Electronic supplementary information

Bismuth oxide nanoparticle as a nanoscale guide to form silver-polydopamine hybrid electrocatalyst with enhanced activity and stability for oxygen reduction reaction

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Dopamine polymerization was clearly verified based on the color-changing reaction of Bi_2O_3 from yellow to dark black during composite formation in reaction mixture within 4 hours.

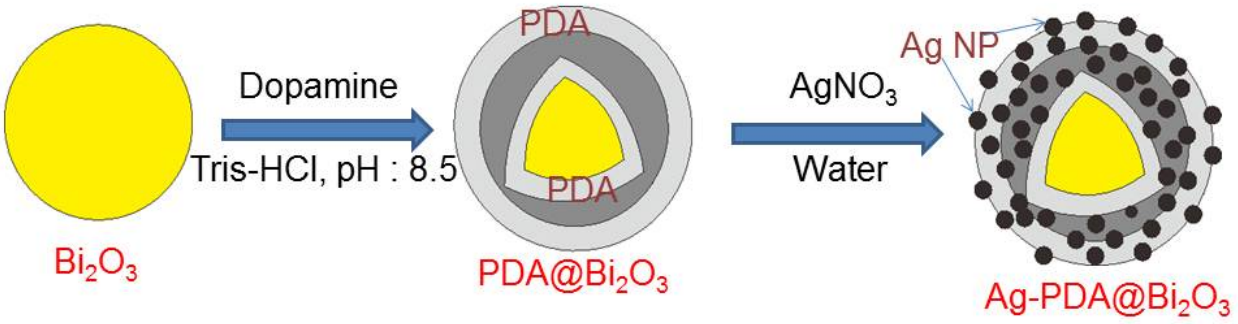

Figure S1: Schematic representation of the Ag-PDA@Bi_2O_3 preparation

1.1 Synthesis of Ag-PDA

Dopamine (100 mg) was dissolved in 10 mM Tris-HCl (pH 8.5) solution under continuous stirring for 12 h. The obtained suspension was centrifuged, washed with DD water and dried at 60°C. After that, 5 mg of PDA powder was dispersed in water with 10 min sonication and 2 mM $AgNO_3$ was added into this solution with 2 h stirring. Then the solution was centrifuged, washed with distilled water and dried at 60°C for further characterization.

1.2 Synthesis of Ag-Bi_2O_3

Bi_2O_3 nanoparticle (5 mg) was dispersed in water with 10 min sonication and 2 mM $AgNO_3$ was added into this solution with 2 h stirring. Then the solution was centrifuged, washed with distilled water and dried at 60°C for further characterization.

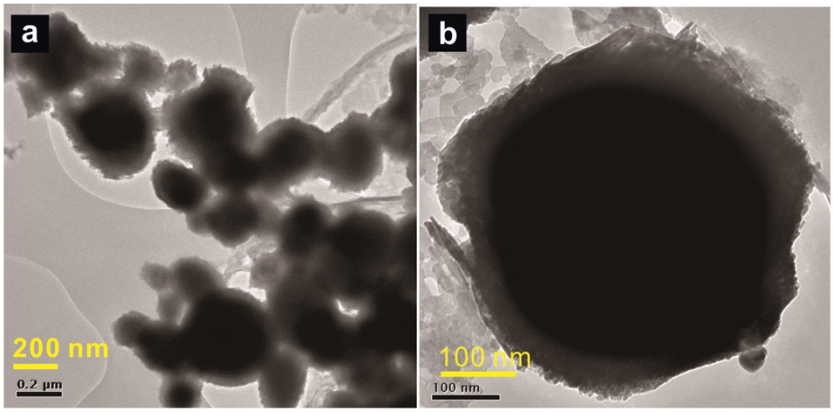

Figure S2: HR-TEM images of different Bi_2O_3 nanoparticle (a) and single TEM image of Ag-Bi_2O_3 (b)

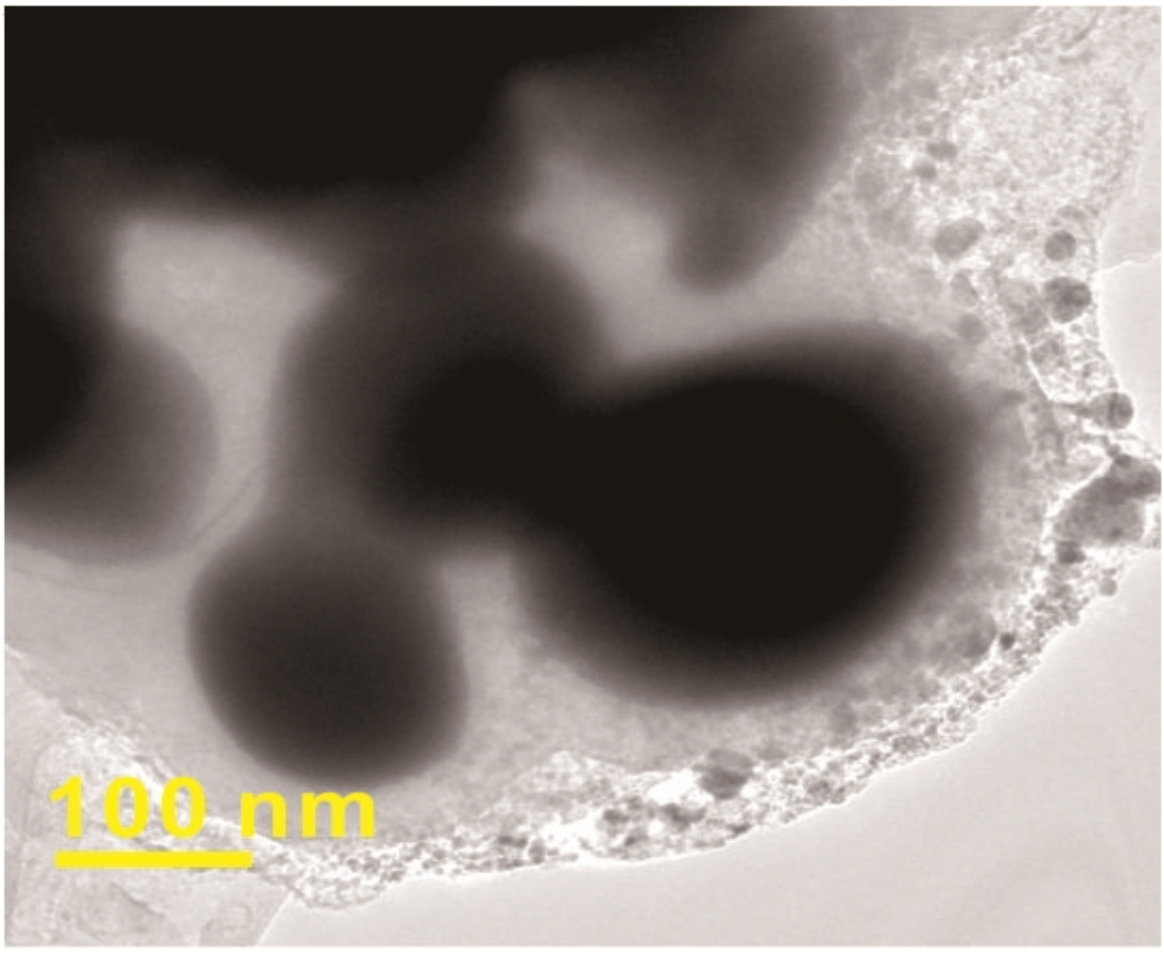

Figure S3: HR-TEM images of Ag-PDA@Bi_2O_3.

47 Table S1: Different particle size variation of Ag on PDA@Bi_2O_3 in HR-TEM image

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No of Particle	Particle size / nm	No of Particle	Particle size / nm
1	57.11	7	31.27
2	39.57	8	27.90
3	42.92	9	45.72
4	17.65	10	21.21
5	34.43	11	36.38
6	32.88	12	27.75
Maximum/nm: 57.11 Minimum/nm: 17.65 Mean/nm: 34.59			

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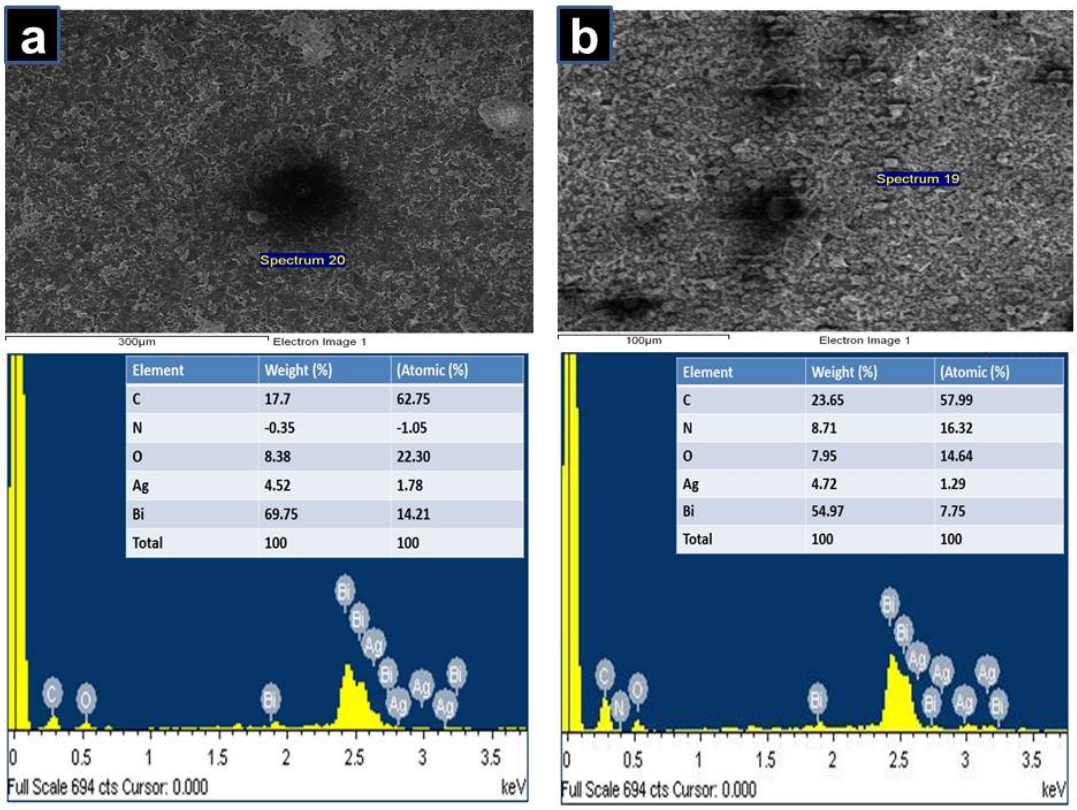


Figure S4: EDX spectrum of Ag-Bi_2O_3 (a) and Ag-PDA@Bi_2O_3 (b)

2. Oxygen reduction reaction:

Electroactive surface area of the modified electrode surface was calculated from the Randles-Sevcik equation:

$$i_P = 0.4463nFAC\left(\frac{nFvD}{RT}\right)^{1/2}$$

where i_p is the current maximum (amps), n is the number of electrons transferred in the redox event, A is electrode Area (cm^2), F is the Faraday constant (C mol^{-1}), D is the diffusion coefficient (cm^2/s), C is the concentration of redox solution, v is the scan rate (V/s). Potassium ferricyanide solution (5 mM) was used as a redox probe (Fe^{3+}/ Fe^{2+}) for calculating electroactive area. Figure S2 shows cyclic voltammetry of ferricyanide redox peak in 0.1 M KNO_3 at a scan rate of 50 mV/s. The redox current was used to evaluate the electroactive surface area.

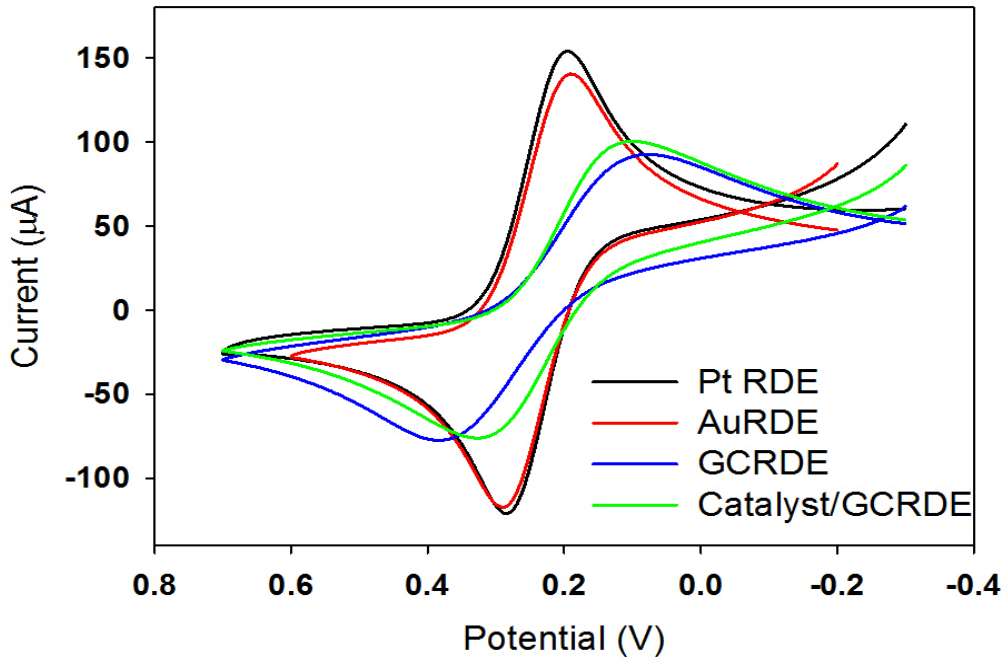


Figure S5: Cyclic voltammetry of ferricyanide redox peak in 0.1M KNO_3 solution

Table S2: Koutecky-Levich plot values calculation for ORR.

	Levich equation				**Koutecky-Levich equation**			
Pt disk (Area = 0.0614 cm^2, Applied potential = −0.38 V)								
ω (rpm)	i	j	ω (rad/s)	ω^(1/2)	1/j	1/B	1/ω^(1/2)	1/jk
150	0.319	4.6366	15.7079	3.963	0.1925	0.6554	0.2523	0.024
200	0.361	5.2470	20.9439	4.576	0.1701		0.2185	
250	0.396	5.7558	26.1799	5.116	0.1551		0.1954	
300	0.424	6.1627	31.4159	5.604	0.1448		0.1784	
500	0.526	7.6453	52.3598	7.235	0.1167		0.1382	
750	0.623	9.0552	78.5398	8.86	0.0986		0.1129	
1000	0.687	9.9854	104.719	10.23	0.0894		0.0978	
Au disk (Area = 0.0588 cm^2, Applied potential = −0.38 V)								
150	0.15	2.5510	15.7079	3.963	0.3920	1.176	0.2523	0.093
200	0.165	2.8061	20.9439	4.576	0.3564		0.2185	
250	0.18	3.0612	26.1799	5.116	0.3267		0.1954	
300	0.192	3.2653	31.4159	5.604	0.3063		0.1784	
500	0.227	3.8605	52.3598	7.235	0.2590		0.1382	
750	0.261	4.4387	78.5398	8.86	0.2253		0.1129	
1000	0.288	4.8979	104.719	10.23	0.2042		0.0978	
GC disk (Area = 0.0389 cm^2, Applied potential = −0.9 V)								
150	0.134	3.4447	15.7079	3.963	0.2903	0.7944	0.2523	0.091
200	0.148	3.8046	20.9439	4.576	0.2628		0.2185	
250	0.159	4.0874	26.1799	5.116	0.2447		0.1954	
300	0.167	4.2930	31.4159	5.604	0.2329		0.1784	
500	0.198	5.0899	52.3598	7.235	0.1965		0.1382	
750	0.222	5.7069	78.5398	8.86	0.1752		0.1129	
1000	0.229	5.8868	104.719	10.23	0.1699		0.0978	
GC+Catalyst (Area = 0.04087 cm^2, Applied potential = −0.38 V)								
150	0.179	4.3797	15.7079	3.963	0.2283	0.637	0.2523	0.055
200	0.197	4.8202	20.9439	4.576	0.2075		0.2185	
250	0.211	5.1627	26.1799	5.116	0.1937		0.1954	
300	0.227	5.5541	31.4159	5.604	0.1800		0.1784	
500	0.27	6.6063	52.3598	7.235	0.1514		0.1382	
750	0.309	7.5752	78.5398	8.86	0.1320		0.1129	
1000	0.338	8.2701	104.719	10.23	0.1209		0.0978	

					n	3.69	ik	18.17

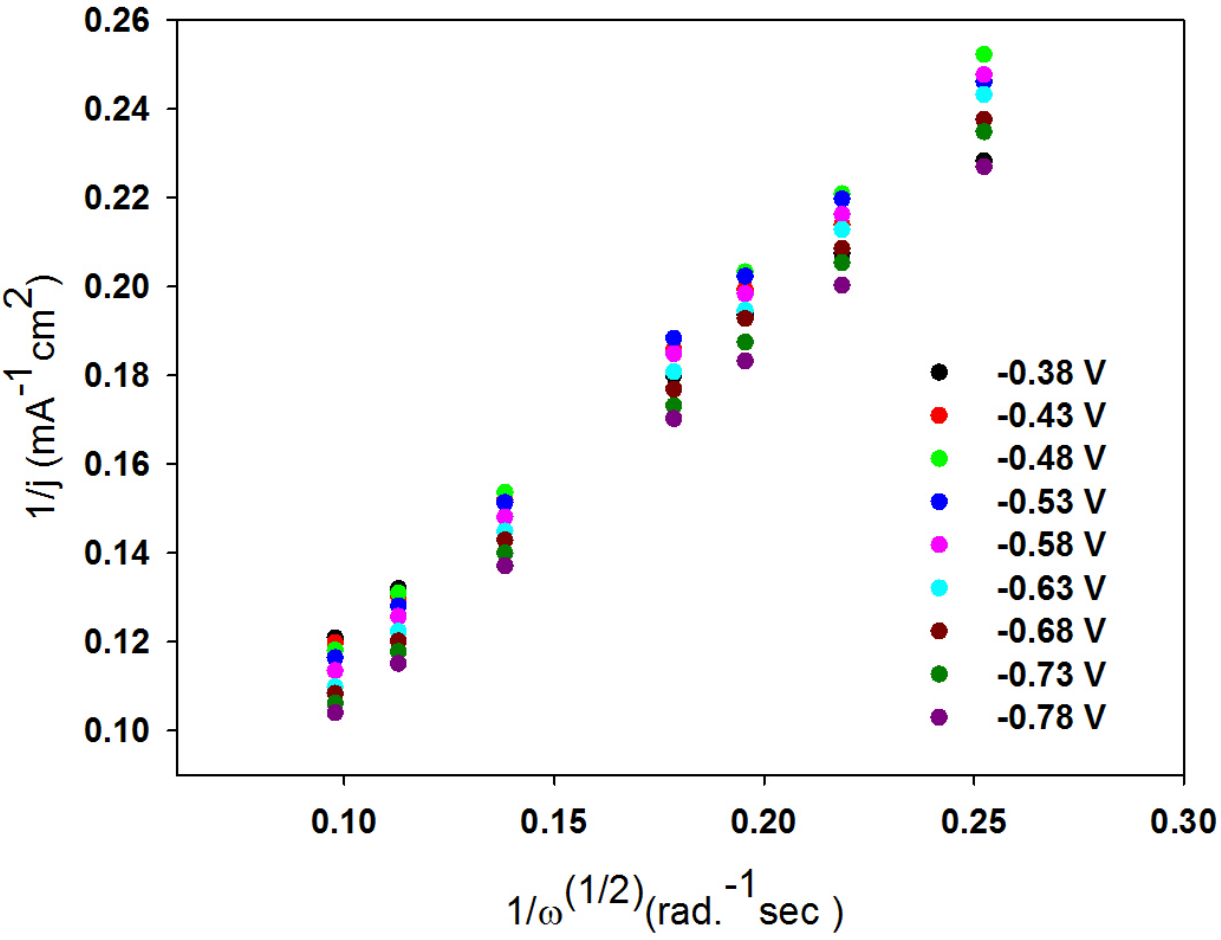
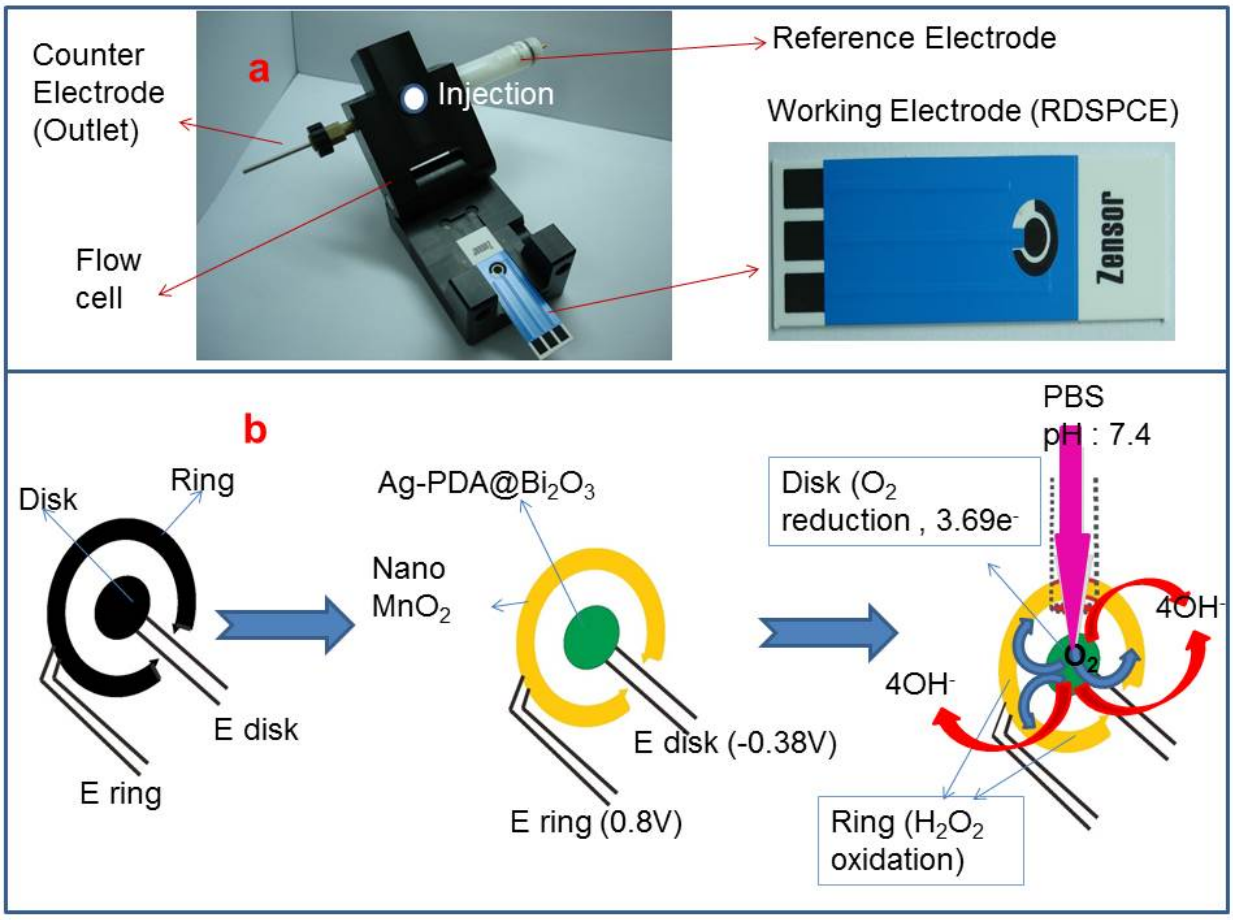


Figure S6: K-L Plots from Figure 4C RDE diffusion curve of different electrode potentials.



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86 Figure S7: Picture of the Flow Injection Analysis system for H_2O_2 monitoring. (a) Flow cell

87 setup and working principle. (b) H_2O_2 monitoring in ORR at Ring and Disk electrode.

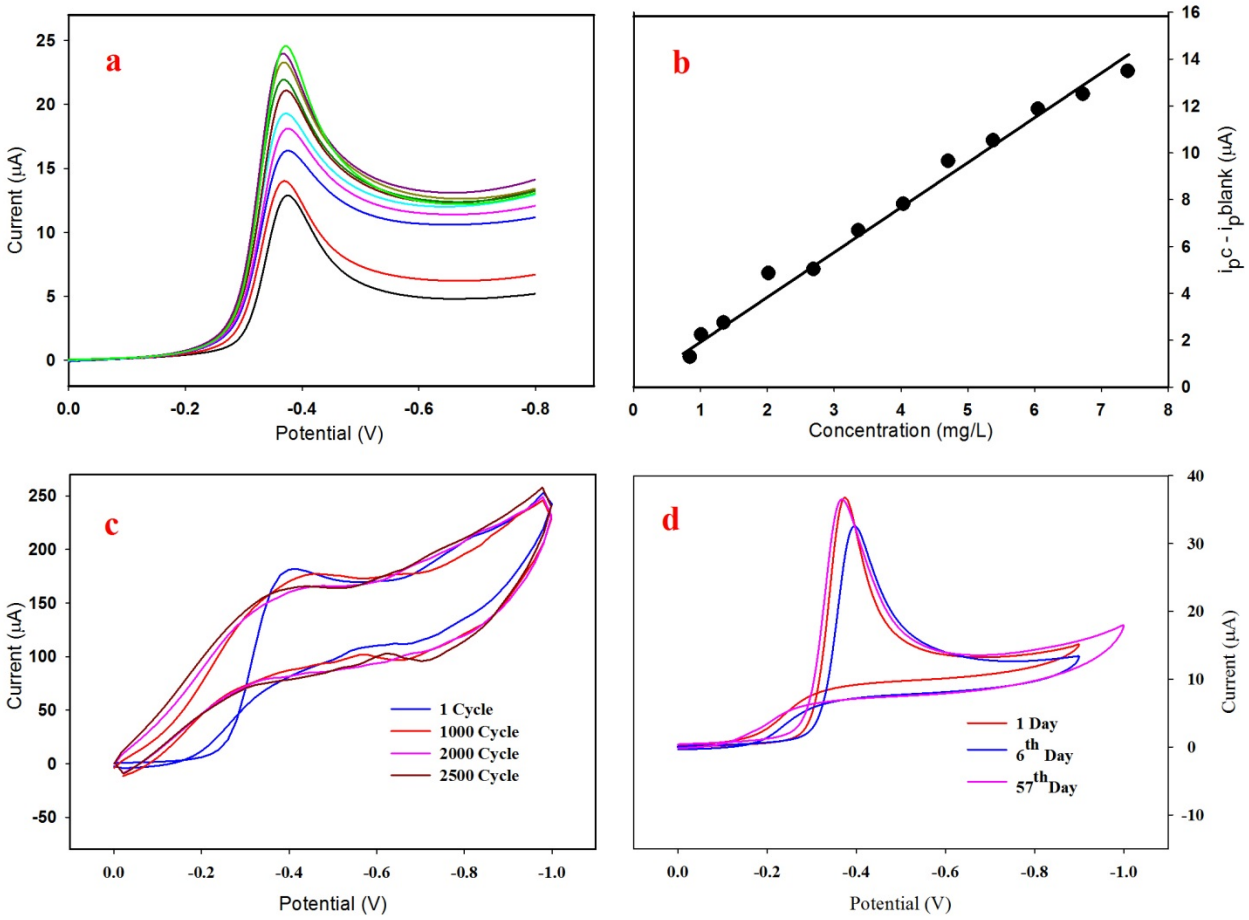

Figure S8: Calibration curve for dissolved Oxygen determination by Linear Sweep Voltammetry (a) (O_2 concentration from black to green is 0.84, 1.34, 2.02, 2.69, 3.36, 4.03, 4.70. 5.38, 6.05, 6.72, 7.39 mg/L) and linear range for dissolved oxygen (b). CV stability of at after 1000, 2000, 2500 cycle in O_2 saturated solution, scan rate 200 mV/s (c). Long time stability CV in dissolved oxygen medium at different days, scan rate 20 mV/s (d).