Supporting information

Facet-energy inspired metal oxide extended hexapod decorated with graphene quantum dots: Sensitive detection of bisphenol A in live cells

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Modification of the working electrode.

To modify the surface of glassy carbon electrode (GCE with 3 mm diameter), 0.3 and 0.05 μm alumina slurry on micro cloth pads was used for polishing and then cleaned with doubly distilled (DD) water. Then, DD water and ethanol were used to wash GCE ultrasonically for one minute and desiccated under N_2 gas purging. A homogeneous mixture of 2 mg of Cu_2O-CuO@GQDs composite in 1 mL of DD water was prepared under strong stirring. Next, 5 μl of above suspension was dispensed on GCE polished surface and dried out at ambient temperature to make Cu_2O-CuO @GQDs/GCE for assessment of electroanalytical performances. The supplementary control materials were also used to modify GCE using the same practice.

Table S1 Elemental composition with textural properties of a series of electrocatalysts

Catalyst	Cu_2O (mg)	GQDs used (mg)	BET (m^2 g^{-1})
Cu_2O NSs	20	0	27.21
Cu_2O-CuO EHPs	20	0	24.69
Cu_2O-CuO @GQDs-I	20	5	50.78
Cu_2O-CuO @GQDs-II	20	7	63.82
Cu_2O-CuO @GQDs-III	20	9	54.11

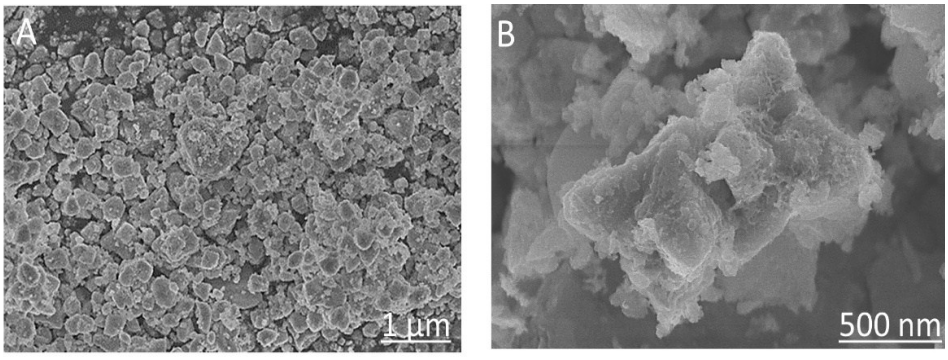

Fig. S1. (A and B) high and low magnification SEM images of Cu_2O-CuO@GQDs (III)

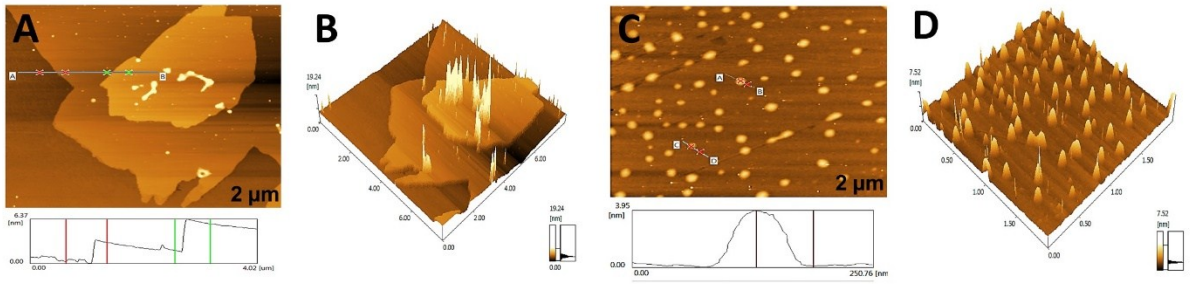

Fig. S2 (A-D) AFM images for size and width study of Cu_2O-CuO@GQDs EHPs and GQDs along with corresponding height profile and 3D images with a scan scale bar of 2×2µm.

Randles–Sevcik equation [1, 2] have been used to calculate the electrochemically active surface area of different electrodes

$$Ip = (2.69 \times 10^5) n^{3/2} AC^* D^{1/2} v^{1/2} \quad (1)$$

Where n A, D, C, v and is electron transfer number, area of the electrode, diffusion coefficient, probe molecules concentration, and scan rate respectively. Now, D is 7.60 (±0.02)10^{-6} cm^2 s^{-1}, the concentration of $[Fe(CN)_6]^{3-/4-}$ is 2.0×10^{-3} M and the estimated electrochemical active surface area of Cu2O-CuO@GQDs/GCE (0.138 cm^2) is greater than GQDs/GCE (0.124 cm^2), Cu2O EHPs/GCE (0.100 cm^2) and bare GCE (0.0712 cm^2) respectively. The enhanced surface area of Cu2O-CuO@GQDs/GCE confirms the synergy effect of Cu2O EHPs and GQDs to offer an active podium in smoothing electron transport between electrodes and the target solution.

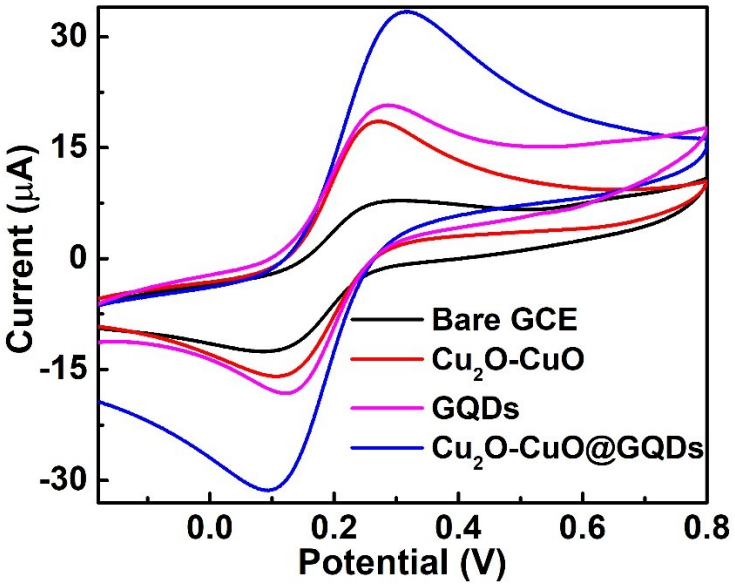

Fig. S3. CV curves of bare GCE, Cu_2O-CuO, GQDs, and Cu_2O-CuO@GQDs modified electron in 0.1 M KCl solution with redox probe of (1:1), $[Fe(CN)_6]^{3-/4-}$

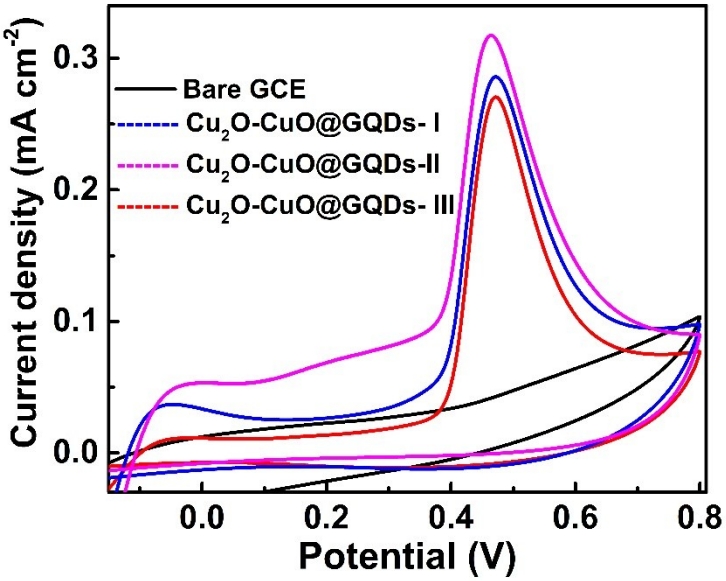

Fig. S4. CV curves of different modified electrodes in the presence of 0.1 M BPA solution

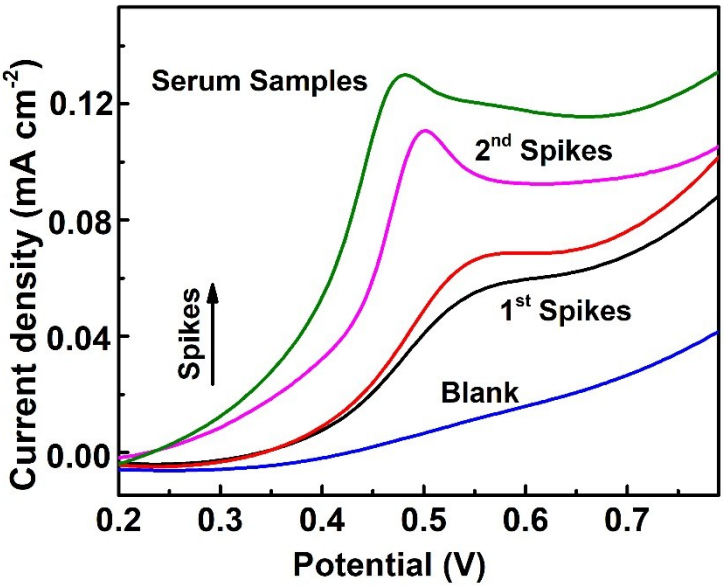

Fig. S5. DPV responses to human serum samples for BPA detection, 1st spikes correspond to 200 nM concentration spikes of BPA in breast cancer serum (black line) and cervical cancer serum (red line), 2nd spikes with 500 nM concentration spike of BPA in breast cancer serum (pink line) and cervical cancer serum (green line).

Table S2. Evaluation of various sensing systems for electrochemical detection of BPA based on nanomaterials stated in the literature.

Electrode Material	Technique	LOD (nM)	Sensitivity ($\mu A\ mM^{-1}\ cm^{-2}$)	Linear Range	Ref.
Gr-AgCuNP/AuE	LSV	110	-	0.1-100 µM	[3]
AuNP/MWCNT/GCE	DPV	4.3	137	0.01-0.7 µM	[4]
Na-doped WO_3/CPE	DPV	28	310	0.0810–22.5 µM	[5]
Tyrosinase/poly(thionine)/GCE	Amperometry	230	-	0.4-50 µM	[6]
Tyr-MWCNT/PE	Amperometry	100	-	1-16 µM	[7]
ILs-LDH/GCE	DPV	4.6	-	0.01-3 µM	[8]
eMIP/e-NIP/SPCE	CV	0.06	-	-	[9]
MIP/GCE	DPV	0.02	-	1 µM- 400 µM	[10]
ZrO2/ZSM-5/GCE	DPV	3	-	6 nM -600 µM	[11]
Cu_2O-CuO@GQDs EHPs	DPV	1	636	2 nM-11 mM	This work

We have investigated the various key features for purposed electrochemical sensing system such as sensitivity, the limit of detection and linear range. The modified Cu_2O-CuO@GQDs/GCE obtained the lowest real detection of 1 nM limit in non-enzymatic sensors employed for BPA oxidation. The excellent sensitivity (636 $\mu A\ mM^{-1}\ cm^{-2}$) modified by present sensors proved better against various sensors reported previously. In the case of selectivity, the modified GCE exhibited outstanding anti-interference aptitude against various potential biomolecules that could possibly co-exist with BPA in blood. The amperometric response records displayed the linear increase in peak current values with increasing BPA concentration range from (2 nM to 11 mM) which is even superior to any other electrochemical system reported previously.

Table S3 Comparison of the proposed biosensor with standard HPLC method to detect BPA in real environmental samples and biological fluids.

Method	Sample	Spiked[c] (μM)	Detected[d] (μM)	RSD	Recovery (%)
ECS[a]	Mineral Water	0	0	0	--
		0.2	0.23 ± 0.22	3.21	115
		0.5	0.52 ± 0.13	0.82	104
	Tap Water	0	0	0	--
		0.2	0.19 ± 0.14	2.22	95
		0.5	0.52 ± 0.16	1.83	104
	Healthy Serum	0	0	0	--
		0.2	0.19 ± 0.12	2.79	95
		0.5	0.53 ± 0.15	2.77	106
	Breast Cancer	0	0	0	--
		0.2	0.22 ± 0.11	1.31	110
		0.5	0.47 ± 0.22	1.28	94
	Cervical	0	0	0	--

	Cancer	0.2	0.21 ± 0.13	0.81	105
		0.5	0.55 ± 0.29	0.27	111
	Mineral Water	0	0	0	--
		0.2	0.21 ± 0.13	1.21	105
		0.5	0.56 ± 0.11	0.75	112
	Tap Water	0	0	0	--
		0.2	0.24 ± 0.24	1.35	120
		0.5	0.54 ± 0.19	0.85	108
HPLC[b]	Healthy Serum	0	0	0	--
		0.2	0.21 ± 0.11	0.31	105
		0.5	0.51 ± 0.22	0.56	102
	Breast Cancer	0	0	0	--
		0.2	0.24 ± 0.13	1.32	120
		0.5	0.52 ± 0.29	0.95	110
	Cervical Cancer	0	0	0	--
		0.2	0.22 ± 0.12	0.44	110
		0.5	0.51 ± 0.15	0.38	102

[a]The electrochemical sensor. [b]High performance liquid chromatography (HPLC-1100, Agilent Inc.) with a reversed-phase column (Hypersil-ODS), λ at 254 nm and detector was UWD. A mixture of water and methanol (30:70) was used as mobile phase and 0.4 mL/minute flow rate. [c]Diluted from 50 μM stock solution at suitable serial dilutions with 0.1 M PBS as a supporting electrolyte. [d]An average value of five analogous measurements (n=5) with RSD ≤ 4%.

References:

1 A. Aziz, M. Asif, M. Azeem, G. Ashraf, Z. Wang, F. Xiao and H. Liu, *Anal. Chim. Acta*, 2019, 1047, 197-207.

2 M. Asif, A. Aziz, H. Wang, Z. Wang, W. Wang, M. Ajmal, F. Xiao, X. Chen and H. Liu, *Microchim. Acta*, 2019, 186, 61.

3 F. Pogacean, A. R. Biris, C. Socaci, M. Coros, L. Magerusan, M.-C. Rosu, M. D. Lazar, G. Borodi and S. Pruneanu, *Nanotechnology*, 2016, 27, 484001.

4 N. B. Messaoud, M. E. Ghica, C. Dridi, M. B. Ali and C. M. Brett, *Sens Actuat. B: Chemical*, 2017, 253, 513-522.

5 Y. Zhou, L. Yang, S. Li and Y. Dang, *Sens Actuat. B: Chemical*, 2017, 245, 238-246.

6 E. Dempsey, D. Diamond and A. Collier, *Biosens. Bioelectron.* 2004, 20, 367-377.

7 D. G. Mita, A. Attanasio, F. Arduini, N. Diano, V. Grano, U. Bencivenga, S. Rossi, A. Amine and D. Moscone, *Biosens. Bioelectron.* 2007, 23, 60-65.

8 T. Zhan, Y. Song, X. Li and W. Hou, *Mater. Sci. Engineering: C*, 2016, 64, 354-361.

9 V. M. Ekomo, C. Branger, R. Bikanga, A. M. Florea, G. Istamboulie, C. Calas-Blanchard, T. Noguer, A. Sarbu and H. Brisset, *Biosens. Bioelectron.* 2018, 112, 156-161.

10 T. S. Anirudhan, V. S. Athira and V. Chithra Sekhar, *Polymer*, 2018, 146, 312-320.

11 B. Kaur, B. Satpati and R. Srivastava, *RSC Advances*, 2016, 6, 65736-65746.