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Electronic Supplementary Information (ESI) for

Probing the Shape Specific Electrochemical Properties of Cobalt Oxide Nanostructures for its Application as Selective and Sensitive Non-Enzymatic Glucose Sensor

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1. FITR Analysis of Cobalt Oxide Nanostructures

FTIR spectra of the calcined samples recorded at room temperature in the range of 450 to 4000 cm^{-1} is demonstrates in Fig. S1. All three spectrums contain two sharp and prominent absorption bands at the positions ≅ 663 and 571 cm^{-1} similar to the reported result of Barakat et al.[1]. The former is originated due to the stretching vibration of tetrahedrally coordinated M-O whereas the next one is associated with the octahedrally coordinated M-O [2, 3]. In this case, M represents Co^{2+} located at tetrahedral sites and Co^{3+} at octahedral sites. Hence, the FTIR analysis again confirms the formation of Cobalt (II, III) oxide. Some other peaks are also observed which are identified as the surface adsorbed stretching (~3400 cm^{-1}) and bending modes (~1600 cm^{-1}) of water molecules.

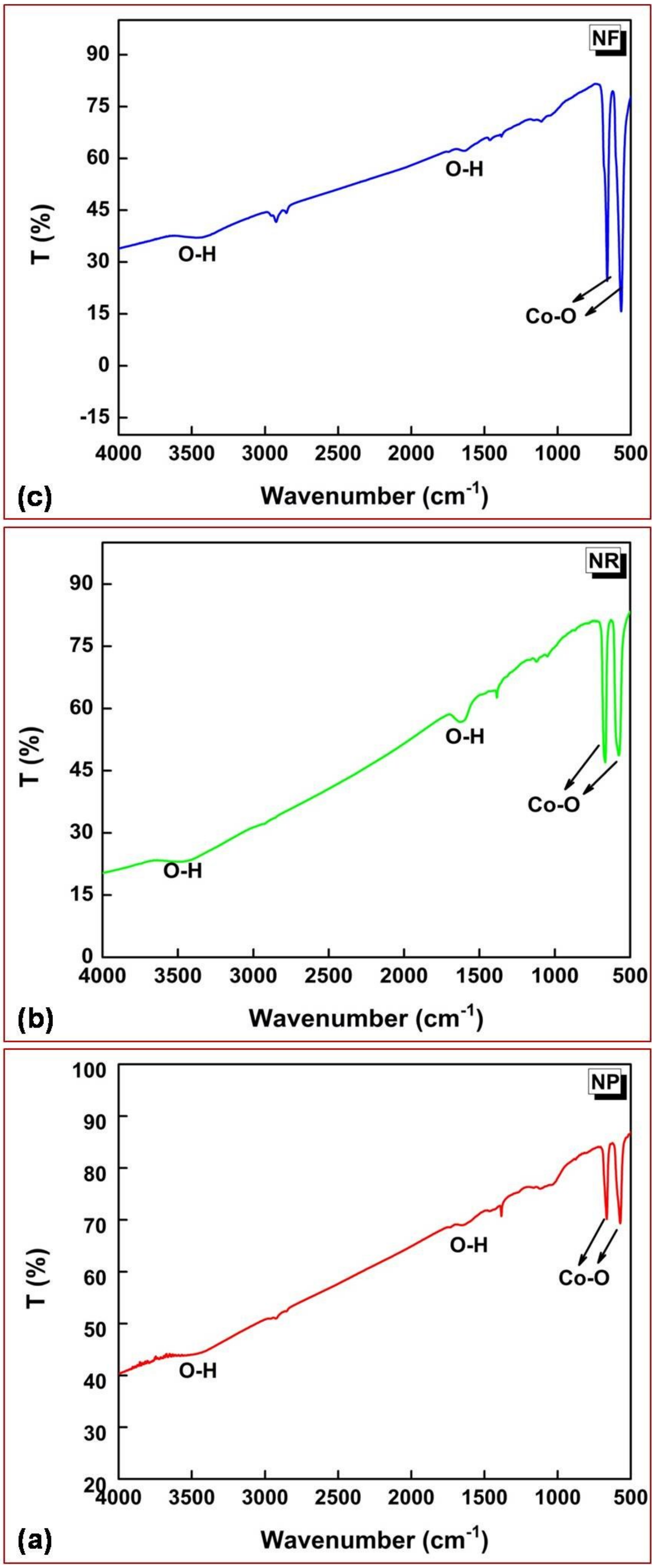


Fig. S1 FTIR spectra of cobalt oxide nanostructures.

2. Electrochemical properties of cobalt oxide nanostructures modified electrodes

Use of modifier is very frequently used technique in order to improve the electrochemical interface and desired detection ability of working electrode[4]. Herein we have used cobalt oxide nanostructures (NP, NR, NF) as modifier for the construction of ultra sensitive electrochemical glucose sensor. Prior to glucose detection, to understand the electrochemical properties of these modified electrodes cyclic voltammetry (CV) is performed using $K_3Fe(CN)_6$ as probe molecule. CV is the most convenient electrochemical technique which gives detailed view of any novel electrode corresponding to the electrochemical processes[5]. Ferricyanide/ferrocyanide redox couple exhibits nearly reversible reaction[6]. That's why it is the most popular choice to determine the electrochemical properties of any novel electrode since years.

The results of the CV taken within the broad potential window of -1.2V to 1.2V with a scan rate of 50mV/s, containing probe molecule in 1mol/L aqueous KCl solution is elucidated in Fig. S2a). All the electrodes show well defined oxidation-reduction peaks corresponding to $Fe(CN)_6^{3-/4-}$. Also, the scan rate dependence (Fig. S2b, c, d) is tested over a wide range of 10-350 mV/s. The redox currents in each case are linearly related to the square root of scan rate (Fig. S2e, f, g) having excellent correlation coefficient of 0.99. This implies that the electrochemical processes on the modified electrodes are diffusion controlled processes. The order of the peak currents obtained by different cobalt oxide nanostructure modified electrodes is NF-PGE >NR-PGE >NP-PGE. The peak to peak separation (ΔE_p) for NP-PGE, NR-PGE and NF-PGE are 0.37, 0.25 and 0.24V respectively. Lower ΔE_p value of NF-PGE indicates greater electron transfer rate compared to the other nanostructures. This higher catalytic current can be attributed to the excessively larger surface area provided by this unique hierarchical architecture and strong adhesion of NF onto the PGE surface. Inter connected nano sized petals of this 3-D structure has effectively improved the direct transportation of electrons. In addition, the anodic and cathodic peak current ratio of the $Fe(CN)_6^{3-/4-}$ for NP-PGE, NR-PGE and NF-PGE are 1.3, 1.2 and 1.1 respectively suggesting better reversibility of NF-PGE compared to other. We have also calculated the real/electroactive surface area, area which participates in electron exchange process[7], using the Randles-Sevcik equation[8] expressed as:

$$i_p = 2.69 \times 10^5 D_0^{1/2} n^{3/2} v^{1/2} C_0 A \qquad (1)$$

[where, i_p is the peak current (A), n represents the no of electron transferred, D_0 is the diffusion coefficient of the electroactive species (cm^2/s), C_0 is the bulk concentration of the same species (mol/L), V is the scan rate (V/s) and A represents the electroactive area of the electrode]. Calculated electroactive areas of the modified electrodes are 0.082 mm^2 (NP), 0.103 mm^2 (NR) and 0.122 mm^2 (NF). Therefore, it is very clear that such larger electroactive area of NF-PGE leads strong potential in electrochemical detection of glucose and most suitable candidate.

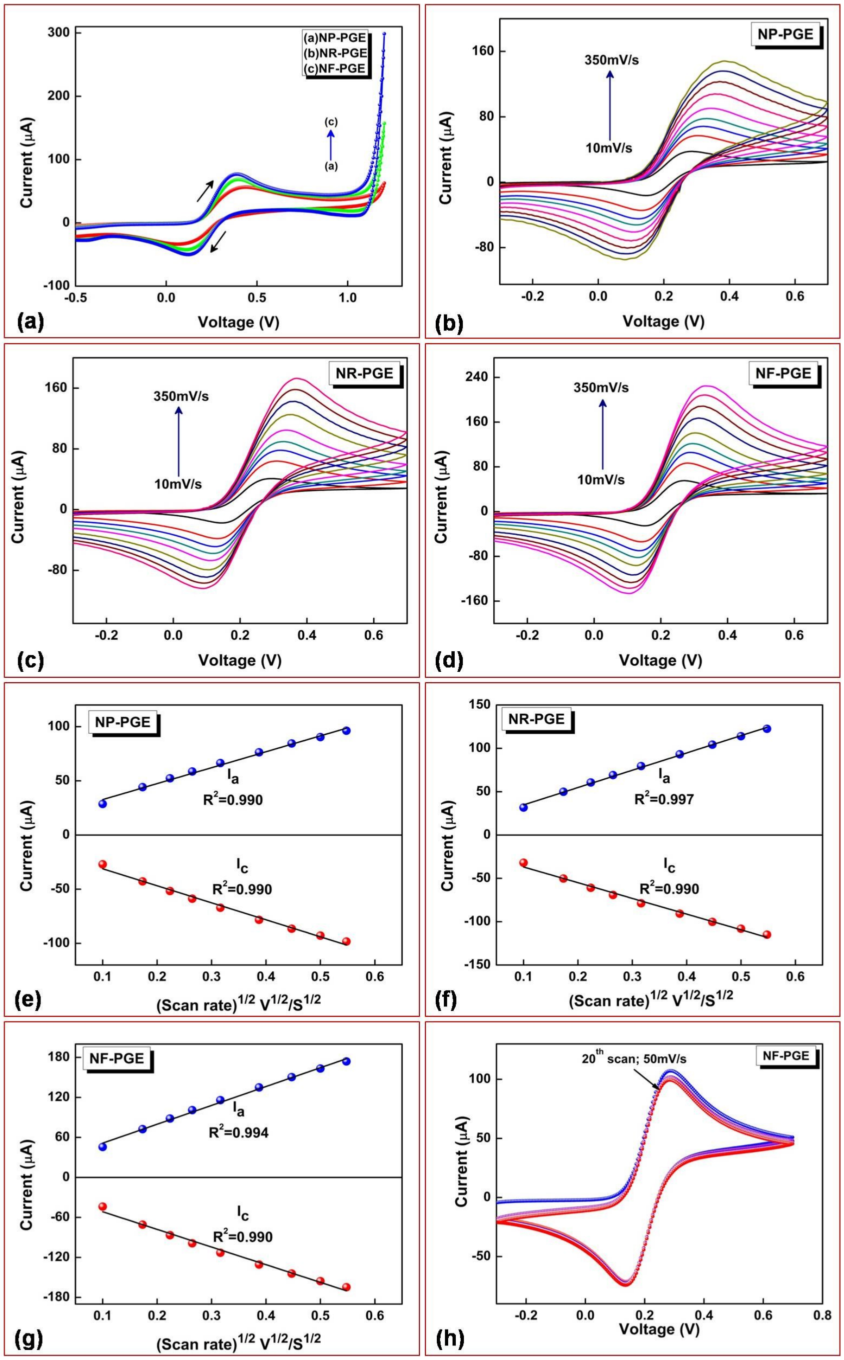


Fig. S2: (a) CV of the prepared electrodes in 1M aqueous KCl solution containing 5mM/L $K_3Fe(CN)_6$ at a scan rate of 50mV/s. (b), (c) and (d) represents CV scans at various scanning potentials for modified electrodes, (e), (f) and (g) Shows the linear fitted plots of peak currents against square root of scan rates for modified electrodes. (h) Repeatability of CONF-PGE for 20 CV runs at 50mV/s.

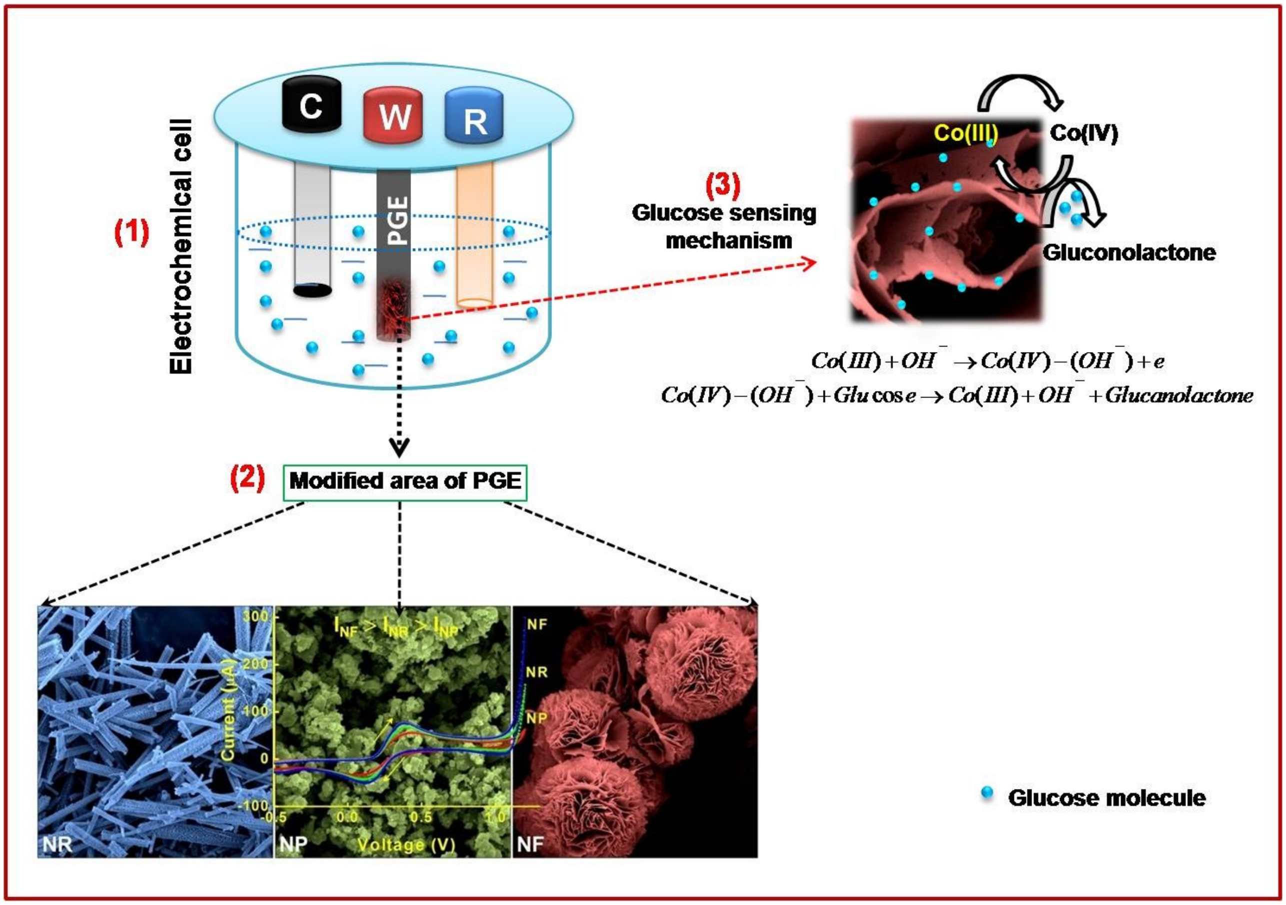
Stability of the modified NF-PGE is observed during the 20 repetitive CV scan at potential sweep of 50 mV/s. Peak current remains almost unchanged (Fig. S2h). Comprehensive results of the obtained electrode parameters for cobalt oxide nanostructures modified electrodes are listed in Table S1.

Table. S1: Electrode parameters calculated from voltammograms; 50mV/s:

Cobalt oxide nanostructure modified electrode	***ΔE_{pp} (V)***	***I_a/I_c***	***Electroactive Area (mm^2)***
NP-PGE	0.37	1.30	0.082
NR-PGE	0.25	1.20	0.103
NF-PGE	0.24	1.10	0.122

Table. S2: Amperometric results for analysis of different soft drink samples by SA method using NF-PGE

Nature of sample	***Sample name***	***Concentration of glucose spiked (mM)***	***Detected concentration (mM)***	***RSD (n=3) (%)***	***Recovery (%)***
Soft drinks	*Pepsi (Pepsico India)*	0.2	0.189	1.6	94.5
	Ditto Mango Drink (HMPC product)	0.2	0.201	1.1	100.5
	7up (Pepsico India)	0.2	0.179	1.4	89.5
Fresh fruits	*Mango*	0.2	0.203	0.8	101.5
	Orange	0.2	0.192	1.1	96.0



Scheme S 1: Shape-specific electrocatalytic oxidation mechanism of glucose.

3. Calculation of LOD:

LOD is defined as the minimum concentration of analyte which can be detected (not quntitated/countable). It signifies the limit if that the analyte is present above this certain value or not[9, 10].

The process of LOD determination is as follows:

- Determine the standard deviation (σ) of the blank measurements by repeating the experiment several times (at signal to noise ratio 3). [Using the inbuilt command *STDEV(Cx:Cy)* of Microsoft excel standard deviation is calculated where Cx and Cy denotes the columns]
- Plot the calibration curve for varying concentration of analyte and find the value of the slope.
- Calculate the LOD using the formula:

$$LOD = \frac{3\sigma}{slope}$$

In our case, the σ value comes out as 0.011.

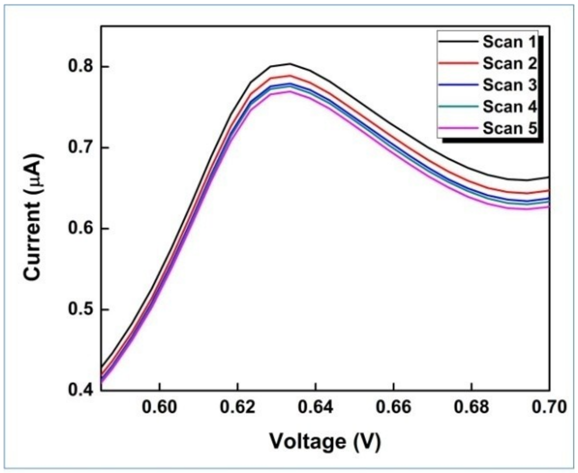


Fig. S3: Blank run of modified electrode.

From the calibration curve, we get two linear filled curves (R^2=0.987):

$Y = 348.05 + 228.03 \times X$ (1)

$Y = 15.22 + 693.02 \times X$ (2)

LOD (1)=0.14 μM and LOD (2)= 0.04 μM

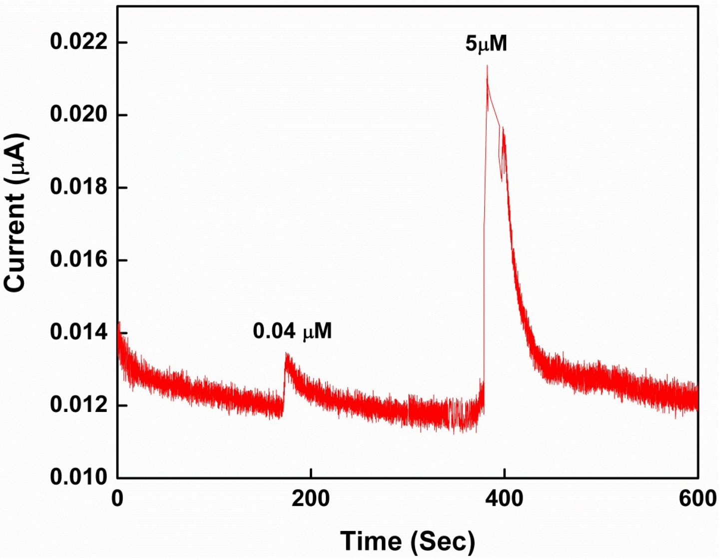


Fig. S4: LOD calculation via experimental process.

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