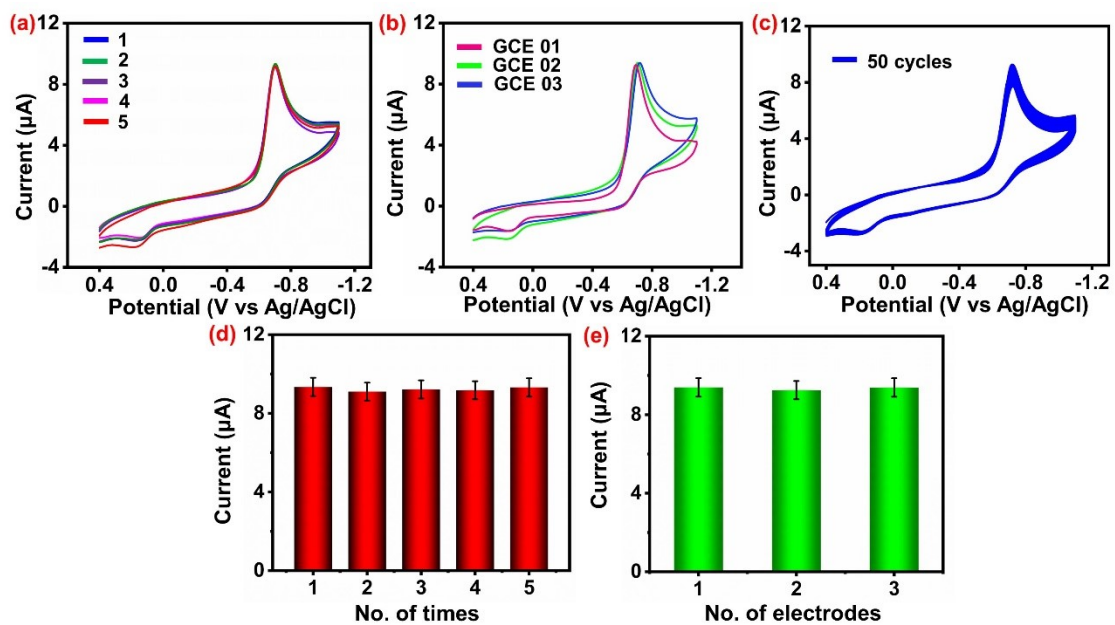

Figure S3. Bar diagram between the potential and pH

Figure S4. **(a)** Repeatability study of LMO/*f*-CNF/GCE with 100 µM of RSN **(b,c)** reproducibility and cycle stability of LMO/*f*-CNF/GCE with 100 µM of RSN and **(d,e)** its corresponding bar diagram
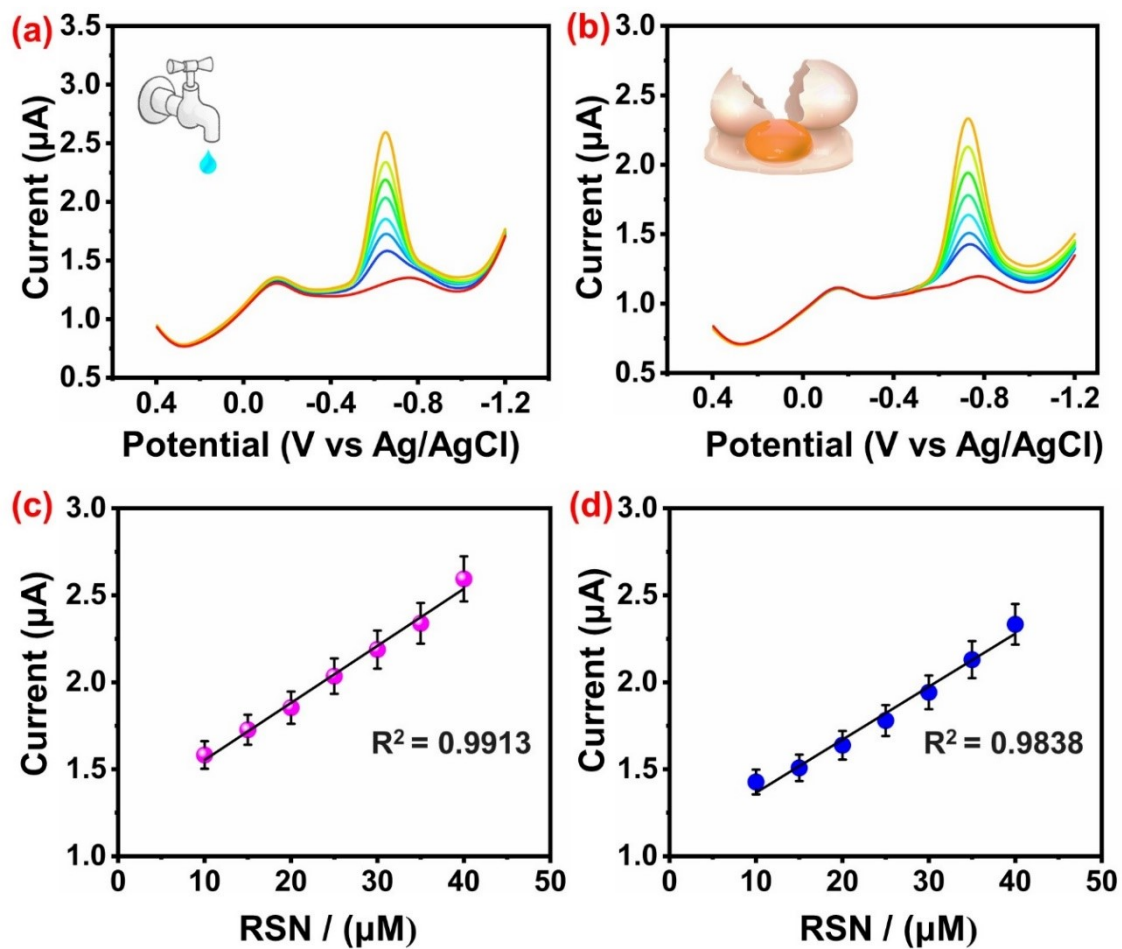
Figure S5. DPV response of real sample **(a,c)** tap water and its calibration plot. **(b,d)** Egg and its calibration plot.

Table S1. Comparison of various electrodes used for RSN detection

Electrodes	Linear Range (μM)	LOD (μM)	Methods	Reference
GCE/CTAB	0.001-0.02	0.0001	SWAdSV	**[39]**
Ti_3C_2/G-MWCNTs/ZnO	0.01-30	3.3	DPV	**[40]**
LaMoO	0.025-2650	0.0124	DPV	**[18]**
HG-AFS	0.011–0.034	0.0015	HPLC	**[41]**
CrNiCo-P/GCN/GCE	1.0-413	31	DPV	**[42]**
MoS_2/S-Ti_3C_2	0.01 – 875.01	2.31 (nm)	DPV	**[43]**
Au/ErGO/SPCE	1.0 – 1000.0	0.014	SWV	**[37]**
LMO/*f*-CNF/GCE	0.01-497	**0.004**	**DPV**	This work

Table S2. Detection of RSN in water and egg samples by using LMO/*f*-CNF/GCE in the presence of different concentrations of RSN.

Real sample	Added (µM)	Found (µM)	Recovery (%)
Tap water	10	9.78	86.11
	15	14.98	98.87
	20	19.97	98.68
	25	24.94	97.06
	30	29.93	96.90
	35	34.90	95.96
	40	39.86	94.69
Egg	10	9.85	86.11
	15	14.90	98.87
	20	19.88	98.68
	25	24.87	97.06
	30	29.84	96.90
	35	34.85	95.96
	40	39.86	94.69