Supplementary information

Quantum-sized Ag nanoparticle conjugates on biofunctionalized La_2O_3–rGO ternary nanocomposite-based platform for the electrocatalytic determination of dopamine

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S1. Materials

Lanthanumnitratehexahydrate $[La(NO_3)_3].6H_2O$, 99%, Silver nitrate $[AgNO_3]$, Cetyltrimethyl Ammonium Bromide $[C_{19}H_{12}BrN]$ (99%), (CTAB) was purchased from SRL Maharashtra India. Sodium Hydroxide (NaOH) pellets from central drug House (P) Ltd. (CDS), New Delhi. Di-sodium hydrogen phosphate dihydrate, $[Na_2HPO_4.2H_2O]$ (99%), Sodium dihydrogen phosphate dihydrate, $[NaH_2PO_4.2H_2O]$ (98-100.5%), Sodium Chloride (NaCl) (99%), Potassium hexa-cyano ferrate(iii), $[C_6FeK_3N_6]$ (98.5%), Potassium Hexacyano ferrate(ii) trihydrate $[C_6FeK_4N_6.3H_2O]$ (98.5%), purchased from Merck Specialties Private Ltd. Mumbai, India. Enzyme Tyrosinase extract from mushroom and dopamine hydrochloride $[C_8H_{11}NO_2.HCl]$ was purchased from SIGMA-ALDRICH, USA. All the chemical used for experiments are of analytical grade and used with no any spare purifications. The ITO sheets (surface reactivity 30-60 sq$^{-1}\Omega$) were purchased from Sigma-Aldrich for electrophoretic deposition.

S2. Characterizations

The shape, structure, and crystalline size of the synthesized L-rGO and L-rGO/Ag nanoparticles has been identified by XRD using BRUKER D8 ADVANCE. FT-IR spectra of the L-rGO and L-rGO/Ag nanoparticles have been taken with the FTIR spectrophotometer (JASCO FT-IR-4700). The TEM, HR-TEM, and EDX of L-rGO/Ag nanoparticles were investigated with JEOL JEM 2100 FX TEM, Japan. The SEM was characterized from carl Zeiss, EVO-18, Research model, Germany. The surface morphology for L-rGO/Ag nanoparticles and Tyr/L-rGO/Ag electrode was studied by the atomic force microscope (NT-MDT, Model-solver Next). The XPS was characterized from PHI 5000 Versa Probe III, using the Al K-α radiation (hν= 1486.6 e.V.). The scanning XPS Al Kα X-ray spot size adjustable from 10 µM through 200 µM and scanning XPS with the dimension up to 1.4 mm. The Raman spectroscopy was performed from WITEC alpha Z00 focus innovation & excitation source 532 nm. The EPD was performed using the direct current power supply unit (Genetix biotech, model GX300C). The CV and DPV have been investigated with the corrtest instrument (single channel model CS350). The electrochemical measurement, conducting on the three-electrode systems where the working electrode is Tyr/L-rGO/Ag electrode the counter electrode is platinum (Pt) wire, and the reference electrode is the saturated Ag/AgCl electrode in the phosphate buffer saline (PBS,50 mM, pH 6.0, 0.9% NaCl) having 5 mM $[Fe(CN)_6]^{3-/4-}$ as mediator.
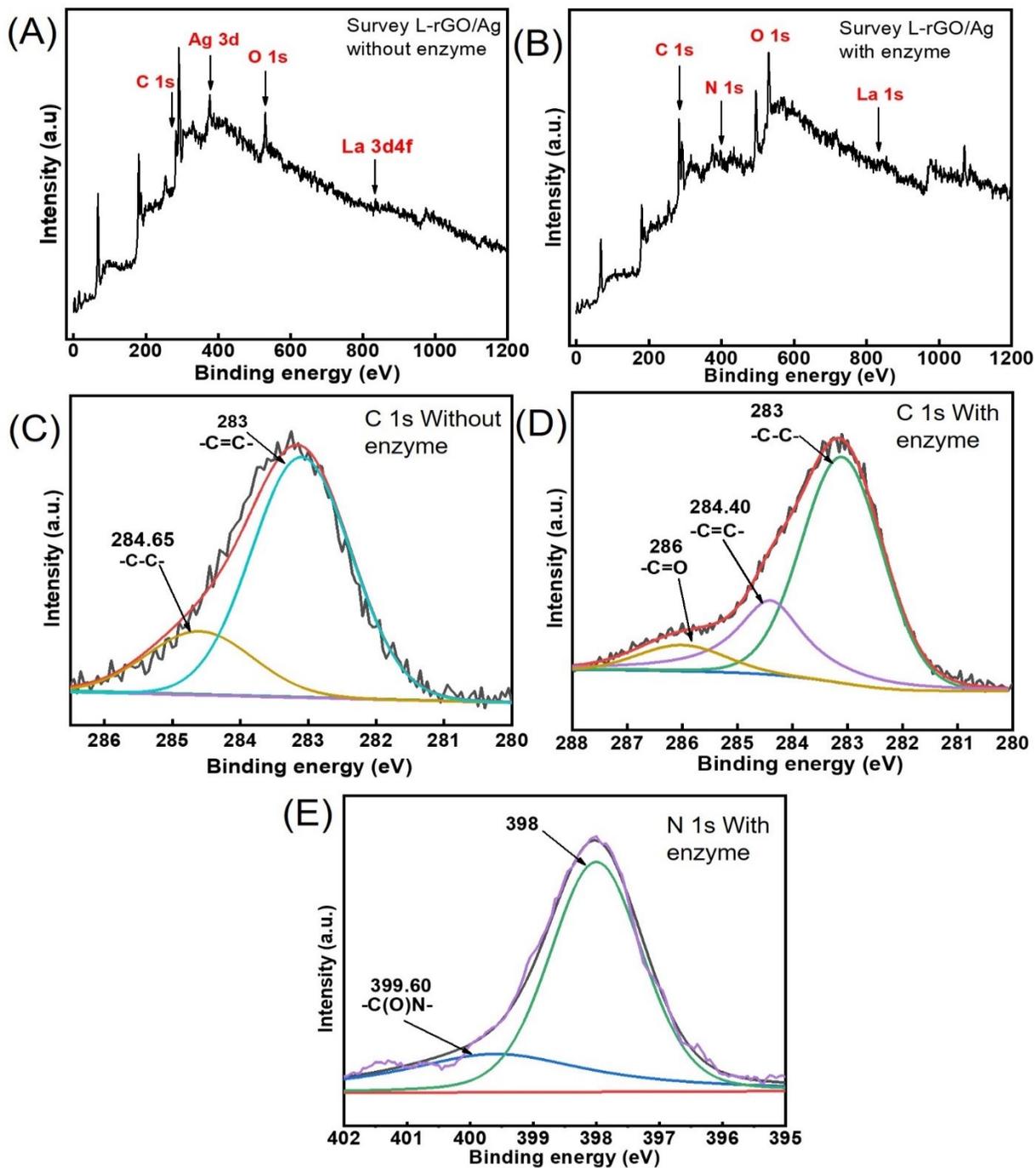
Fig. S1. *(A) Shows the XPS spectra of survey image for L-rGO/Ag without enzyme and (B) is the survey image for Tyr/L-rGO/Ag with enzyme. (C) are the XPS core level spectra of individual compounds for C 1s without enzyme & (D) is the C 1s with enzyme and the image (E) is for core level spectra of N 1s of enzyme.*
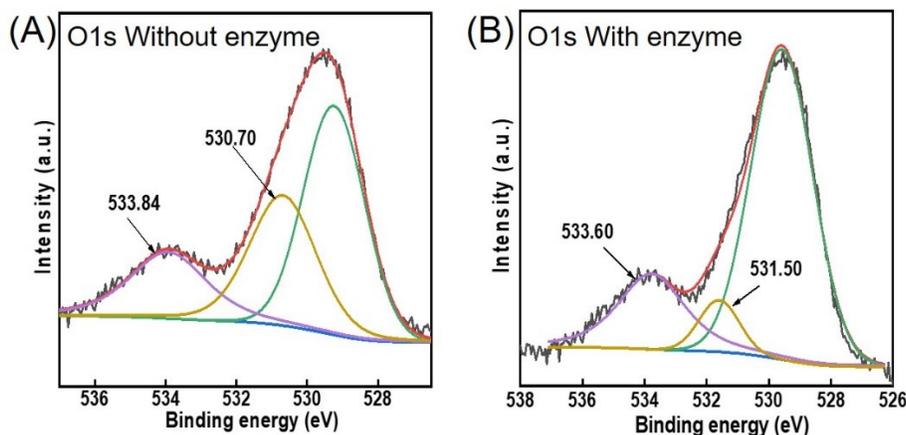
Fig. S2. *(A) is the XPS spectra of L-rGO/Ag for core level spectra of individual compounds of O 1s without enzyme and (B) is the spectra of Tyr/L-rGO/Ag for core level spectra of O 1s with enzyme.*

S3. Electrochemical response study of dopamine by Cyclic voltammetry (CV)

The electrochemical response for the sensing study has been demonstrated for the Tyr/LGO/Ag/ITO electrode, as an active function of dopamine, in the same 50 mM PBS saline solution and 50 mV s^{-1} scan rates varying the concentration range from 0 μM to 20 μM (**Fig. S3A**) The CV studies observation reveals the information with increasing concentration of dopamine, the oxidative and reductive peak current were found to increased and decreased respectively in linear manner, which inform the prepared bioelectrode is effectively sensitive to dopamine analysis. More over this, it has been also observed that the oxidative peak current (I_{pa}) and reductive peak current (I_{pc}) having the linear relationship at various concentration ranges, with the linear regression coefficient value R^2=0.990, (**Fig. S3B**) appreciating the current obtained at the oxidation (I_{pa})/reduction (I_{pc}) for the various concentration range. The LOD value (limit of detection) can be obtained by applying the formula (3×SD/Sensitivity) where, SD denotes to standard deviation of the calibration plot of current vs. concentration. In this sequence the

sensitivity has been obtained from the slope divided by active surface area of bioelectrode, from the plot of the current vs. concentration used in the sensing experiments, which was obtained 0.011mA/µM/cm^2, informed the fabricated electrode was significantly sensitive for the dopamine interpretation. Including this the limit of detection (LOD) value has been obtained 0.52 µM. Moreover, the Michaelis menton constant (K$_m$) value has been obtained -2.02 µM, **Fig. S3C**. Thus, electrochemical study reveals the information for fabricated bioelectrode, from prepared material is much promising for the dopamine estimation and sensing application, which support to establishment as an efficient material for fabricating the electrochemical device. The linear regression coefficient equation has been given in **Eq. S1**.

$$I_p(mA) = 2.8E\text{-}3 \cdot C\ (\mu M) + 1.05\ (R^2 = 0.996),\ [0\text{-}35\ \mu M] \qquad \textbf{Eq. S1}$$
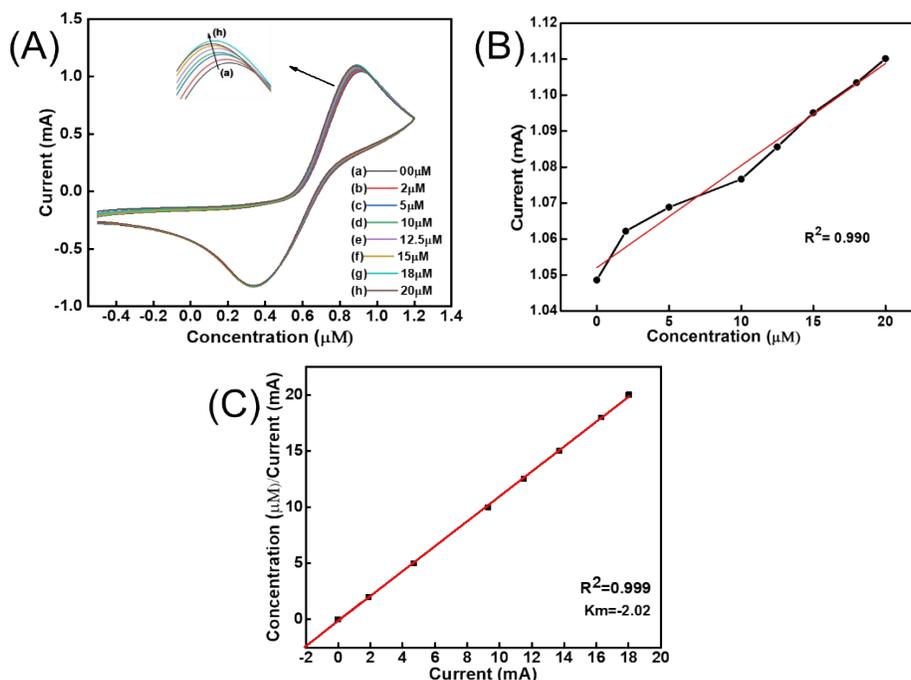
Fig. S3. *(A) is the CV sensing curve of dopamine detection, from 0-20 µM concentration range. (B) is the calibration curve of the dopamine sensing for anodic peak current. (C) is the Michaelis menton constant (Km), plotted concentration/current vs. concentration taken for sensing study.*
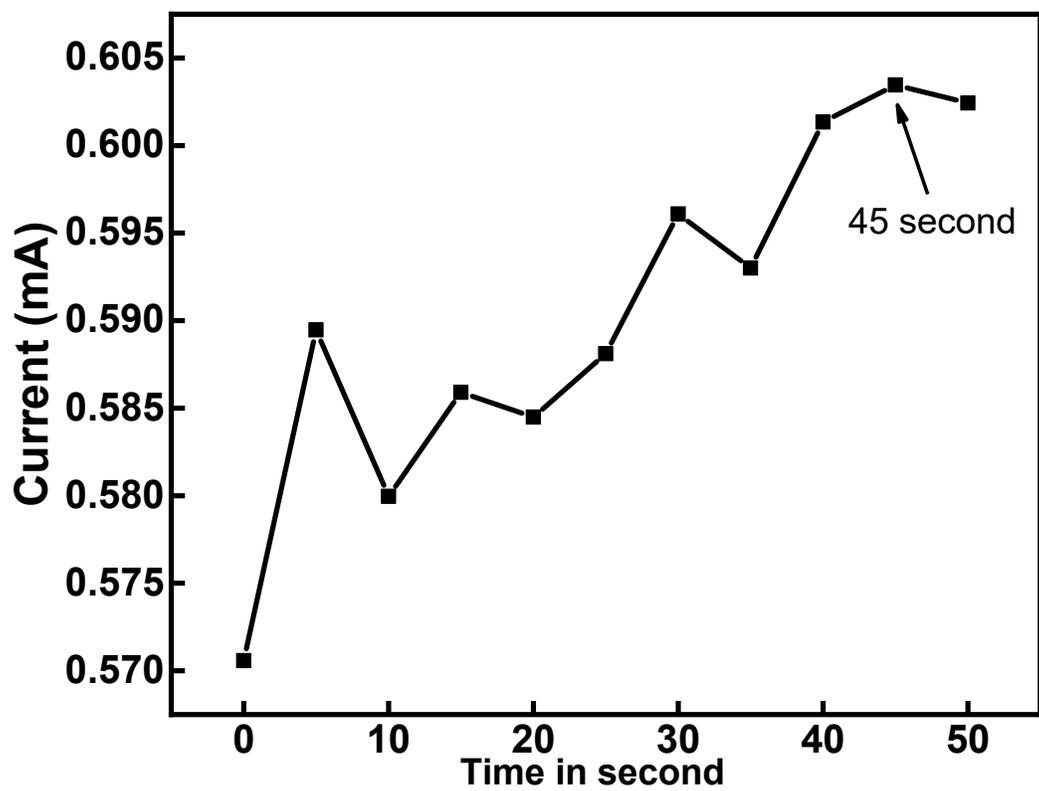
Fig. S4. *Shows response time study for the Tyr/L-rGO/Ag electrode.*

Table S1. *Shows the result obtained from the atomic force microscopy.*

	Rms-Rq	Ra	Max. area peak height
(a)	93.63	72.97	205.24
(b)	10.47	8.21	70.28
(c)	10.32	5.99	99.12

Table S2. *Shows the anodic peak (I_{pa}) current obtained from the CV and DPV experiments.*

Electrodes	CV current increase in %	DPV current increase in %
Bare ITO	-	-
L-rGO/ITO	44.71	12.46
L-rGO/Ag/ITO	99.56	24.13
Tyr/L-rGO/Ag/ITO	144.77	38.13

Table S3. *Shows the results obtained in the form of LOD and Michaelis menton constant values from the DPV sensing for the dopamine detection.*

	Lower concentration	Higher concentration
Linearity	0-35µM	40-95 µM
Sensitivity	6.08×10^{-4} mA/µM/cm^2	6.96×10^{-4} mA/µM/cm^2
LOD	1.03 µM.	-
Km	-3.70 µM	-

Table S4. *Shows the results obtained from the stability and reusability experiments.*

Days	Stability current in %	Scan no	Reusability current in %
40	100	8	100
45	99.85	9	99.82
50	99.42	10	99.69
55	99.0	-	-
60	98.74	-	-

Table S5. *Shows the representation of the %RSD value obtained from the interference study.*

Dopamine with interfering substances (40 µM each)	Cathodic peak current (I_p; mA)	% RSD
DA	4.11	0.0
DA + Urea	3.98	4.05
DA + AsA	4.48	8.99
DA + Glu	4.55	10.74
DA + LA	4.67	13.48
DA + UA	4.11	2.43
DA + Urea +AsA + Glu + LA	4.38	6.43