Hybridized sulfated-carboxymethyl cellulose/MWNT nanocomposite as high-selective electrochemical probe for trace detection of arsenic in Real Environmental Samples

Youssef O. Al-Ghamdi[a,*], Mahjoub Jabli[a], Mona H.Alhalafi[a], Ajahar Khan[b,**], Khalid A. Alamry[c,***]

[a]Department of Chemistry, College of Science Al-Zulfi, Majmaah University, Al-Majmaah 11952, Saudi Arabia

[b]Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

[c]Department of Food and Nutrition, Bionanocomposite Research Center, Kyung Hee University, 26 Kyungheedae-ro, Dongdaemun-gu, Seoul, South Korea

Corresponding Author.

****Corresponding Author.***

*****Corresponding Author.***

E-mail addresses: yo.alghamdi@mu.edu.sa (Youssef.O.Al-Ghamdi), arkhan.029@gmail.com (Ajahar Khan), kaalamri@kau.edu.sa (K.A.Alamry)

Supporting Information

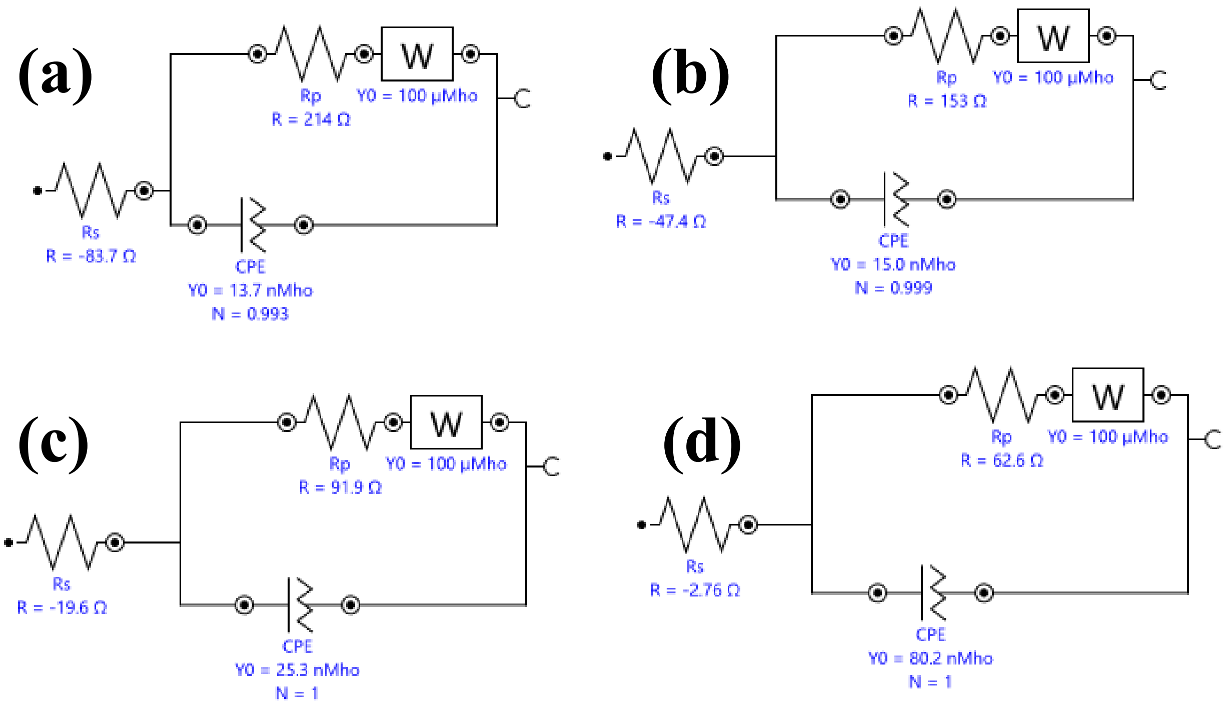

Fig. S1 Equivalent circuit models for (a) blank, (b) CMC-S@GCE, (c) CMC-S/MWMNT^{1}@GCE, and (d) CMC-S/MWMNT^{2}@GCE showing charge transfer resistance (Rp=Rct), solution resistance (Rs), W-Warburg impedance, and CPE-constant phase element.

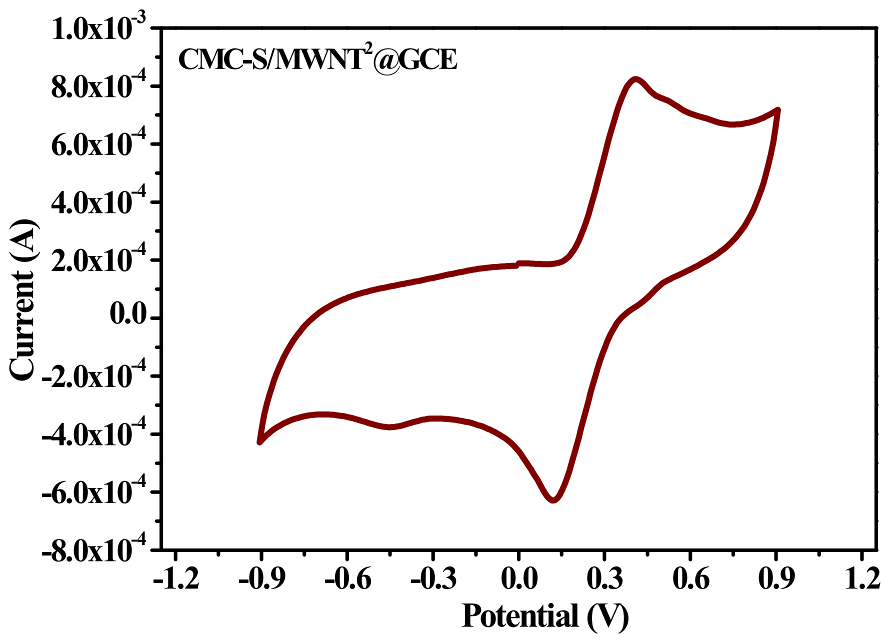

Fig. S2. CV hysteresis curve of CMC-S/MWNT²@GCE in the presence of $[Fe(CN)_6]^{3-/4-}$ (0.5 mM)couple/ KCl(0.1 M) at scan rate=100 mV s^{-1}.

S3.1 Limit of Detection (LOD) of the CMC-S/MWNT²@GCE probe

$$LOD = \frac{3 \times SD}{b}$$

where S represents the standard deviation of the blank response, and b represents the Slope of the calibration plot.

SD= 1.8319×10^{-8}

b = 2.21×10^{-6}

LOD= $0.0248\pm4.3\times10^{-4}$ nM

S3.2 Limit of Quantification (LOQ) of the CMC-S/MWNT²@GCE probe

$$LOQ = \frac{10 \times SD}{b}$$

LOQ= 10 ×1.8319×10^{-8}/ 2.21×10^{-6} nM

LOQ= 0.0828±1.5×10^{-4} nM

S3.3 Sensitivity of the CMC-S/MWNT^2@GCE probe

$$Sensitivity = \frac{Slope\ of\ calibration\ plot}{Surface\ area\ of\ GCE}$$

Slope of calibration plot = 2.21×10^{-6} AnM^{-1}

Surface area of electrode = 0.0316 cm^{-2}

Calculated sensitivity = 69.93±7.9×10^{-2} $\mu AnM^{-1}cm^{-2}$

S4: Statistical Analysis

S4.1 Interferents Effect

Stripping peak current response (A): 0.000346272, 0.00033889, 0.000329784, 0.000328084, 0.000318594, 0.00031806, 0.000318098, 0.00031544, 0.000314143, 0.000310162, and 0.000310101.

Mean= 0.00032251

Standard deviation= 2.04029×10^{-5}

$$Relative\ standard\ deviation\ \%\ (RSD) = \frac{Standard\ deviation}{X\ (mean\ value)} \times 100$$

RSD(%)= 6.32

S4.2 Stability over a period of 28 days

Stripping peak current response (A): 0.000366997, 0.000346273, 0.000337889, 0.000329802, and 0.000310203.

Mean= 0.00033823

Standard deviation = 2.091×10^{-5}

RSD(%) = 6.18

Drop of current (%) = 15.48

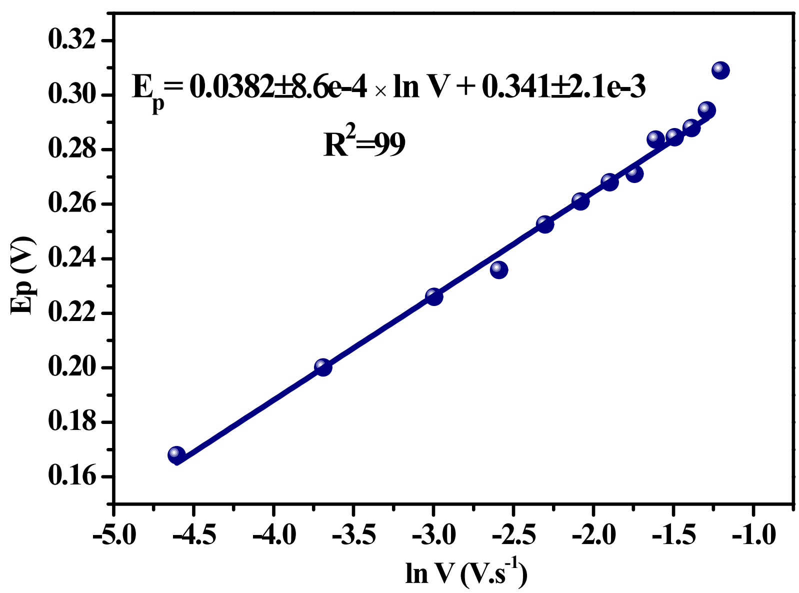

Fig. S3. Plot of peak potential (Ep) against the logarithm of scan rate (ln ν) for 0.1 mM As (III) at CMC-S/MWNT2@-GCE in 0.1 M PBS of pH 5.7.

S5. Ampirometric response

Response time was examined in a solution of 0.1 M PBS 5.7, including 0.1 mM As(III), to show the accumulation time. A quick response time of CMC-S/MWNT^2@-GCE was found (**Fig. S4**), proving that steady-state current was reached in less than 20 s. The amount of time that it takes to reach steady-state current can be used to describe response time. Therefore, the proposed modified GCE is suggested to be useful, particularly for in-situ analysis.

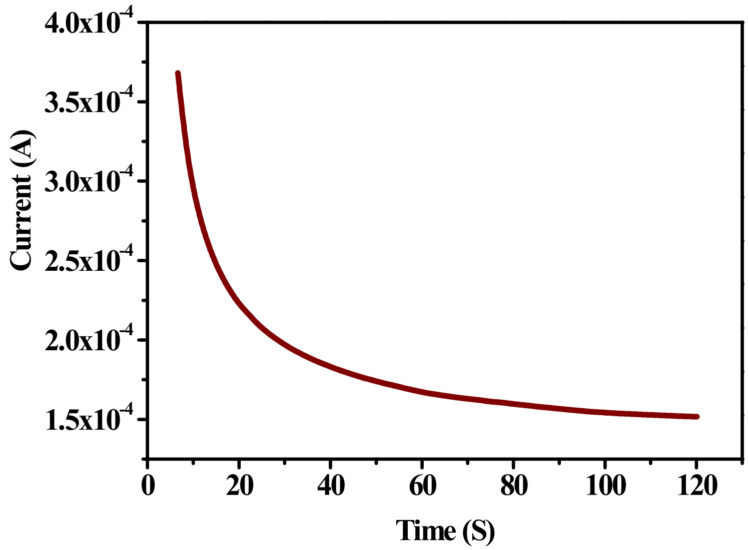

Fig. S4. Response time CMC-S/MWNT^2@-GCE in the presence of As(III).

S6. CV response at different concentration

The stripping current response of CMC-S/MWNT^2@-GCE towards As (III) in PBS was also investigated by recording CV response between ±0.9 V at 0.1 Vs^{-1} (**Fig S5)**. The CMC-S/MWNT^2@-GCE shows a high response towards As(III). I-V hysteresis voltammograms result suggested that the peak current value escalated with the As(III) concentration increase.

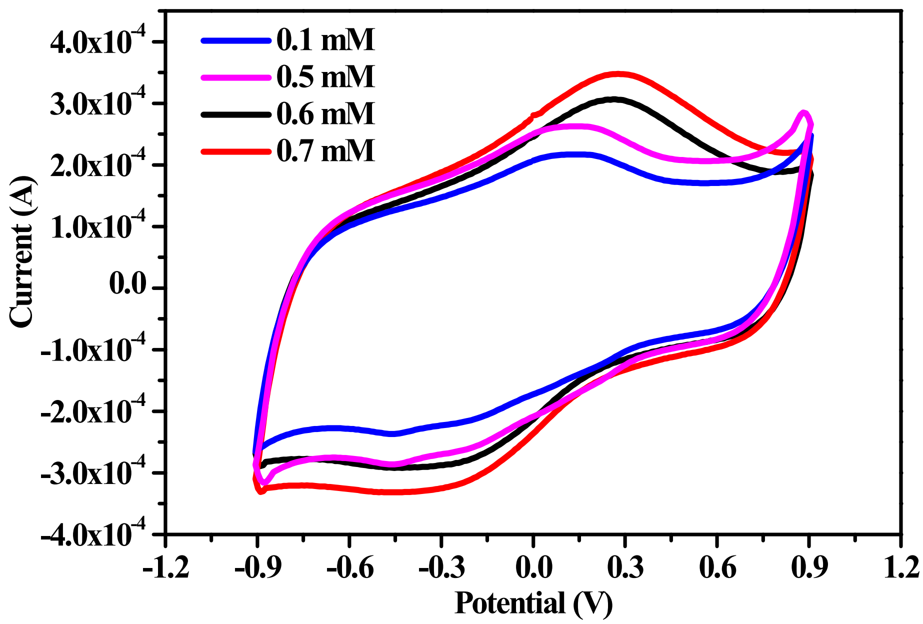

Fig. S5. CV response of CMC-S/MWNT^2@-GCE in the presence of 0.1, 0.5, 0.6, 0.7 mM As(III).

Table S1. Comparison of electrochemical sensing performance of CMC-S/MWNT^2@GCE with various previously reported modified electrodes toward As(III)

S.No.	Modified GCE	Analytical technique	LOD (nM)	LDR (nM)	Ref
1	(Fe_3O_4-Ag/Au hollow-nanoshell-rGO nanosheet	CV	0.05	0.50-101.09	[1]
2	Pt-nanoparticle/GCE	SWASV	28	100-500	[2]
3	Au-nanoparticles/GCE	SWASV	2.0	130-16000.1	[3]
4	Amino-functionalized graphene oxide NH_2-GO	SWASV	8.97	5.05-50.54	[4]
5	Reduced graphene oxide-magnetic nanocomposite	DPASV	0.51	10.1-1516.4	[5]

	($rGO-Fe_3O_4$)				
6	Co nanoparticles and reduced graphene oxide (CO-rGO)	SWASV	1.56	0.51-252.73	[6]
7	Reduced graphene oxide /Fe_3O_4 composite	SWASV	1.51	10.1-101.09	[7]
8	Silver nanoparticle-graphene oxide (AgNPs-GO)	SWASV	0.24	13.33-375.19	[8]
9	Graphene-platinum nanocomposite (Gr-nPt)	SWASV	10-100	1.1	[9]
10	Au-reduced graphene oxide (Au/rGO)	ASLSV	2.31–153.95	0.76	[10]
11	Poly(3,4-ethylenedioxythiophene) /Pd nanoparticles/GCE	DPASV	7.0	10-160	[11]
12	CMC-S/MWNT^2@GCE	DPV	0.024	0.05-90	This work

Differential pulse anodic stripping voltammetry (DPASV); square wave anodic stripping voltammeter (SWASV); anodic stripping linear sweep voltammetry (ASLSV)

References

1 Z. Zhao, C. Li and H. Wu, *Microchim. Acta*, 2019, **186**, 226.

2 X. Dai and R. G. Compton, *Analyst*, 2006, **131**, 516.

3 A. O. Idris, N. Mabuba and O. A. Arotiba, *Int. J. Electrochem. Sci.*, 2017, **12**, 10–21.

4 M. Yang, T.-J. Jiang, Y. Wang, J.-H. Liu, L.-N. Li, X. Chen and X.-J. Huang, *Sensors Actuators B Chem.*, 2017, **245**, 230–237.

5 A. B. Chimezie, R. Hajian, N. A. Yusof, P. M. Woi and N. Shams, *J. Electroanal. Chem.*, 2017, **796**, 33–42.

6 A. Jimana, *Int. J. Electrochem. Sci.*, 2018, 10127–10140.

7 Z. Xie, J. Xu, F. Xie and S. Xiong, *Anal. Sci.*, 2016, **32**, 1053–1058.

8 R. A. Dar, N. G. Khare, D. P. Cole, S. P. Karna and A. K. Srivastava, *RSC Adv.*, 2014, **4**, 14432–14440.

9 R. Kempegowda, D. Antony and P. Malingappa, *Int. J. Smart Nano Mater.*, 2014, **5**, 17–32.

10 W.-W. Li, F.-Y. Kong, J.-Y. Wang, Z.-D. Chen, H.-L. Fang and W. Wang, *Electrochim. Acta*, 2015, **157**, 183–190.

11 S. Dash and N. Munichandraiah, *Analyst*, 2014, **139**, 1789–1795.