Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Boosting the charge for selective photoelectrochemical oxidation of hydroquinone in hazardous environments using fine-tuned heterojunction catalyst

Mohamed G. Abdelkader[a], Nada F. Atta[a*], Ahmed Galal[a*]

Chemistry Department, Faculty of Science, Cairo University, 12613 Giza, Egypt

E-mail: galal@sci.cu.edu.eg

Supplementary Materials

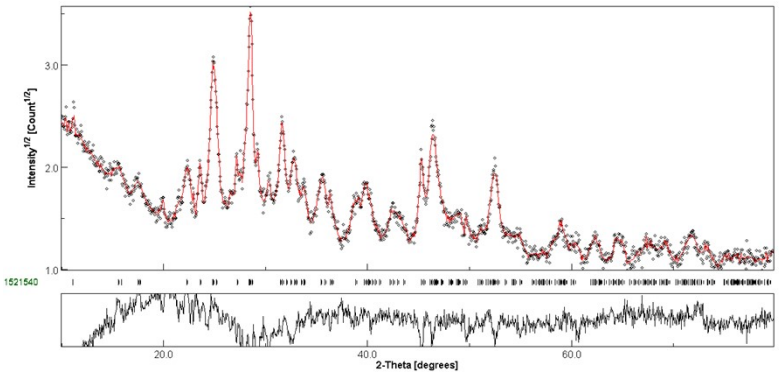
The SAED pattern of Figure 3C expresses the crystalline nature of the nanorods shown in Figure 3A. The indexing of the pattern resulted in the following cell parameters: a = 11.01 Å, b = 11.94 Å, c = 3.89 Å which are in acceptable agreement with the XRD results. The lattice spacing of 0.50 nm corresponds to the separation between two (200) planes. The nanorods preferentially grow along the (001) direction of the c-axis. Again the SAED data are in good agreement with those obtained from XRD measurements. The following indices of the planes deduced from the SAE pattern are: (130), (211), (221), (301) are identified.

Supplement 1A. Bi_2S_3 SAED analysis

Figure 3F displays the SAED pattern of $BiFeO_3$ nanoparticles. The sharp diffraction spots indicate that the structure is crystalline in nature. The indexing of the pattern reflects the following line parameters: $a = b$ = 5.67 Å, c = 13.91 Å that are in good agreement with the data deduced from the XRD measurement. The interplanar spacing of 0.12 nm ascertains the presence of (012) plane diffraction fringe. The planes indices identified from the SAE pattern are: (113), (202), (024) and (211) planes.

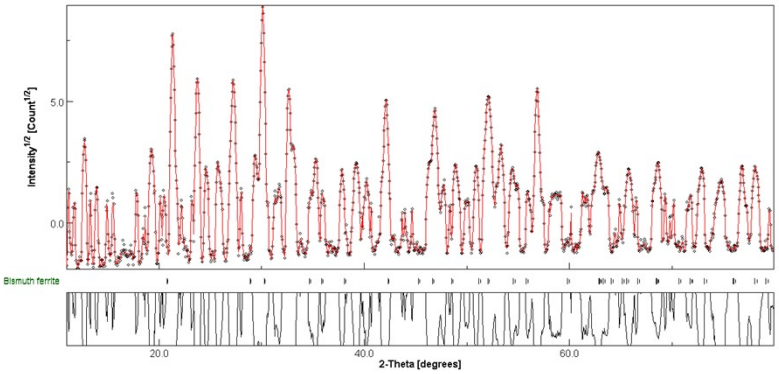
Supplement 1B. $BiFeO_3$ SAED Indexing table

Supplement 2. Rietveld refinement pattern and the corresponding parameters using MAUD program for: $BiFeO_3$ (a); Bi_2S_3 (b); and $Bi_2S_3/BiFeO_3$ heterojunction. Errors are reported in parentheses.



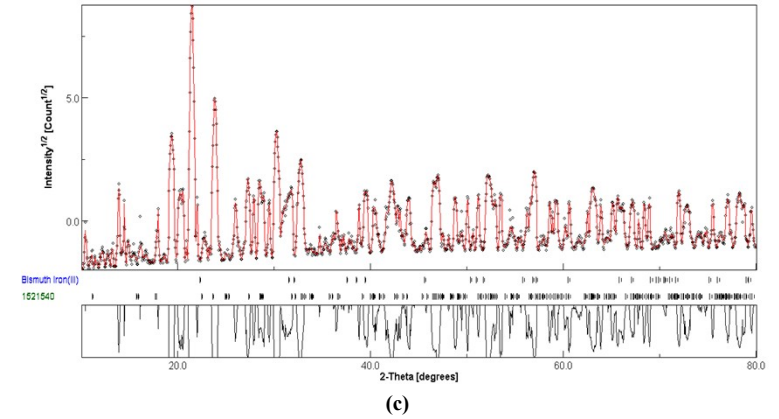
(a)

Phase	**Bi_2S_3 [Pnma]**
$Bi_{Occup.}$	Bi: 0.4
$S_{Occup.}$	S: 0.6
$Bi_x/Bi_y/Bi_z$	1.0 / 1.0 / 0.0 (4.04×10^{-4})
$S_x/S_y/S_z$	1.0 / 1.0 / 0.0 (4.04×10^{-4})
$B_{iso\ Bi/S}$	Bi: 0.620 (0.258) S: 0.847 (0.258)
R_w (%)	12.311
R_b(%)	18.512
R_{exp}(%)	21.592
χ^2	1.194



(b)

Phase	$BiFeO_3$ [*R3c*]
$Bi_{Occup.}$	Bi: 1.0
$Fe_{Occup.}$	Fe: 1.0
$O_{Occup.}$	O: 3.0
$Bi_x/Bi_y/Bi_z$	1.0 / 0.0 / 0.0 (3.37×10^{-4})
$S_x/S_y/S_z$	1.0 / 0.0 / 0.0 (3.37×10^{-4})
$O_x/O_y/O_z$	0.44 / 0.14 / 0.94 (5.21×10^{-4})
$B_{iso\ Bi/Fe/O}$	Bi: 1.661 (0.092) S: 1.661 (0.092) O: 3.539 (0.129)
R_w (%)	29.213
R_b(%)	18.816
R_{exp}(%)	17.239
χ^2	1.224

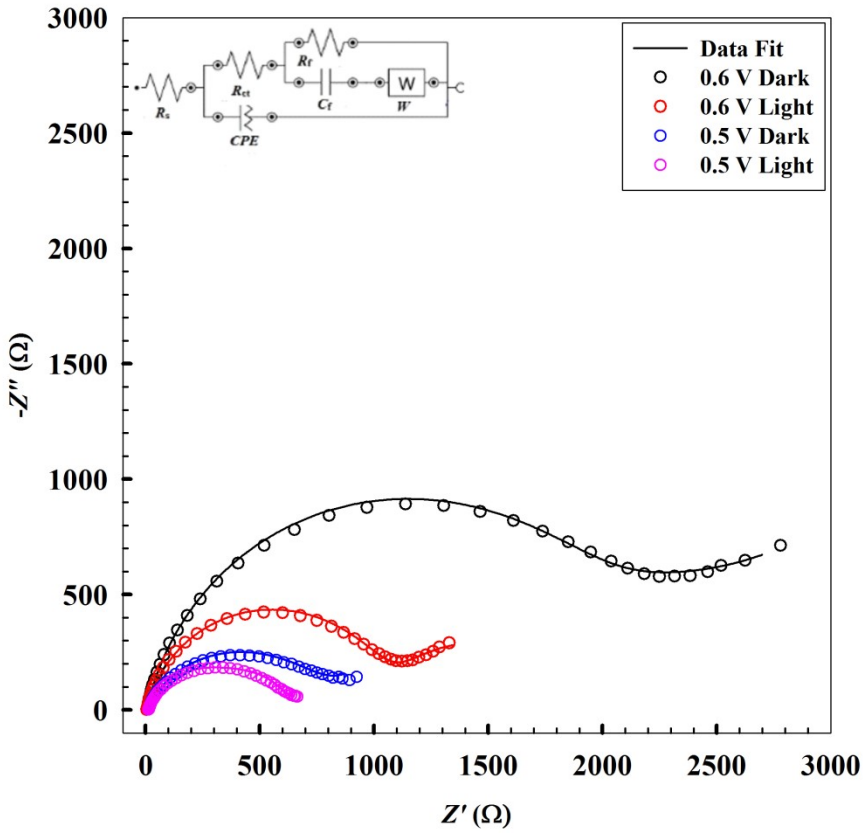


(c)

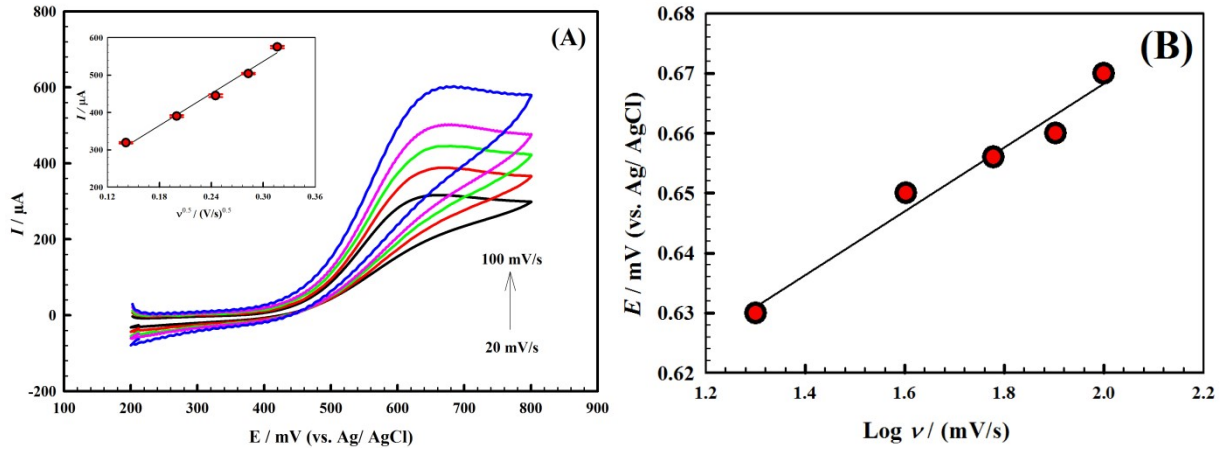
Phase	Bi_2S_3 / $BiFeO_3$
$Bi_{Occup.}$	Bi1: 0.4/Bi2: 1.0
$S_{Occup.}$	S: 0.6
$Fe_{Occup.}$	Fe: 1.0
$O_{Occup.}$	O: 3.0
$Bi_x/Bi_y/Bi_z$	1.0 / 1.0 / 0.0 (3.15×10^{-4}) 1.0 / 0.0 / 0.0 (4.46×10^{-4})
$S_x/S_y/S_z$	1.0 / 1.0 / 0.0 (5.67×10^{-4})
$B_{iso\ Bi/S}$ $B_{iso\ Bi/Fe/O}$	Bi1: 0.704 (0.314) S1: 0.889 (0.314) Bi2: 1.895 (0.131) S2: 1.895 (0.131) O: 3.755 (0.342)
R_w (%)	18.865
R_b(%)	15.236
R_{exp}(%)	19.862
χ^2	1.886

Electrode	*E*pa (mV)	*I*pa (μA)	*E*pc (mV)	*I*pc (μA)
Pt	611	247	61	80
(Pt/$BiFeO_3$-Bi_2S_3) – Dark	637	283	69	110
(Pt/$BiFeO_3$-Bi_2S_3) – Light	657	388	–	–

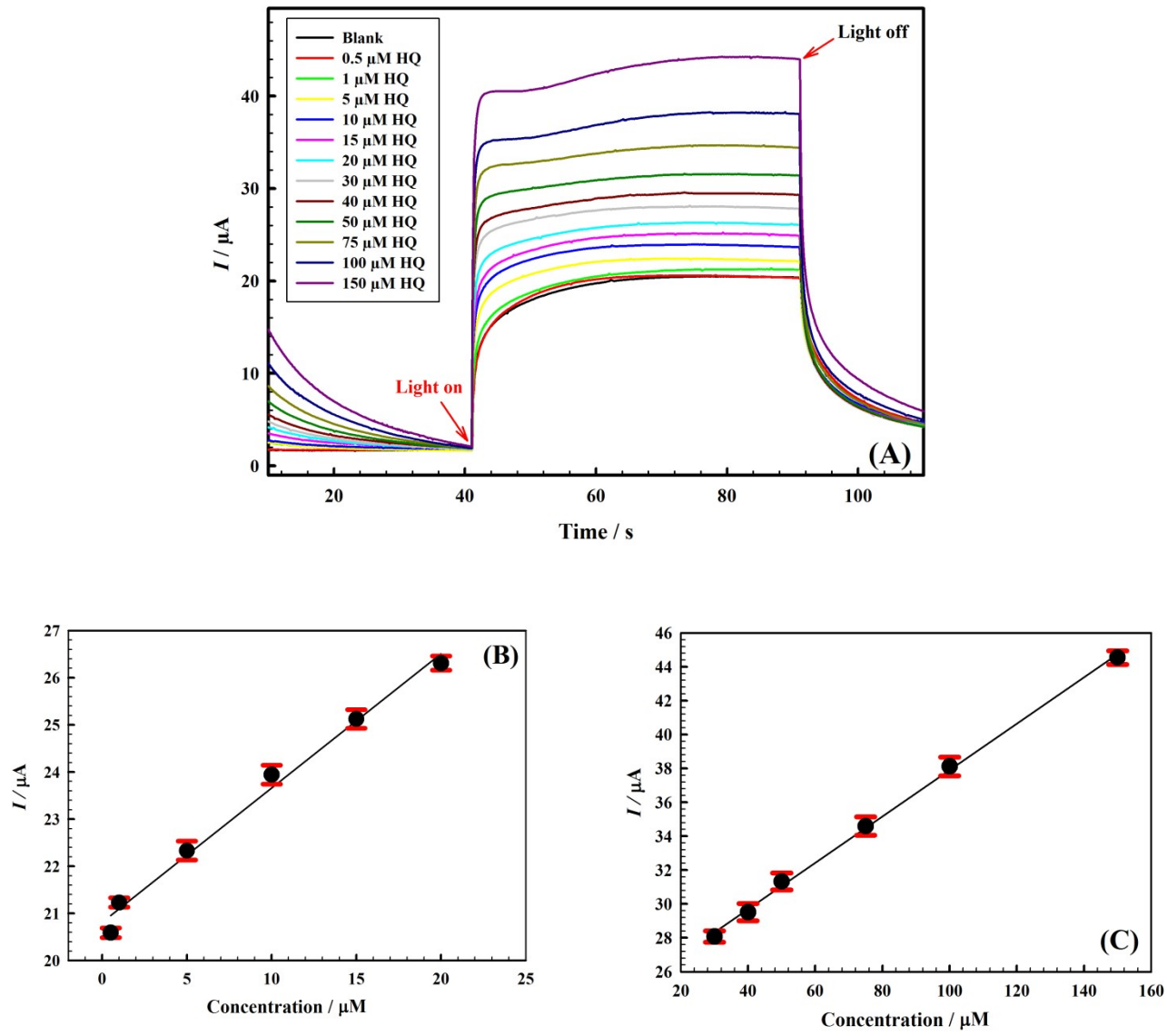
Supplement 3. Electrochemical data from the CVs of Figure 1; the scan rate: 50 $mV.s^{-1}$ in 1 mM HQ/0.1 M H_2SO_4. Light source: Optical intensity is 30 $mW.cm^{-2}$; Operating current intensity is 700 mA. All potentials are listed in reference to Ag/AgCl electrode.



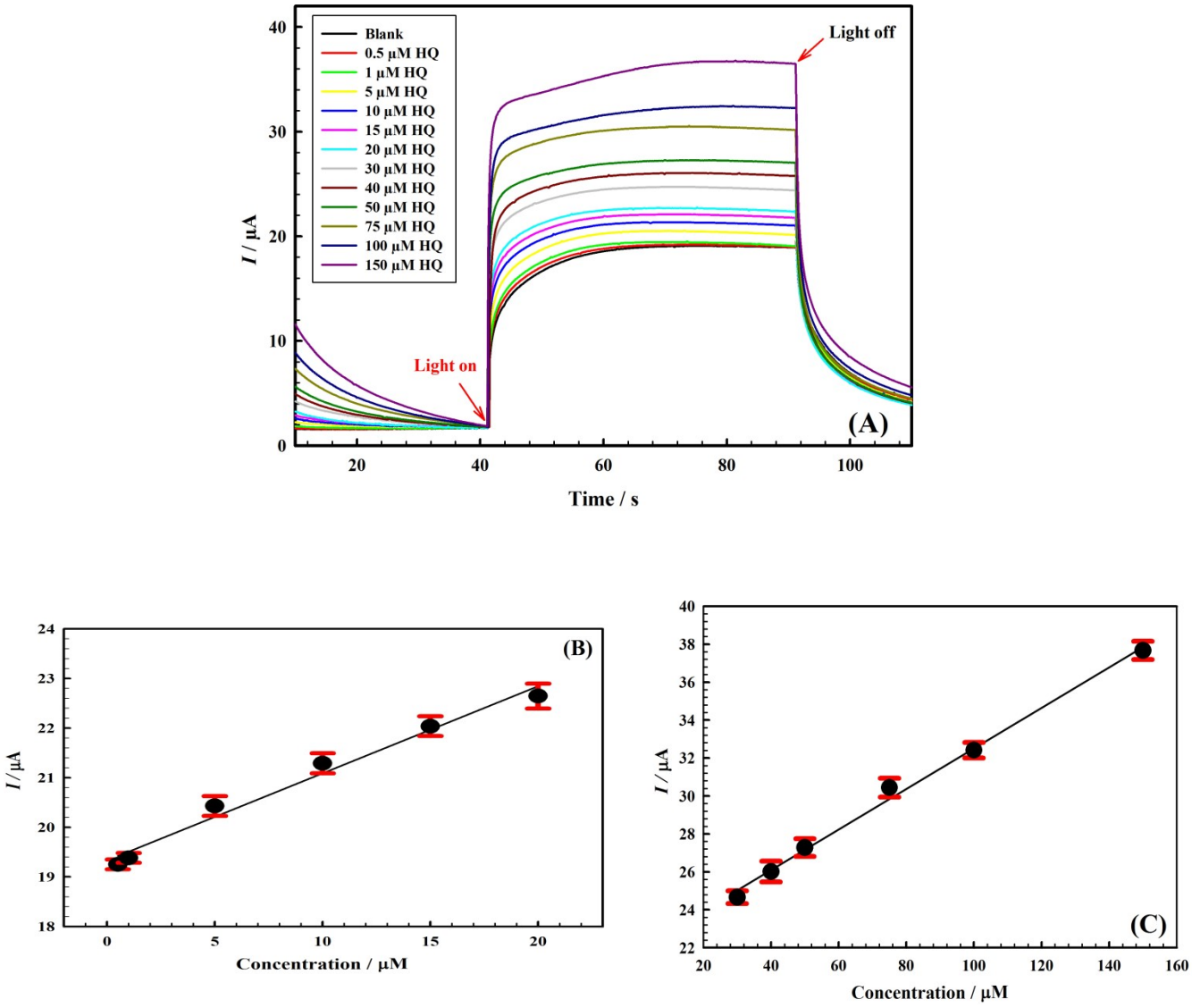
Supplement 4. Nyquist plots showing the effect of applied potential in presence and absence of light exposure



Supplement 5. **A:** Effect of increasing the scan rate on the cyclic voltammetry response of the $Bi_2S_3/BiFeO_3$ electrode in dark and under illumination (Inset: Relation between oxidation peak current of HQ and square root of scan rate); **B:** Relation between oxidation peak potential of HQ and log scan rate. Electrolyte: 0.05 M HQ in 0.1 M H_2SO_4



Supplement 6. **(A):** Amperomteric response of $Bi_2S_3/BiFeO_3$ electrode under illumination upon successive in HQ batch concentrations from 0. 5 μM to 150 μM (under illumination); **(B):** Calibration curve for HQ in the concentrations from 0.5 to 20 μM; **(C):** Calibration curve for HQ in the concentrations from 30 to 100 μM. Electrolyte: 0.1 M H_2SO_4; Applied potential 0.65 V.



Supplement 7. **(A):** Amperomteric response of $Bi_2S_3/BiFeO_3$ electrode under illumination upon successive in HQ/tap water batch concentrations from 0. 5 µM to 150 µM (under illumination); **(B):** Calibration curve for HQ in the concentrations from 0.5 to 20 µM; **(C):** Calibration curve for HQ in the concentrations from 30 to 150 µM. Electrolyte: 0.1 M H_2SO_4; Applied potential 0.65 V.

Concentration Added (μM)	Concentration Found (μM)	Standard Error	SD	RSD (%)	Recovery
10	10.252	0.126	0.178	1.779	102.516
20	19.765	0.117	0.166	0.830	98.827
50	51.109	0.554	0.784	1.568	102.217
100	99.110	0.445	0.630	0.630	99.110

Supplement 8. Recovery data of HQ in tap water as derived from results in supplement 7

Conc. Added (μM)	Conc. Found (μM)	Standard Error	SD	RSD%	Recovery
10	10.107	0.0533	0.075	0.754	101.067
20	19.440	0.280	0.396	1.980	97.200
50	50.773	0.387	0.547	1.094	101.547
100	99.780	0.110	0.156	0.156	99.780

Supplement 9. Recovery data of HQ concentrations in sewage wastewater

Conc. Added (μM)	Conc. Found (μM)	Standard Error	SD	RSD%	Recovery
10	9.696	0.152	0.215	2.150	96.962
20	20.700	0.350	0.495	2.477	103.503
50	49.434	0.283	0.400	0.800	98.870
100	100.177	0.089	0.125	0.125	100.177

Supplement 10. Recovery data of HQ in industrial wastewater dump

Electrode	Technique	Medium	LOD (µM)	Sensitivity (µA/µM)	Linear range (µM)	Applied in	Ref
ZnO/Co_3O_4/MCPE	CV	0.2 M PBS pH = 7.4	3.22	Not mentioned	10-100	Tap water	[84]
MNi/GCE	DPV	0.1 M PBS pH = 7	5.3	0.2871	(0.03-3) (3-15)	River and waste water	[85]
PPy/CB/ZnO/GCE	Amperometry	0.1 M PBS pH = 7	0.0229	0.5405 (low range) 0.3006 (high range)	(0.9-772) (772-6528)	Tap water	[86]
AuNPs/ITO	Irradiated Amperometry	0.1 M PBS pH = 7	0.1	0.0743	0.25-150	Not applied	[87]
Gr-SiNWs-Si/Pt	Irradiated Amperometry (at 0 bias)	0.1 M PBS pH = 7	0.3	0.36	10-300	Not applied	[88]
$FeC_4Pc@TiO_2$	PEC Cronoamperometry	0.1 M PBS pH = 3	0.078	-0.00151	0.2-78	River water	[89]
CSS/SPE	PEC Cronoamperometry	0.1 M $Na_2C_2O_2$ pH = 7.18	2.7	0.07	3-23	Tap water	[46]
CdS/SnS_2/CNTs	PEC Cronoamperometry	0.1 M PBS pH = 7	0.1	0.446 (low range) 0.073 (high range)	(0.2-4) (4-100)	Tap and lake water	[47]
$BiPO_4$-$GQD_{s\ 0.1}$/ITO	Signal off PEC Cronoamperometry	0.1 M PBS pH = 7	0.034	-0.0647	0.05-3	River water	[45]
$BiFeO_3$-Bi_2S_3 /Pt	PEC Cronoamperometry (Irradiation on/off)	0.1 M H_2SO_4	0.038	0.285 (low range) 0.137 (high range)	(0.5-20) (30-150)		**This work**
		Tap water with 0.1 M H_2SO_4 supporting electrolyte	0.046	0.176 (low range) 0.107 (high range)	(0.5-20) (30-150)	Tap water	
	Irradiated Amperometry	0.1 M H_2SO_4	0.00273	14.9 (low range) 0.463 (high range)	(0.025-0.5) (1-100)		
	Dark Amperometry	0.1 M H_2SO_4	0.0492	0.239	(0.1-100)		
		Sewage water with 0.1 M H_2SO_4 supporting electrolyte	0.132 (low range) 0.401 (high range)	0.150	(10-100)	Sewage water	
		Industrial dump water with 0.1 M H_2SO_4 supporting electrolyte	0.121 (low range) 0.366 (high range)	0.164	(10-100)	Industrial dump water	

CSS/SPE: Carbon spherical shell / screen printed electrode

Gr-SiNWs-Si/Pt: Graphene / silicon nanowires decorated with n-silicon/platinum(Si-Pt)

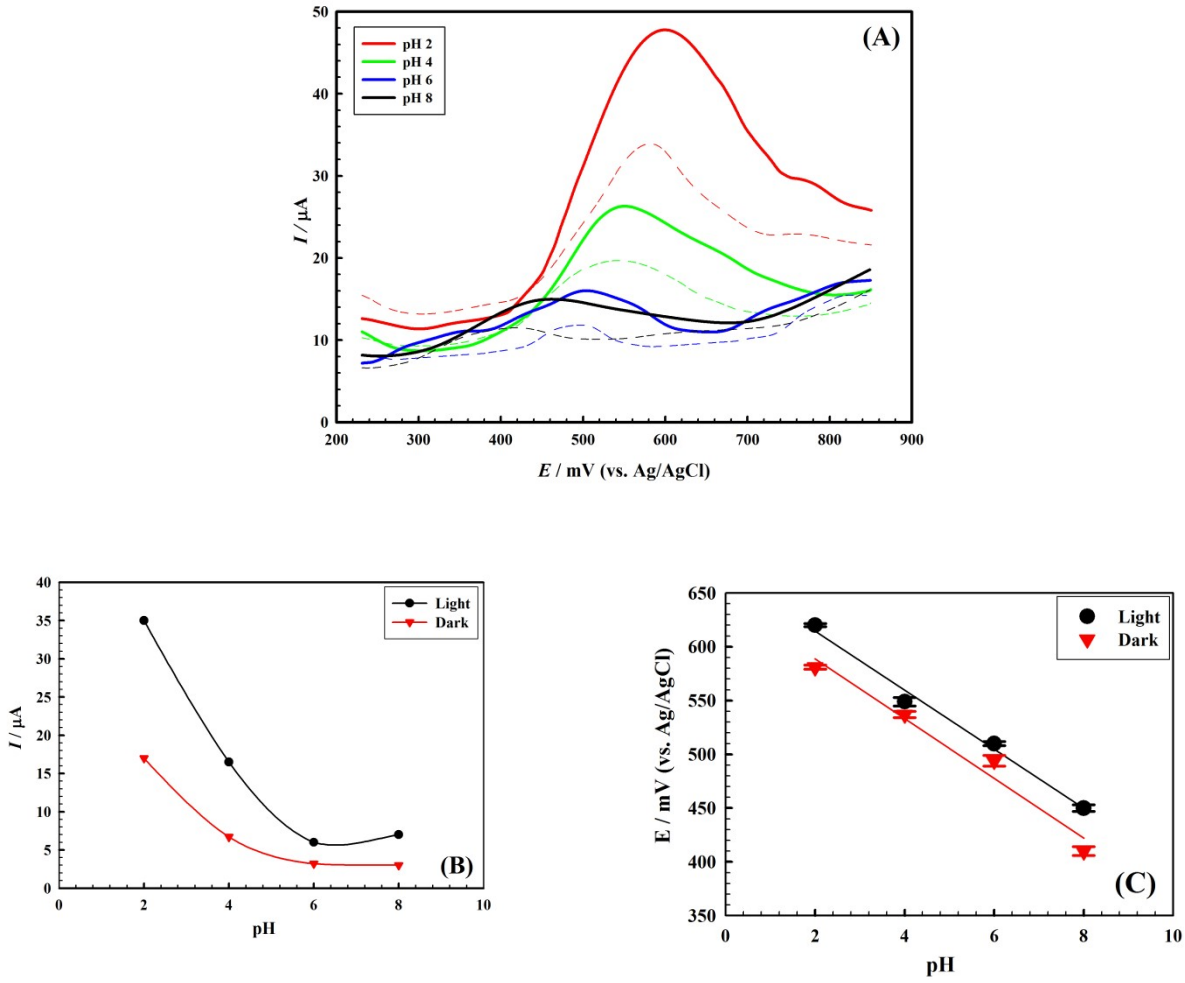
$FeC_4Pc@TiO_2$: Anatase TiO_2 nanoparticles with iron(III) tetracarboxyl phthalocyanine

MCPE: Modified carbon paste electrode

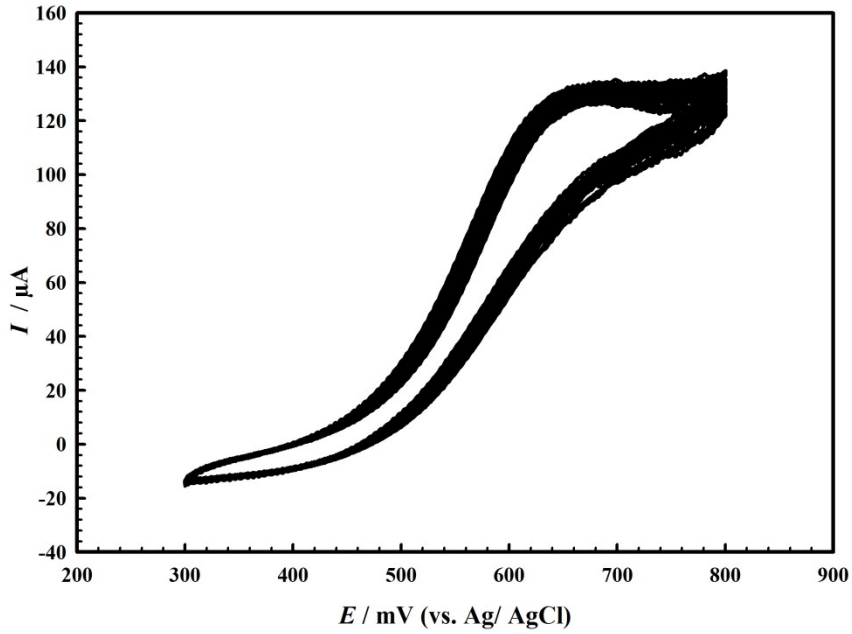
MNi/GCE: Mesoporous nickel / glassy carbon

PPy/CB/ZnO/GCE: Polypyrrole-carbon black doped ZnO / glassy carbon

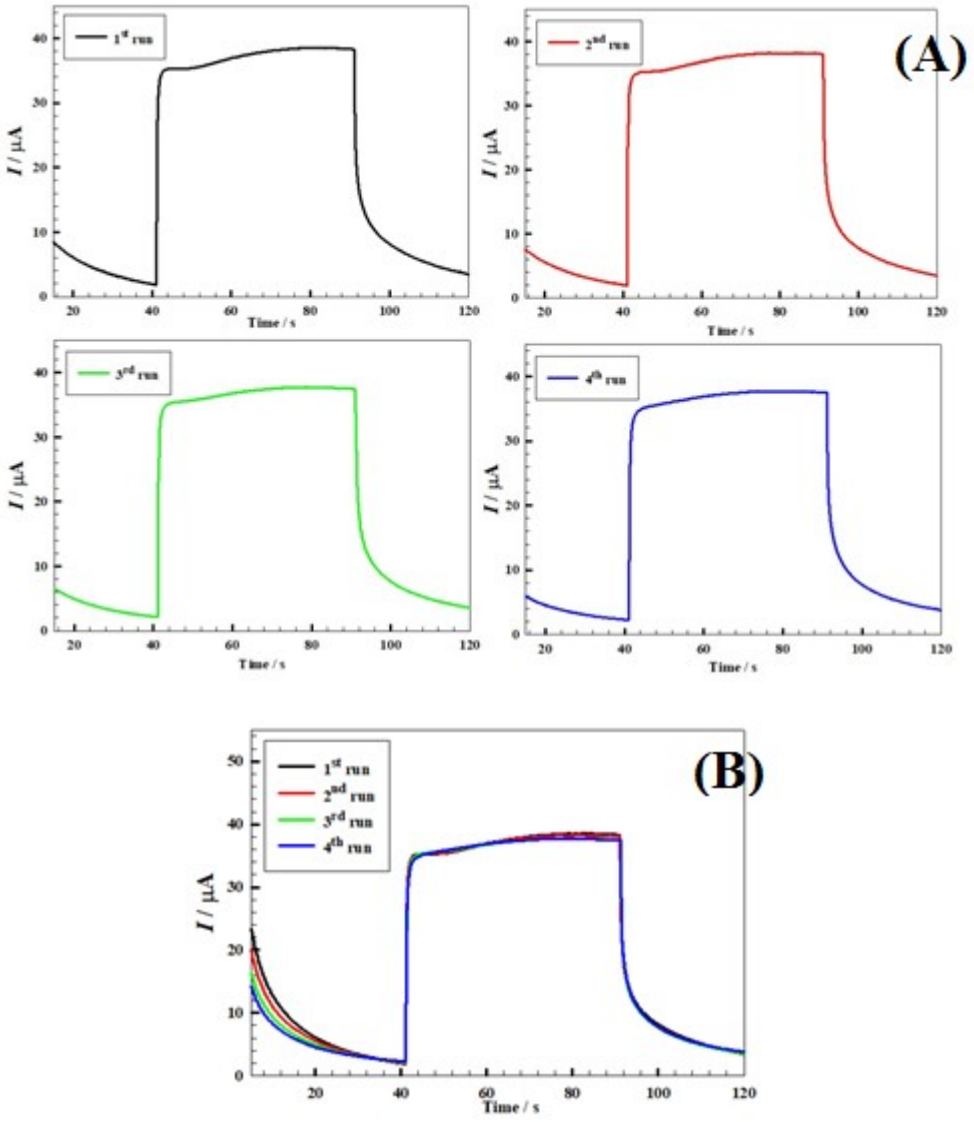
Supplement 11. Comparison of figures of merits of different sensors and PEC sensors in the previously reported literature to the present proposed sensor in this work



Supplement 12. (A): Effect of changing the pH of supporting electrolyte on the linear sweep voltammograms of the $Bi_2S_3/BiFeO_3$ electrode for the oxidation of HQ under illumination and in dark; **(B):** The relations between the PEC current under illumination and in dark at different pH values; **(C):** The relations between the oxidation potential values of HQ in different pH values.



Supplement 13. Effect of repeated cycles of the voltammograms (40 cycles) of the $Bi_2S_3/BiFeO_3$ electrode under illumination in 0.05 M HQ in 0.1 M H_2SO_4 showing the stability of the PEC catalyst



Supplement 14. Evaluation of the reusability of the PEC ($Bi_2S_3/BiFeO_3$).

(A): Chronoamperometry graphs of inter-day intervals (2 days apart), the same PEC is used in freshly prepared 100 µM HQ in 0.1 M H_2SO_4; **(B):** The overlay of the four runs shows the stability of the PEC reusability.