

Zn@ZrO₂ Nanoparticles Decorated on Naringin - Based Sensor for Electrochemical Detection of *p*-Nitrophenol and *o*-Nitrophenol

**Ramesh Madhaiyan^a, Umamatheswari Seeman^{a*}, Sankar Chinnusamy^{b*},
and Jayavel Ramasamy^c**

^aPG and Research Department of Chemistry, Government Arts College (Affiliated to Bharathidasan University), Tiruchirappalli - 620 022, Tamil Nadu, India.

^bDepartment of Chemistry, Velammal College of Engineering and Technology, Madurai – 625 009, Tamil Nadu, India.

^cCentre for Nanoscience and Technology, Anna University, Chennai - 600 025, Tamil Nadu, India.

* Corresponding author, Tel.; +91-8438288510
E. mail: drsumamatheswari@gmail.com (Dr. S. Umamatheswari)
* Corresponding author, Tel.; +91-9944585257
E. mail: sankchem@gmail.com (Dr. C. Sankar)

1.1. Characterization

The crystalline planes of the Zn@ZrO₂/NG nanocomposite were analyzed by XRD (BRUKER Eco D8 advance with Cu - K α radiations = 1.54 Å). The absorption spectrum were further analyzed by FT-IR (IRTRACER-100), HR-SEM and EDX measurements were performed on (HR - SEM, Thermo scientific Apreos), HR-TEM measurements were performed on (HR-TEM, JEOL, JEM - 2100 plus, Japan), XPS measurements were conducted on (PHI Versaprobe III).

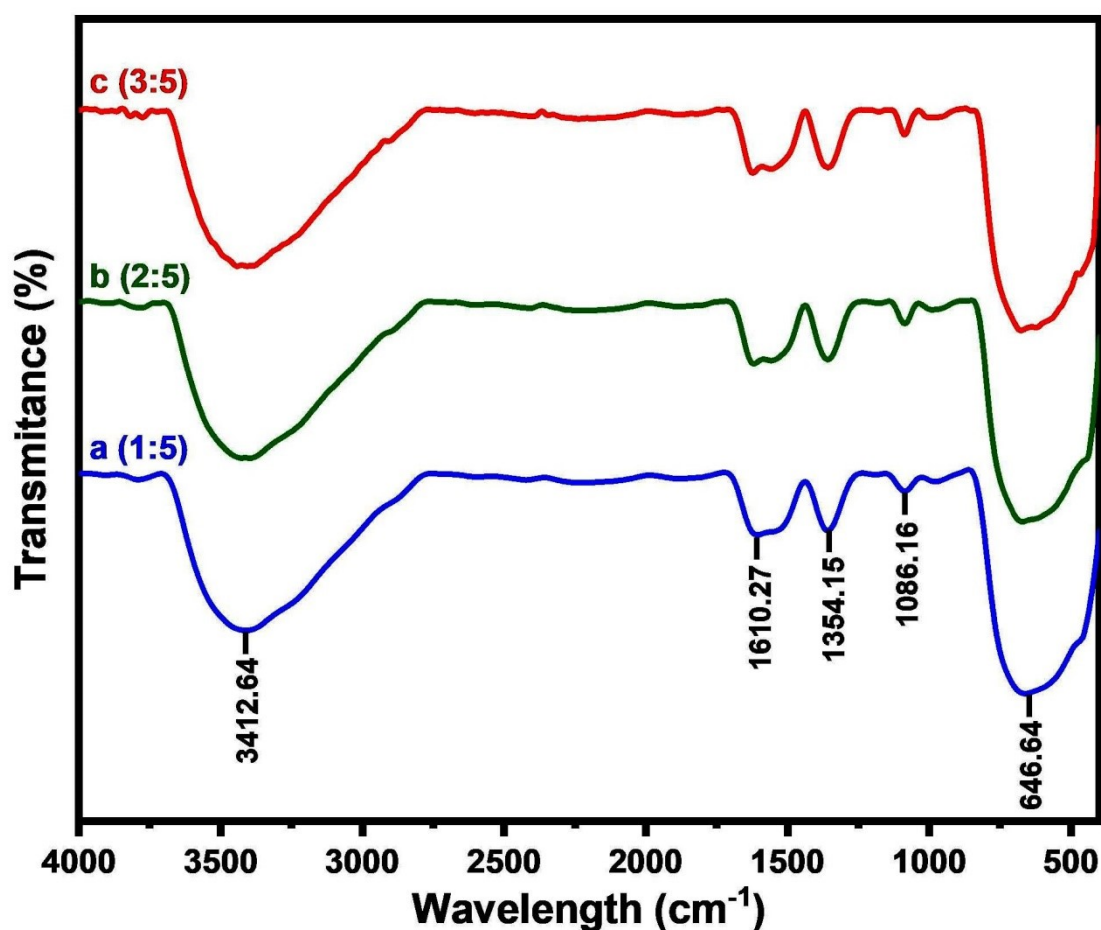


Fig. S1: FT-IR spectrum of different Zn@ZrO₂ combined with NG nanocomposites.

Effect of Zn@ZrO₂ concentration and pH

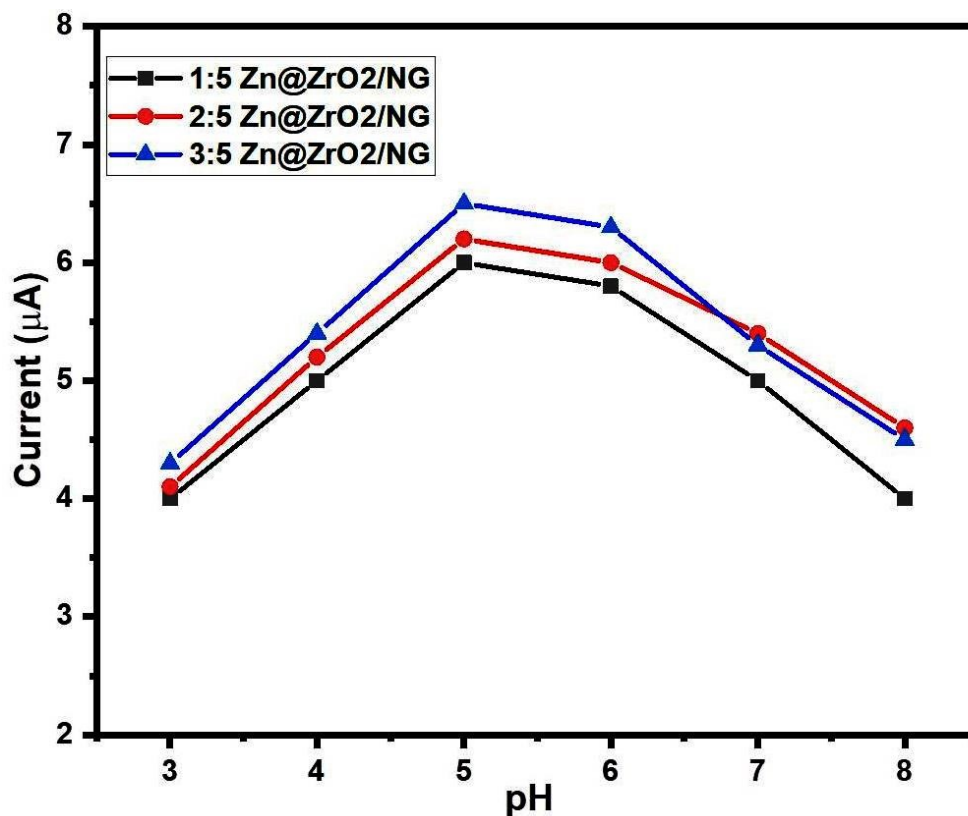


Fig. S2: Comparison plot of different Zn@ZrO₂ combined with NG with different pH.

In a bid to find the ideal operating pH and additive amount, the responses of Zn@ZrO₂/NG sensors with different Zn@ZrO₂ content (1:5, 2:5 and 3:5) combined with NG to 10 µM PNP were measured at various operating pH. The sensor exhibiting a concentration of Zn@ZrO₂/NG (3:5) displays the most significant reaction in detecting PNP when compared to the other concentrations. Additionally, the sensor's reaction to PNP detection is influenced by the operating pH. Each curve demonstrates a peak reaction at the optimal pH of 5. Based on the previously mentioned findings, it is evident that the Zn@ZrO₂/NG (3:5) sensor has a superior response and operates at a lower pH compared to the other sensors. Therefore, subsequent experiments were conducted using the identical composition Zn@ZrO₂/NG (3:5) and optimal pH (5) in order to examine the sensing capabilities of PNP and ONP.

Table. S1. Concentration of PNP and ONP for DPV analysis

S. No	Sets	PNP	ONP
1.	1	1 μM	1 μM
2.		2 μM	2 μM
3.		3 μM	3 μM
4.		4 μM	4 μM
5.		5 μM	5 μM
6.	2	10 μM	10 μM
7.		20 μM	20 μM
8.		30 μM	30 μM
9.		40 μM	40 μM
10.		50 μM	50 μM
11.	3	100 μM	100 μM
12.		200 μM	200 μM
13.		300 μM	300 μM
14.		400 μM	400 μM
15.		500 μM	500 μM

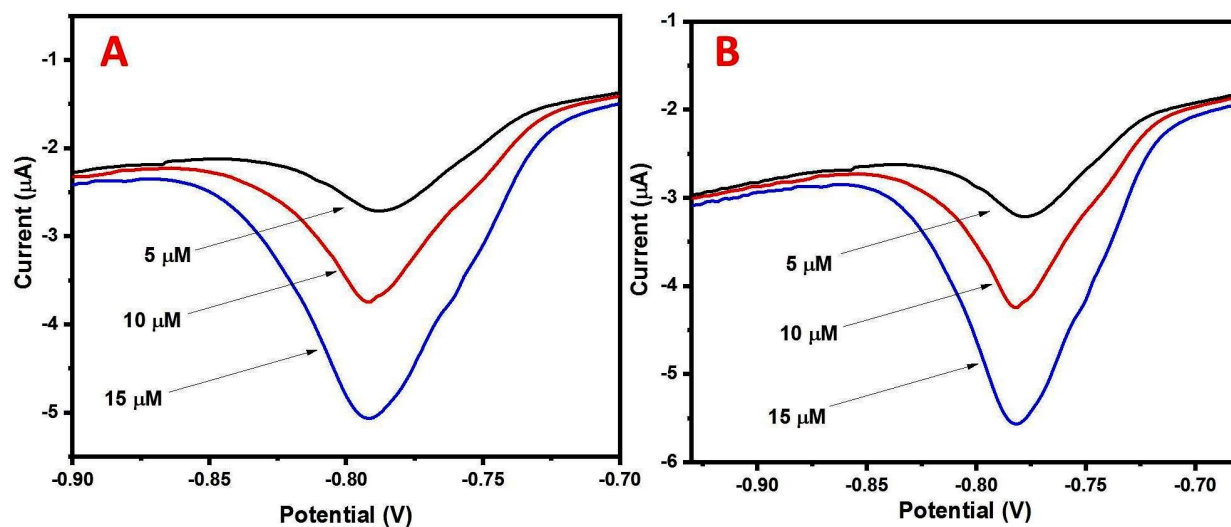


Fig. S3: A) PNP detection in tap water samples. B) PNP detection in river water samples.

Table. S2. Comparison of previously reported electrochemical detection of PNP

Materials	Linear range (μM)	LOD (μM)	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	References
ZnO/GCE	10 – 1000	13	404.35	1
meso-ZnCo ₂ O ₄ /GCE	1 – 4000	0.3	0.318	2
Fe ₃ O ₄ @AT-COFs	10 – 3000	0.2361	–	3
Nano-gold/GCE	10 – 100	8	–	4
AgPd@UiO-66-NH ₂	100 – 370	0.032	–	5
Cu-curcumin	0.1 – 1030	0.068	1.57	6
DVD@NP.Au/Hg	5 – 250	1	–	7
γ -Fe ₂ O ₃ -N-rGO	0.1 – 1000	0.1	0.6	8
GCE/Ag NPs-chi	0.07 – 2	0.07	–	9
Zn@ZrO ₂ /NG-GCE	1 – 500	1.14	5.05	Present work

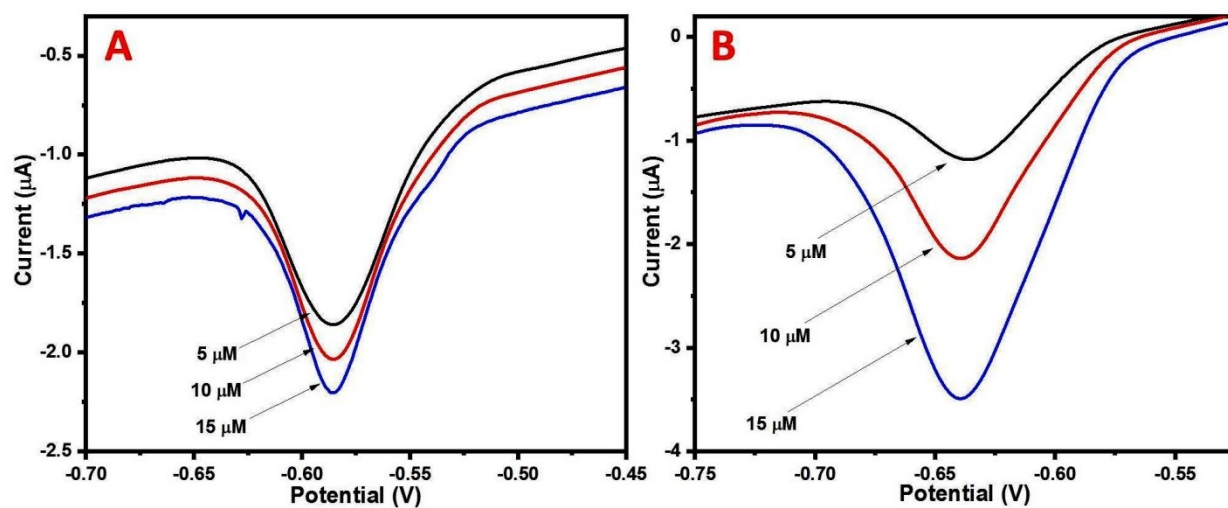


Fig. S4: A) ONP detection in tap water samples. B) ONP detection in river water samples.

Table. S3. Comparison of previously reported electrochemical detection of ONP

Materials	Linear range (μM)	LOD (μM)	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	References
RGO@CuO@Mn ₂ O ₃	0.5 – 126	0.021	4	10
Fe ₃ O ₄ @AT-COF	10 – 3000	0.657	0.041	11
C/N-Au-600e/GCE	0.1 – 320	0.043	–	12
C/N-Au	0.1 – 320	0.049	–	13
FeSe ₂	10 – 100	0.036	–	14
Mn-MOF@RGO/GCE	0.5 – 180	0.078	–	15
CoC@Mn	5 – 100	0.16	–	16
Zn@ZrO ₂ /NG-GCE	1 – 500	1.03	3.38	Present work

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