

Supporting information

Highly sensitive enzyme-free amperometric sensing of hydrogen peroxide in real samples based on Co_3O_4 nanocolumn structures

Palanisamy Kannan,^{a*} Thandavarayan Maiyalagan,^b Alagarsamy Pandikumar,^c Longhua Guo,^{a,d*} Pitchaimani Veerakumar,^e and Perumal Rameshkumar^f

^a College of Biological, Chemical Sciences and Engineering, Jiaying University, Jiaying, 314001, PR China.

^b SRM Research Institute, Department of Chemistry, SRM University, Kattankulathur – 603203, Chennai, India.

^c Electrochemical Materials Science and Functional Materials Division, CSIR-Central Electrochemical Research Institute, Karaikudi, 630003, India.

^d Institute of Nanomedicine and Nanobiosensing; MOE Key laboratory for analytical science of food safety and biology; Fujian Provincial Key Laboratory of Analysis and Detection Technology for Food Safety; College of Chemistry, Fuzhou University, Fuzhou, 350116, PR China.

^e Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, 10617 Taiwan.

^f Department of Chemistry, Kalasalingam University (Kalasalingam Academy of Research and Education), Krishnankoil, India.

* Corresponding Authors: ktpkannan@mail.zjxu.edu.cn (Kannan); Tel: +86-19857386580; Fax: +86-573 83643264; guolh@fzu.edu.cn (Guo); Tel: +86 15280077696, Fax: +86 591 22866135.

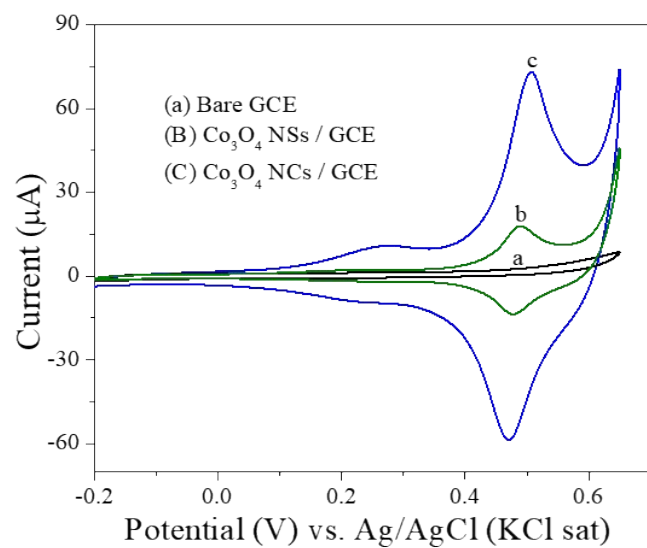


Figure S1. CVs obtained at bare GCE (a), Co_3O_4 NSs GCE (b), and Co_3O_4 NCs GCE (c) in Ar saturated 0.1 M NaOH aqueous solution at a scan rate of 50 mV s^{-1} .

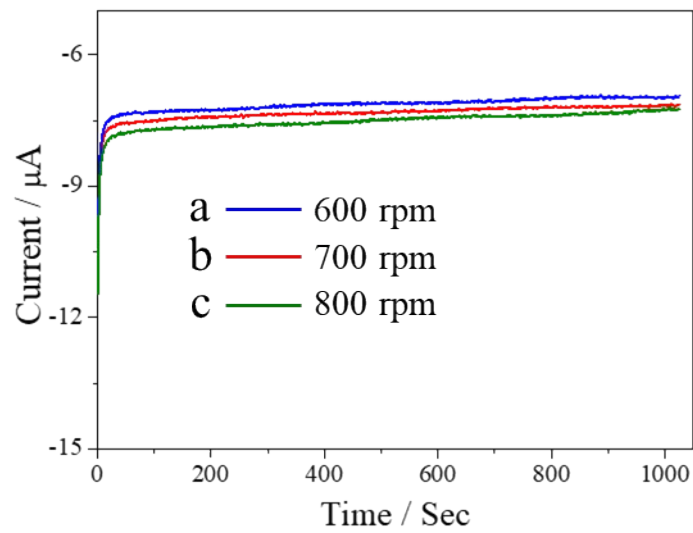


Figure S2. Optimization of stirring rate for amperometric detection of H_2O_2 using Co_3O_4 NCs / GCE in 0.1 M NaOH solution.

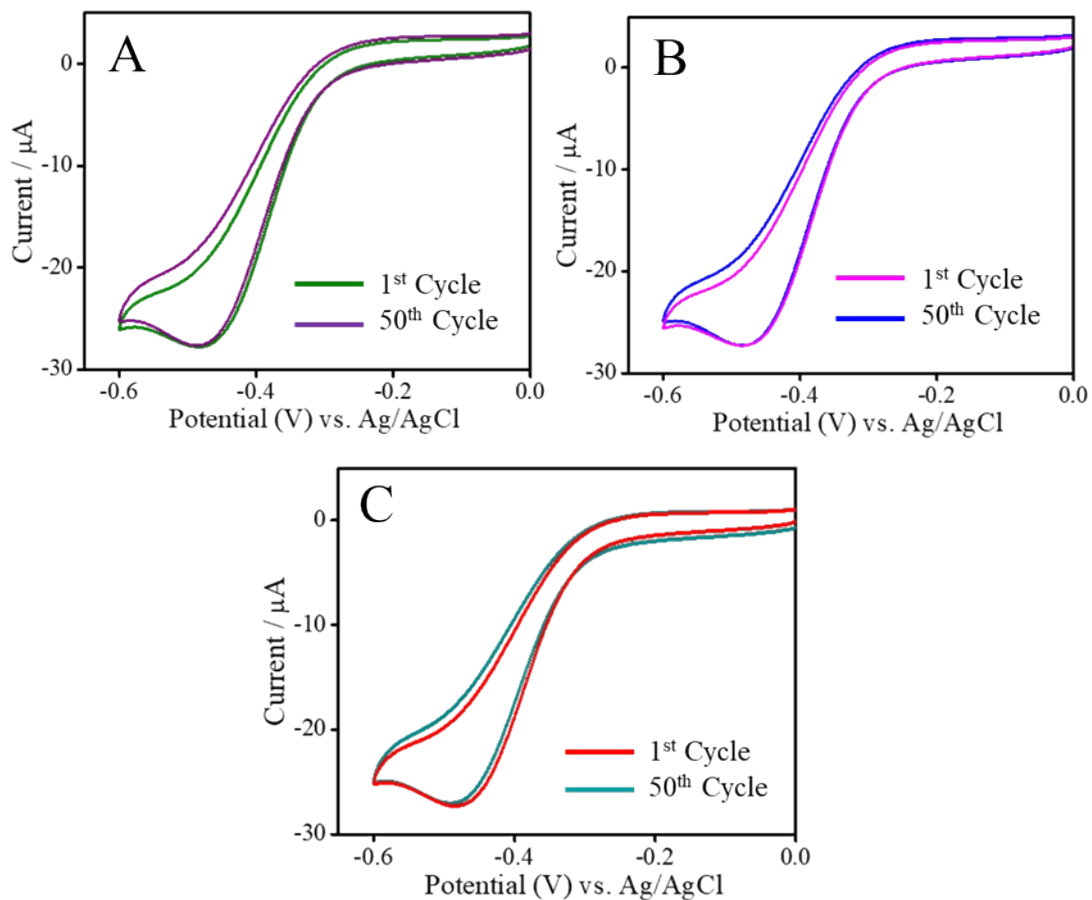


Figure S3: Reproducibility analysis of H_2O_2 electroreduction at three-different batch Co_3O_4 NCs electrodes.

Table S1. Comparison of the detection limit of the proposed non-enzymatic H₂O₂ sensor vs. other Co₃O₄ or Co₃O₄ based composite nanomaterials.

S. No	Electrodes	Detection Techniques	Detection limit (μM)	References
1	Co ₃ O ₄ nanoparticles	Amperometry	4.40	[1]
2	Vertically aligned Co ₃ O ₄ nanowalls	Amperometry	2.80	[2]
3	Co ₃ O ₄ nanoporous thin film	Amperometry	200.0	[3]
4	Nafion/exfoliated graphene oxide–Co ₃ O ₄ nanocomposite	Amperometry	0.30	[4]
5	Co ₃ O ₄ nanoparticles on mesoporous carbon nanofibers	Amperometry	0.50	[5]
6	Co ₃ O ₄ nanoparticles and multi-walled carbon nanotubes	Amperometry	0.74	[6]
7	Binary Mn-Co Oxides decorated graphene nanocomposites	Amperometry	0.80	[7]
8	Co ₃ O ₄ nanoparticles anchored to porous silicon	Amperometry	0.80	[8]
9	Interconnected 1D Co ₃ O ₄ nanowires on reduced graphene oxide	Amperometry	2.40	[9]
10	Co ₃ O ₄ Nanoparticles anchored to multi-walled carbon nanotubes	Amperometry	2.46	[10]
11	Hexagonal CoAl-layered double hydroxide nanoshales/carbon nanotubes composite	Amperometry	10.0	[11]
12	Co ₃ O ₄ nanoparticles anchored on nitrogen-doped reduced graphene oxide	Amperometry	100.0	[12]
13	CoFe ₂ O ₄ hollow nanostructures	Amperometry	2.50	[13]
14	Co₃O₄ nanocolumns arrays	Amperometry	0.28	This work

Table S2. Determination of H₂O₂ in 8: 2 ratio of river water + 0.1M NaOH and antiseptic solution + 0.1M NaOH based on the Co₃O₄ NCs arrays electrode.

River Water Sample	Added (mM)	Found (mM)	RSD (%) ^a	Recovery (%)
1	1	0.96	2.51	96.00
2	2	1.93	2.23	96.50
3	3	2.92	2.06	97.33
4	5	4.91	1.98	98.20
5	7	6.89	2.01	98.42
Antiseptic Sample	Added (mM)	Found (mM)	RSD (%)	Recovery (%)
1	1	0.97	2.63	97.00
2	2	1.88	2.91	94.00
3	3	2.81	3.06	93.00
4	5	4.74	2.84	94.80
5	7	6.68	2.72	95.42

^a Relative standard deviation was obtained from three independent measurements.

References

- [1] J. Mu, L. Zhang, M. Zhao, Y. Wang, Co₃O₄ nanoparticles as an efficient catalase mimic: Properties, mechanism and its electrocatalytic sensing application for hydrogen peroxide, *Journal of Molecular Catalysis A: Chemical*, 378, (2013) 30-37.
- [2] W. Jia, M. Guo, Z. Zheng, T. Yu, E.G. Rodriguez, Y. Wang, Y. Lei, Electrocatalytic oxidation and reduction of H₂O₂ on vertically aligned Co₃O₄ nanowalls electrode: Toward H₂O₂ detection, *Journal of Electroanalytical Chemistry*, 625, (2009) 27-32.
- [3] G.S. Cao, R. Wang, P. Wang, X. Li, Y. Wang, G. Wang, J. Li, Electrochemical Co₃O₄ nanoporous thin films sensor for hydrogen peroxide detection, *Nano*, 09, (2014) 1450047.
- [4] A.A. Ensafi, M. Jafari-Asl, B. Rezaei, (2013) A novel enzyme-free amperometric sensor for hydrogen peroxide based on Nafion/exfoliated graphene oxide-Co₃O₄ nanocomposite, *Talanta*, 103, 322-329.
- [5] Y. Ni, Y. Liao, M. Zheng, S. Shao, In-situ growth of Co₃O₄ nanoparticles on mesoporous carbon nanofibers: a new nanocomposite for nonenzymatic amperometric sensing of H₂O₂, *Microchimica Acta*, 184, (2017) 3689-3695.
- [6] C. Kaçar, B. Dalkiran, P.E. Erden, E. Kiliç, An amperometric hydrogen peroxide biosensor based on Co₃O₄ nanoparticles and multiwalled carbon nanotube modified glassy carbon electrode, *Applied Surface Science*, 311, (2014) 139-146.
- [7] Su-Juan Li, Yun Xing, Hong-Yuan Yang, Jia-Yan Huang, Wen-Tian Wang, R.-T. Liu, Electrochemical Synthesis of a Binary Mn-Co Oxides Decorated Graphene Nanocomposites for Application in Nonenzymatic H₂O₂ Sensing, *International Journal of Electrochemical Science*, 12, (2017) 6566-6576.
- [8] A. Farzad, F. Khalil, E. Habibollah, A.M. Mokhtari, M. Rahim, Cobalt nanoparticles anchored to porous silicon as a novel modifier for the construction of enzyme-free hydrogen peroxide screen-printed sensor, *Journal of the Chinese Chemical Society*, 65, (2018) 1082-1089.
- [9] L. Kong, Z. Ren, N. Zheng, S. Du, J. Wu, J. Tang, H. Fu, Interconnected 1D Co₃O₄ nanowires on reduced graphene oxide for enzymeless H₂O₂ detection, *Nano Research*, 8, (2015) 469-480.
- [10] H. Heli, J. Pishahang, (2014) Cobalt oxide nanoparticles anchored to multiwalled carbon nanotubes: Synthesis and application for enhanced electrocatalytic reaction and highly sensitive nonenzymatic detection of hydrogen peroxide, *Electrochimica Acta*, 123, 518-526.
- [11] H. Heli, J. Pishahang, H.B. Amiri, Synthesis of hexagonal CoAl-layered double hydroxide nanosheets/carbon nanotubes composite for the non-enzymatic detection of hydrogen peroxide, *Journal of Electroanalytical Chemistry*, 768, (2016) 134-144.
- [12] T. Zhang, C. He, F. Sun, Y. Ding, M. Wang, L. Peng, J. Wang, Y. Lin, Co₃O₄ nanoparticles anchored on nitrogen-doped reduced graphene oxide as a multifunctional catalyst for H₂O₂ reduction, oxygen reduction and evolution reaction, *Scientific Reports*, 7, (2017) 43638.
- [13] K. Vasuki, K. J. Babu, S. Sheet, G. Siva, A. R. Kim, D. J. Yoo, G. G. Kumar, Amperometric hydrogen peroxide sensor based on the use of CoFe₂O₄ hollow nanostructures, *Microchimica Acta* 184 (2017)2579–2586.