# Online Supporting Information for

# Self-assembled $IrO_2$ Nanoparticles on DNA Scaffold with Enhanced Catalytic and Oxygen Evolution Reaction (OER) Activities

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**Instruments.**

The synthesized DNA-$IrO_2$ NPs were characterized using several spectroscopic techniques. The UV-visible (UV-Vis) absorption spectra were recorded in a double beam UV-Vis spectrophotometer purchased from Unico (model 4802) equipped with a 1 cm quartz cuvette holder for liquid samples. The transmission electron microscopy (TEM) analysis was done with JEOL-JEM 2010 and Tecnai model TEM instrument (Tecnai$^{TM}$ G2 F20, FEI) with an accelerating voltage of 200 KV. The Energy Dispersive X-ray Spectroscopy (EDS) analysis was done with the FE-SEM instrument (Oxford) with a separate EDS detector connected to that instrument. A thin film of the $IrO_2$ NPs solutions was made on a glass substrate and the fabricated thin films were characterized by X-ray diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FT-IR) analyses. The XRD analysis was done with a scanning rate of 5° $min^{-1}$ in the $2\theta$ range 10-80° using a Bruker X-ray powder diffractometer (XRD) with Cu Kα radiation ($\lambda$ = 0.154 nm). The FT-IR analysis was done with the model Nexus 670 (FTIR), Centaurms 10X (Microscope) having spectral Range 4,000 to 400 $cm^{-1}$ with a MCT-B detector. The $^1H$ NMR study was done with Bruker (Germany), 400 MHz, FT-NMR spectrometer. Electrochemical analyzer BAS 100B potentiostat was used for the entire OER and related studies. Hg/HgO reference electrode was used along with a Pt counter electrode and $IrO_2$ catalyst. DNA-$IrO_2$ nanocatalyst solution was drop casted on a glassy carbon (GC) electrode surface which was then used as a working electrode.

**Preparation of Sample for Other Various Characterizations.**

The synthesized DNA-$IrO_2$ NPs were characterized using UV-Vis, TEM, EDS, XRD, XPS and FT-IR analysis studies. The DNA-$IrO_2$ NPs solutions were directly used for the absorption measurement in UV-Vis spectrophotometer. The same liquid solution was used for the TEM sample preparation and other thin films preparation. The samples for TEM was prepared by placing a drop of the as synthesized DNA capped $IrO_2$NPs solution onto a carbon coated Cu grid followed by slow evaporation of solvent at ambient conditions. For EDS, XRD, XPS and FT-IR analysis, glass slides were used as substrates for the preparation of thin films. The slides were cleaned thoroughly in acetone and sonicated for about 30 min. The cleaned substrates were covered on one side with the DNA capped $IrO_2$NPs and then dried in air. After the first layer was deposited, subsequent layers were deposited by repeatedly adding more DNA capped $IrO_2$NPs solutions and dried. Final samples were obtained after 10-12 depositions and then analyzed using the above techniques. For catalysis study, the sample preparation procedure has already been said above. For OER study, a three electrode electrochemical cell was taken which contained 20 mL of 0.1M NaOH solution, a pair of Hg/HgO reference electrode and a Pt foil counter electrode. The working electrode was fabricated by drop casting 6 μL of the $IrO_2$ nano-catalyst solution at the finely polished GC electrode surface and dried at RT for 8 h. Then the working electrode was also introduced in the electrochemical cell. All three electrodes were connected to a BAS 100B potentiostat for the OER studies.

**Determination of Turn Over Frequency (TOF).**

With reference to the work of Wehner et al. (Ref 88 in the main text) turn over frequency (TOF) of our catalyst in electrochemical water oxidation is calculated as follows by taking the current observed at 1505 mV which is $4.12\times 10^{-3}$ A.cm$^2$. The surface concentration of Ir atom on the modified GC electrode is $1.128 \times 10^{14}$ which is also calculated with reference to the work of Wehnerwt et al. (Ref 88 in main text). In general, the TOF is calculated by using the following formula

$$\mathbf{TOF= I \times N_A / A \times F \times n \times \Gamma}$$

Where,

i = Current

$N_A$ = Avogadro Number

A = Geometrical surface area

F = Faraday constant

n = Number of electrons

Γ = Surface concentration

Hence,

$TOF_{1.505\ V} = [(4.12\times 10^{-3})\ (6.023\times 10^{23})] / [(0.0723)\ (96485)\ (4)\ (1.128 \times 10^{14})]$

$TOF_{1.505\ V} = 7.88\ s^{-1}$

**Prediction of Number of Electrons Transferred During OER on the Basis of Tafel Slope.**

As per theory, the Tafel behavior at larger anodic overpotential will give a slope represented as.

$$\text{Slope} = (1-\alpha)\ n\ F / 2.303\ R\ T$$

Where, n is the number of electron transferred and a is the anodic Tafel slope.

If n = 1 and at 25 °C, $\text{Slope} = (1-\alpha)(1)\ F / 2.303\ R\ T$

$$\text{Slope} = 120\ \text{mV/dec}$$

Since, OER is an electrochemical reaction which occur at larger anodic overpotential. Hence, we adapted this method to predict the number electrons transferred at lower and higher overpotentials respectively. Water oxidation could be a 1 to 4 electron transfer which mainly depends on the conditions and the applied potential. The observed overpotentials at lower and higher overpotentials are 32 mV/dec and 90 mV/dec which corresponds to four electron and two electron transfer. This means that the water oxidation falls within the allowed order of Tafel slopes and the OER kinetics is facile with DNA@$IrO_2$ NPs.(References 90-92 in main text).

**Post cycle Linear Sweep Voltammetry (LSV) after chronoamperometry analysis.**

To check the efficiency of our DNA-$IrO_2$ NPs modified GC electrode even after the chronoamperometry analysis a linear sweep voltammogram was obtained under the identical conditions as done prior to the chronoamperometry analysis. The resultant iR corrected LSV is given in Figure S2. It is clear from Figure S2 that electrocatalytic activity is almost retained and the loss in the overpotential observed is extremely low and negligible too. From this we conclude here that our catalyst is able to deliver almost the same efficiency even after 12 h.

**Control experiments on OER activity.**

As explained in the main text, few controlled experiments were carried out to check the influence of GC electrode, DNA and $IrO_2$ particles prepared using the same wet chemical route but without the DNA scaffold. Linear sweep voltammogram for each of them were obtained separately under the same condition in which the actual study was carried out. All of them are given together with the LSV curve of DNA-$IrO_2$ NPs modified GC for comparison purposes below in Figure S3 where line a is for bare GC, line b is for GC modified with only DNA, line c for $IrO_2$ modified GC and line d is for DNA-$IrO_2$ NPs modified GC and all are iR corrected. From Figure S3, it is clear that none of them alone was able to catch the catalytic efficiency achieved by our catalyst. As consequence of this result we conclude here that for an efficient catalytic activity both the presence of DNA and $IrO_2$ are necessarily to be bound together.

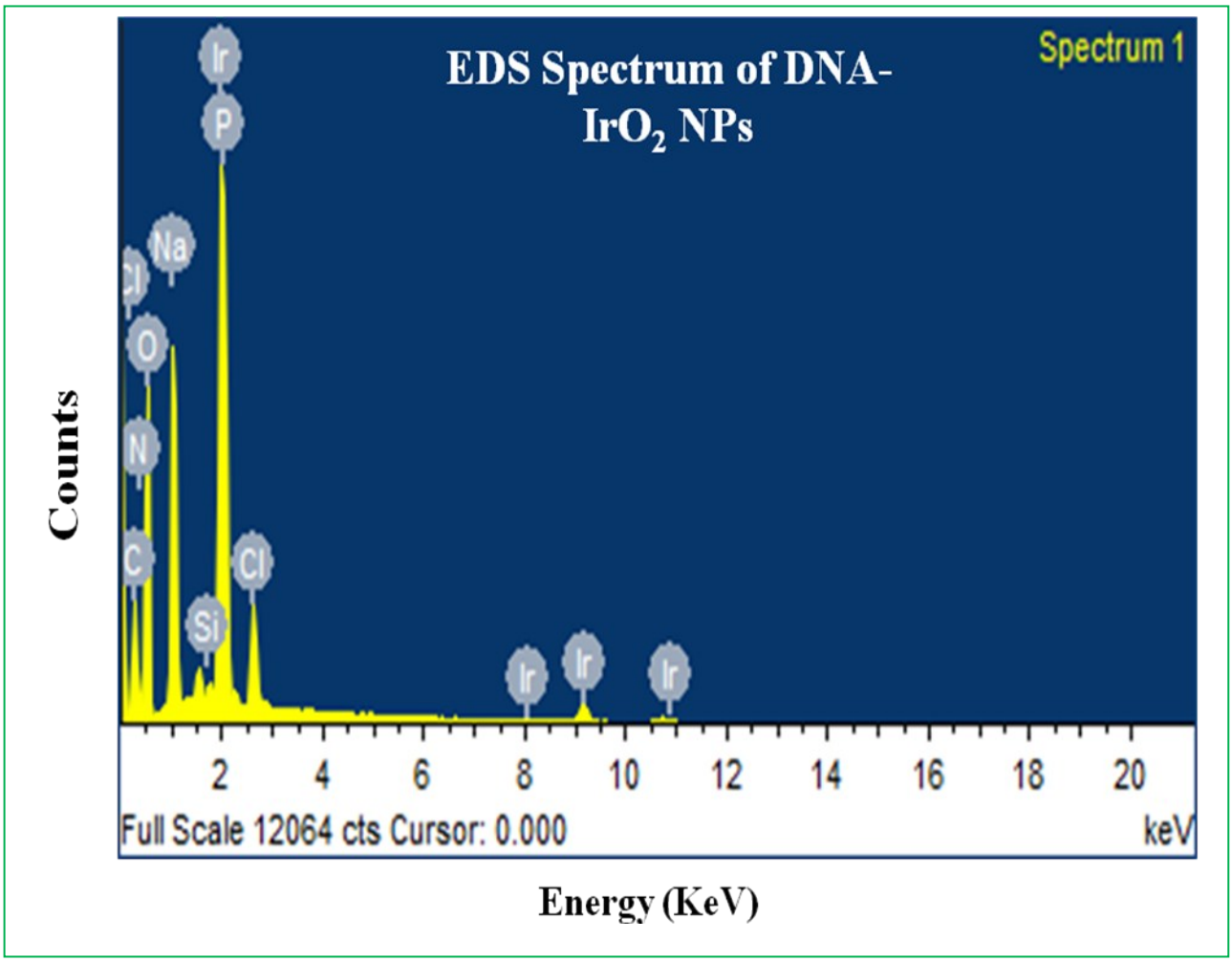



**Figure S1:** The energy dispersive X-ray spectroscopic (EDS) analysis of self-assembled $IrO_2$ NPs on DNA scaffold that possess the expected peaks for Ir, Cl, O, Ca, Si, P and Na.

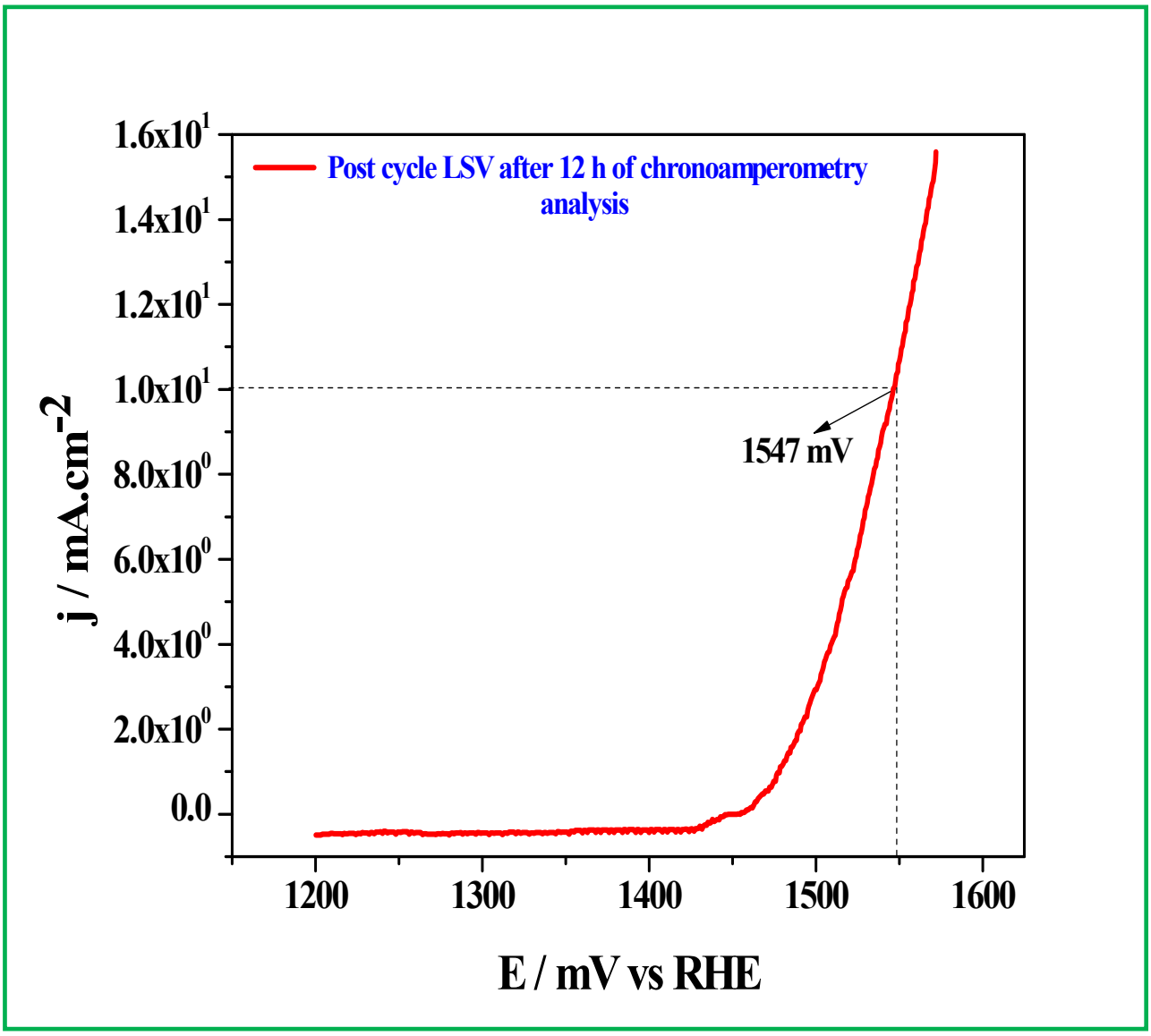



**Figure S2:** iR corrected linear sweep voltammogram of DNA-$IrO_2$ NPs modified GC after the chronoamperometry analysis at a sweep rate of 0.01 $V.s^{-1}$.

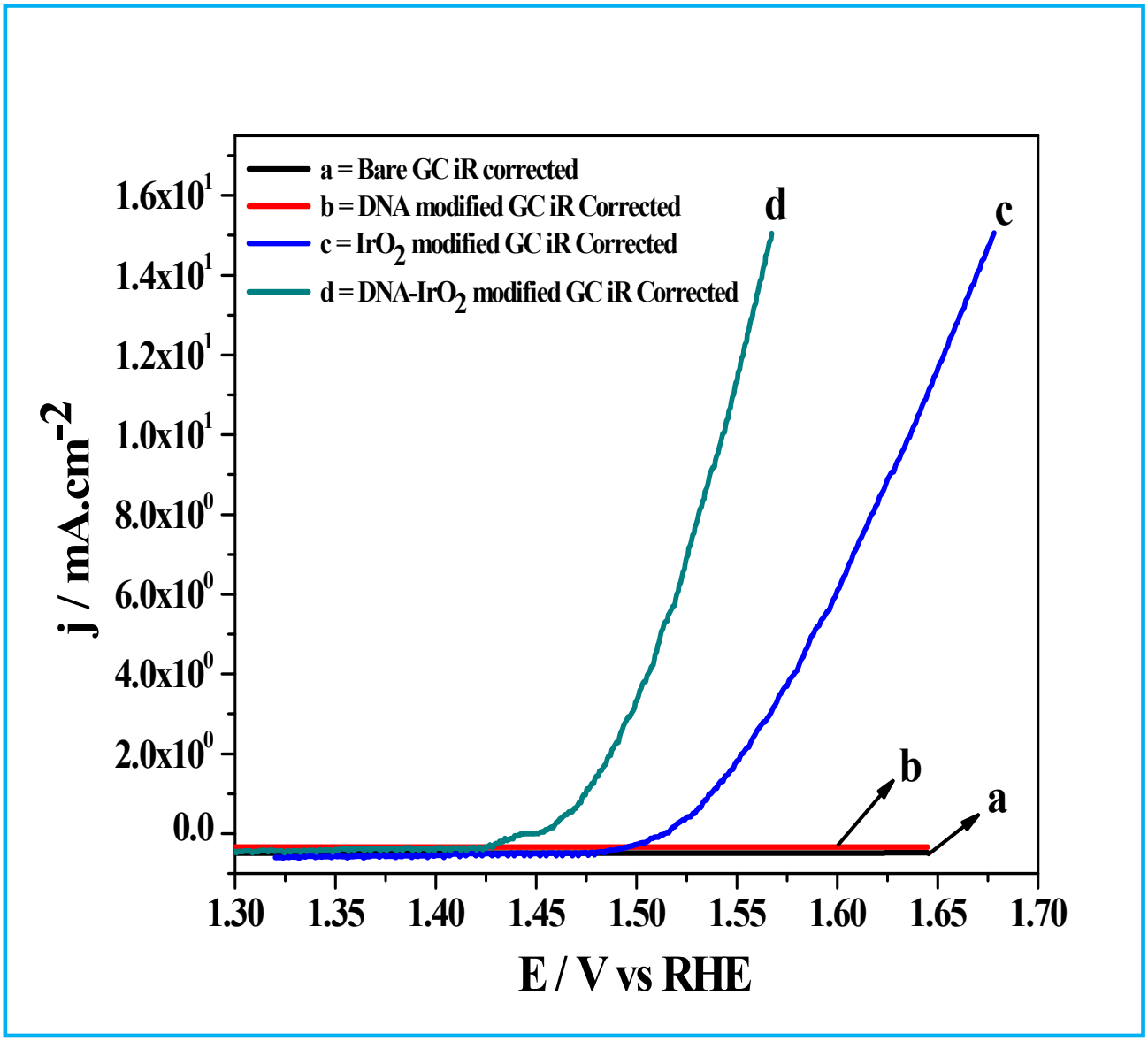
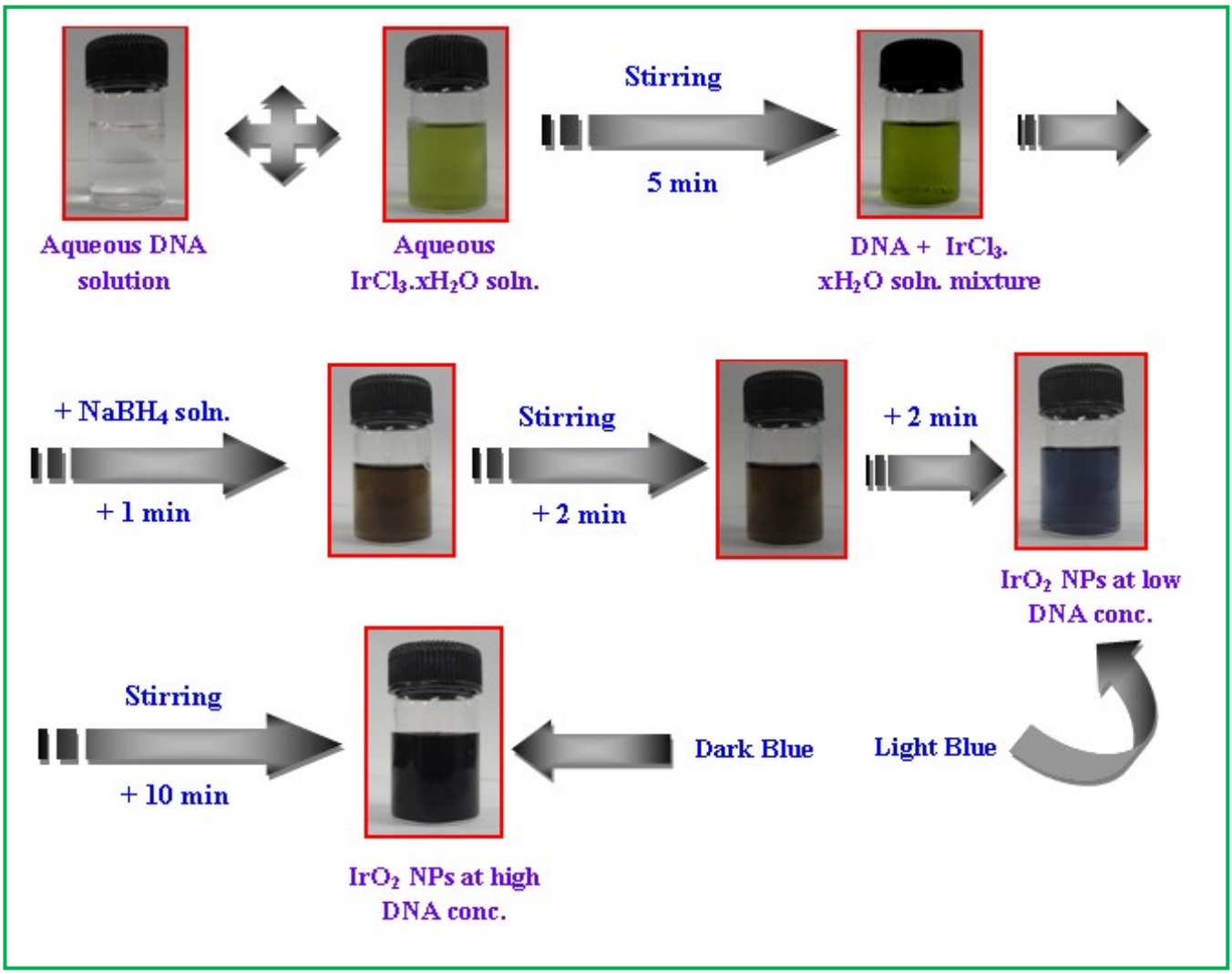



**Figure S3:** iR corrected linear sweep voltammograms of GC electrode (a); DNA modified GC electrode (b); $IrO_2$ modified GC electrode (c); and of DNA-$IrO_2$ NPs modified GC electrode (d).

**Table S1:** Experimentally observed FT-IR bands for DNA and the reported DNA bands with band assignments.

| **FT-IR bands - de-oxyribo nucleic acid (DNA)-Experimental and Reported values** | | |
|---|---|---|
| **FT-IR bands ($cm^{-1}$) (experimentally observed)** | **FT-IR frequency range ($cm^{-1}$) (reported value)[34]** | **Absorbing bonds/vibration types** |
| 3606, 3738 | 3100-3750 | ν (OH group in DNA/water) |
| 2852, 2987 | 2800-2950 | Symmetric stretching vibration (C-H bonds in $–CH_2$ group) |
| 1678 | 1732-1595 | C=O, C-N, N-H[34] |
| 1488 | 1492-1480 | Bending (δ) of C-H bond in $CH_2$ |
| 1220, 1273 | 1170-1300 | Asymmetric stretching of $PO_2^-$ group |
| 1105 | 1140-950 | ν (C-O-C, C-C)[34] |
| 560, 812 | 400-1000 | De-oxyribose region |

Reference number 34 is given in main text.




**Scheme S1:** The schematic depiction of the overall preparation process for the formation of self-assembled DNA@$IrO_2$ NPs.