

# Enhanced Non-enzymatic Electrochemical Sensor Based on Bi<sub>2</sub>S<sub>3</sub>-TiO<sub>2</sub> Nanocomposite with HNT's for the individual and simultaneous Detection of 4-Nitrophenol and Nitrofurantoin in environmental samples.

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## Supplimentary data

### **S1 Formation mechanism of the Bi<sub>2</sub>S<sub>3</sub>-TiO<sub>2</sub>/HNTs nanocomposite:**

Firstly, the hydrolysis of Ti (OBu)<sub>4</sub> occurs upon the addition of water. Ti (OBu)<sub>4</sub> undergoes hydrolysis to form titanium hydroxide (Ti (OH)<sub>4</sub>) and butanol (C<sub>4</sub>H<sub>9</sub>OH). During the condensation phase, the Ti (OH)<sub>4</sub> molecules undergo condensation reactions to form a network structure of Ti—O—Ti bridges. After multiple condensation events, large polymeric structures are formed [1].

Secondly, bismuth nitrate (Bi (NO<sub>3</sub>)<sub>3</sub>) dissolves in the ethanol-water mixture, releasing Bi<sup>3+</sup> ions. Thiourea ((NH<sub>2</sub>)<sub>2</sub>CS) decomposes in the presence of water and ammonia, releasing S<sup>2-</sup> ions. The Bi<sup>3+</sup> ions react with S<sup>2-</sup> ions to form bismuth sulfide (Bi<sub>2</sub>S<sub>3</sub>) through precipitation. The Bi<sub>2</sub>S<sub>3</sub> and TiO<sub>2</sub> particles then integrate during the sol-gel process, forming a nanocomposite material with both Bi<sub>2</sub>S<sub>3</sub> and TiO<sub>2</sub> phases. The calcination step at 500°C promotes the crystallization of TiO<sub>2</sub> and further stabilizes the Bi<sub>2</sub>S<sub>3</sub>-TiO<sub>2</sub> nanocomposite.

Thirdly, the formation of the composite between Bi<sub>2</sub>S<sub>3</sub>-TiO<sub>2</sub> and HNTs is achieved through a simple sonication method. Here, the Bi<sub>2</sub>S<sub>3</sub>-TiO<sub>2</sub> and HNTs are mixed in equal proportions and sonicated, which creates a force of attraction between the two nanomaterials.

**Table S2.** Emphasizes the Comparison of Electrochemical Performance of various reported electrodes with Bi<sub>2</sub>S<sub>3</sub>-TiO<sub>2</sub>/HNT's

Material	Limit of detection		Linear range		References
	NFT (nM)	4-NP (nM)	NFT (μM)	4-NP(μM)	
NiFe/f-MWCNT	30	-	0.1–352.4	-	2
MgFe <sub>2</sub> O <sub>4</sub>	33	7	0–342.6	0–342.6	3
M-MWCNTs	167	165	0.56	0.55	4
NiO/BCN	10.0	-	0.05–230.0	-	5
SVG-2/GCE	8.7	-	0.035–672.3	-	6
BDDFE	8.2	-	0.497–5.66	-	7
AuNP/RGO	-	10	-	0.05–2.0	8
GO/GCE	-	20	-	0.1–120	9

rGO-HNT-AgNP/SPCE	-	48	-	0.1–363.9	10
Nb <sub>2</sub> CTX/ Zn-Co-NC	-	70	-	1– 500	11
<b>Bi<sub>2</sub>S<sub>3</sub>-TiO<sub>2</sub>/HNT's</b>	3.2	3.5	0 -260	0-260	This work

**Table S3:** Simultaneous determination of NFT and 4-NP in pond water samples using the Bi<sub>2</sub>S<sub>3</sub>-TiO<sub>2</sub>/HNT's sensor

Sample	Added (μM)	Found (μM)	HPLC Method	Recovery (%)	RSD (%)
Pond water	50	49.0	49.5	<b>96.5</b>	<b>2.12</b>
	100	98.5	99.2	<b>98.4</b>	<b>3.23</b>
	150	149.2	149.3	<b>98.2</b>	<b>3.12</b>
Tap Water	50	48.6	49.8	<b>97.6</b>	<b>2.62</b>
	100	99.4	98.9	<b>99.5</b>	<b>3.55</b>
	150	149.5	148.9	<b>99.6</b>	<b>3.58</b>

## References

1. Sukharevska, N., Bederak, D., Dirin, D., Kovalenko, M. and Loi, M.A., (2020). Energy Technology, **8(1)**, 1900887.
2. Hwa, K. Y., & Sharma, T. S. K. (2020). Scientific reports, **10**, 12256.
3. Baby, J. N., Sriram, B., Wang, S. F., & George, M. (2020). ACS Sustainable Chemistry & Engineering, **8**, 1479-1486.
4. Dighole, R. P., Munde, A. V., Mulik, B. B., Zade, S. S., & Sathe, B. R. (2022). New Journal of Chemistry, **46**, 17272-17281.
5. Kokulnathan, T., & Wang, T. J. (2019). Composites Part B: Engineering, **174**, 106914.
6. Babulal, S. M., Koventhan, C., Chen, S. M., & Hung, W. (2022). Composites Part B: Engineering, **237**, 109847.
7. de Lima-Neto, P., Correia, A. N., Portela, R. R., da Silva Julião, M., Linhares-Junior, G. F., & de Lima, J. E. (2010) Talanta, **80**, 1730-1736.
8. Tang, Y., Huang, R., Liu, C., Yang, S., Lu, Z., & Luo, S. (2013). Analytical methods, **5**, 5508-5514.
9. Li, J., Kuang, D., Feng, Y., Zhang, F., Xu, Z., & Liu, M. (2012). Journal of hazardous materials, **201**, 250-259
10. Hwa, K. Y., Sharma, T. S. K., & Ganguly, A. (2020). Inorganic Chemistry Frontiers, **7**, 1981-1994.
11. Huang, R., Liao, D., Liu, Z., Yu, J., & Jiang, X. (2021). Sensors and Actuators B: Chemical, **338**, 129828.