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Ultrasonic-assisted Preparation and Characterization of Magnetic ZnFe₂O₄/g-C₃N₄ Nanomaterial and their Applications towards Electrocatalytic Reduction of 4-Nitrophenol

Sathishkumar Chinnapaiyan^a, Tse-Wei Chen^b, Shen-Ming Chen^{a,*}, Z. Abdullah Alothman^c,

M. Ajmal Ali^d, S. M. Wabaidur^c, Fahad Al-Hemaid^d, Shih-Yi Lee^{e*}, Wen-Han Chang^{f,g,h}

^aDepartment of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan, Republic of China ^bDepartment of Materials, Imperial College London, London, SW7 2AZ, United Kingdom.

^cAdvanced Materials Research Chair, Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia.

^dDepartment of Botany and Microbiology, College of Science, King Saud University, P.O. Box 2455, Riyadh, 11451, Saudi Arabia.

^eDivision of Pulmonary and Critical Care Medicine, MacKay Memorial Hospital; MacKay Medicine, Nursing and Management College.

^fMacKay Memorial College Department of Cardiology, MacKay Memorial Hospital, Taiwan. ^gDepartment of Emergency Medicine, MacKay Memorial Hospital, Taiwan.

^hGraduate Institute of Injury Prevention and Control, Taipei Medical University; Department of Medicine, Taiwan.

Corresponding Author:

*E-mail: smchen1957@gmail.com (S.-M.Chen), leesyi5538@yahoo.com.tw (S.-Y. Lee).

Abstract:

Nanoball-structured ferromagnetic zinc ferrite nanocrystals (ZnFe₂O₄ NPs) entrapped with graphitic-carbon nitride (g-C₃N₄) was produced via straightforward and facile sonochemical synthetical technique (titanium probe; 100 W/cm² and 50 KHz). The morphological (SEM), elemental (EDS), diffraction (XRD), XPS, and electrochemical studies (CV) have been carry out to verify the nanostructure and shape of the materials. The ZnFe₂O₄ NPs/g-C₃N₄ electrode (GCE) was constructed which displayed outstanding electrochemical ability towards toxic 4-nitrophenol (NTP). A sensitive, selective, reproducible, and durable electrochemical NTP sensor was developed by ZnFe₂O₄ NPs/g-C₃N₄ modified electrode. The modified sensor exhibited a high sensitivity and 4.17 nanomolars of LOD. It's greater than the LOD of previously reported NTP modified sensors. The real-time experiments of the modified electrochemical (ZnFe₂O₄ NPs/g-C₃N₄ electrode) sensor were successfully explained in various water (river and drinking) samples and its showed high standard recoveries. Therefore, sonochemical synthetical method and fabrication of modified electrode were developed this work based on environmental analysis of NTP sensor.

Keywords: Sonochemical approach; Graphitic Carbon Nitride; Electrochemical detection; Bimetal oxide; ZnFe₂O₄; Toxic chemical sensor.

1. Introduction

Ultrasound is an acoustic wave, which paves the route for several chemical reactions by inducing chemical damage during the sonication process which leads to the growth, formation and bubbles implosion within the liquid solution by its acoustic cavitation phenomenon [1-3]. On sonication, the reaction condition such as a change in vapor pressure, collapsing of bubbles with transient pressure and temperature were observed with the utilization of ultrasound waves [4-8]. In today's world, the ultrasonication assisted synthesis of nanocomposite has attracted the researchers due to its wide range of applications in various fields such as medical, chemical, industrial and environmental fields [8-10]. Recently, a great deal of research has been addressed to develop the hierarchical nanostructure of transition bimetal oxide such as nanorods, nanoflowers, nanotubes, nanoparticles, nanosphere and layered sheets using facile sonochemical approach due to its optical, and electronic properties [4, 11].



Scheme 1. Sonochemical synthesis of $ZnFe_2O_4(a)g-C_3N_4$ nanomaterials and sensor.

The spinel ferrites with chemical composition (MFe₂O₄, M = Zn, Ni, Co, and Cd) has gained attention among researchers because of its excellent magnetic, chemical, catalytic and

physical properties [12-14]. Among these, the synergistic action of Zn and Fe in zinc ferrite (ZnFe₂O₄) enrich the redox reaction in electrochemistry and was extensively applied in diverse fields like photocatalysis, solar cells, photochemical hydrogen production, chemical sensors and batteries [15-18]. Hence, ZnFe₂O₄ is an excellent candidate owing to its high abundance, low cost, less toxic, environmental friendly, high electrochemical activity and high active surface area [19, 20]. The synthesis of ZnFe₂O₄ with various structural morphologies like ZnFe₂O₄ nanoparticles, ZnFe₂O₄ nanobelts [21], and ZnFe₂O₄ nanorods has been reported [22]. One of the fascinating methods to attain high electrochemical performance is to incorporate carbon-based conductive material like CNT, graphene or graphitic carbon nitride (g-C₃N₄) with ZnFe₂O₄ [23, 24]. Besides, the polymeric 2D semiconductor, g-C₃N₄ has emerged as a potential candidate due to its distinct electronic structure, low-cost, high stability, facile synthesis, high thermal stability, low density, electrocatalytic and photochemical properties which have been exhaustively employed in various fields such as sensing, photo-catalysis, and bio-imaging [25-29].

The significant advances in industrialization and technology over the globe have created a huge demand to detect hazardous environmental pollutants such as heavy metals, dyes, and pesticides from industrial wastewater. These harmful chemicals have a deleterious impact on the ecology as well as mankind [30-33]. Among them, phenolic derivative 4-nitrophenol (NTP) is a toxic, non-degradable nitro aromatic compound that is extensively employed in dyes, explosives, pharmaceuticals, petroleum, textile, and paper industries [34]. Owing to its toxicity, the US environmental protection agency (EPA) has categorized NTP as a priority pollutant with a permissible limit of less than 20 ppb in water. Intake or inhalation of NTP leads to severe health impacts on human, which affects the kidney, nervous and blood system by causing nausea, inflammation, cyanosis, drowsiness and methemoglobinemia [34-36]. Therefore, a simple,

effective, rapid, cheap and sensitive methodology for detecting NTP in water and food samples is of urgent need. To date, several methodologies, such as capillary electrophoresis, fluorescence, high-performance liquid chromatography, spectrophotometry, flow injection, and gas chromatography, have been widely used for the quantitative and qualitative detection of NTP. Nonetheless, these methods are highly sensitive but are time-consuming, require complicated operations with trained operators, high cost and need substantial sample manipulation. Moreover, the electrochemical method is identified as a promising analysis tool for its low cost, high-speed measurement, simple implementation, easy handling, reduced instrument size, and ultrasensitive detection.



Scheme 2. Fabrication of modified electrode and its application in water samples

In this work, we aimed to synthesize $g-C_3N_4$ incorporated on highly stable $ZnFe_2O_4$ for effective electrochemical detection of NTP using the facile sonochemical approach. The $ZnFe_2O_4/g-C_3N_4$ modified glassy carbon electrode (GCE) exhibits beneficial sensing ability over NTP with a lower limit of detection, broad dynamic range, high reproducibility, stability, and sensitivity. The as described modified electrode delivers excellent practicability in biological samples.

2. Experimental section

2.1. Preparation of ZnFe₂O₄/g-C₃N₄ nanocomposites

One mol of zinc source ($Zn(NO_3)_2 \cdot 6H_2O$) and two mol of iron nitrate nonahydrate were dissolved in 50 mL of Milli-Q water to form suspension (materials and method given in supporting information file). Then, 100 mg of carbon nitride (C_3N_4) powder was subsequently added to the pre-prepared mixture solution under magnetic stirrer. The suspension was ultrasonic agitated for 1 h (100 W/cm² and 50 KHz) and then mechanically stirred for 30 minutes at 30 °C temperature. Finally, the obtained precipitate (PPT) was collected using centrifuged and washed process with Milli-Q water and ethanol thoroughly and heated in vacuum dry oven at 80 °C for 12 h. For controlled material, pure $ZnFe_2O_4$ electro-catalyst was also prepared using same procedure without an addition of graphitic carbon nitride powder. Then, it also using for electrochemical experiments

2.2. Electrode modification using ZnFe₂O₄/g-C₃N₄ nanocomposite

The alumina powders (0.3 μ m) were applied to polish (clean) the glassy carbon electrode (GCE), and then the glassy carbon electrode was cleaned with water and ethanol sequentially. After, washed glassy carbon electrode was dried, at electric oven for 30 min. Then, 8 μ L ZnFe₂O₄/C₃N₄ suspensions (2 mg/mL) were drop casted on GCE (glassy carbon electrode) and then, composite drop casted electrode was dried at electric oven for 30 min. Furthermore, the C₃N₄ modified GCE and ZnFe₂O₄ modified GCE were prepared with a similar way. Then, all the modified electrodes were applied to electrochemical analysis.



Figure 1. TEM analysis of $g-C_3N_4$ nanosheets (A-B), TEM analysis of $g-C_3N_4/ZnFe_2O_4$ (C-E) and graphical structure (stick and ball) of the $g-C_3N_4/ZnFe_2O_4$ nanocomposite (F).

3. Results and discussions

3.1. Characterizations of ZnFe₂O₄/g-C₃N₄ nanocomposite

Figure 1A, shows the TEM analysis of graphitic carbon nitride (A-B) and $g-C_3N_4/ZnFe_2O_4$ composite (C-E). Pure graphitic carbon nitride shows an aggregated multi-layered nanostructure with smooth surface in Figure 1A-B. $ZnFe_2O_4$ particles are 200 nanometers larger and also its nano-balls like shaped (Figure 1C). Moreover, $ZnFe_2O_4$ particles are covered with graphitic carbon nitride sheets and it's like multilayered nanocomposite (Figure 1D-E). Figure 1F depicts the synthetic model of nanocatalyst (g-C₃N₄/ZnFe₂O₄) and the ball-stick model structure of the graphitic carbon nitride with $ZnFe_2O_4$ catalyst.



Figure 2. X-ray powder diffraction analysis of graphitic carbon nitride/ZnFe₂O₄ composite.

Figure 2, explained the X-ray powder diffraction patterns of $g-C_3N_4/ZnFe_2O_4$ composite. Furthermore, the X-ray powder diffraction peaks at 29.34°, 35.01°, 36.24°, 43.19°, 53.21°, 56.42°, and 63.34° with much intensity, can be assigned to (200), (311), (222), (400), (422), (511), and (440) diffraction planes of spinel-type zinc ferrite (JCPDS 22–1012) [37-39]. Figure 2, can be seen the graphitic carbon nitride has two distinct peaks in XRD analysis. A week peak at 28.71°, correspond to (002) plane with in-planar distance of graphitic carbon nitride (JCPDS 87–1526) and it is attributed to the long-range in-planar and stacking of aromatic units with one more peak at 13.74°. Its high-intensity and can be designated to (100) XRD peak, which correspond to tri-s-triazine part and also the interlayer stacking of graphitic carbon nitride. Moreover, the ZnFe₂O₄ nanoparticles combined with g-C₃N₄ was confirmed by XRD analysis in Figure 2. Therefore, the formation of nanocomposite has been achieved from X-ray powder diffraction examination.



Figure 3. X-ray photoelectron spectroscopy (XPS) analysis of $g-C_3N_4$ nanosheets@ZnFe₂O₄ nanocomposite

In this study, we are used X-ray photo-electron spectroscopy (XPS) method to analyses the physical and chemical properties of the g-C₃N₄/ZnFe₂O₄ nanocomposite with surface and structural character. Figure 3A shows the Zn 2p, Fe 2p, O 1s, N 1s and C 1s spectra of g-C₃N₄/ZnFe₂O₄ catalysts [41]. Zn 2p^{3/2} was deconvoluted into two XPS peaks. That is binding energy of 1020 to 1055 eV and it's due to Zn²⁺ as shown in Figure 3B. Furthermore, Fe 2p^{3/2} was deconvoluted into two XPS peaks. That is binding energy of 710 to 735 eV and it's due to Fe³⁺ as shown in Figure 3C. Moreover, the peak intensity of the higher oxidation state Fe³⁺ is enhancing with the increase of graphitic carbon nitride in the g-C₃N₄/ZnFe₂O₄ nanocomposite [41]. Then, O 1s XP-spectra contains four distinct XPS peaks. Two low binding energy peaks are located at 528.3 eV and 530.2 eV and it's ascribed to the lattice oxygen O²⁻ species in the ZnFe₂O₄ nanoparticles (Figure 3D). The N 1s XPS spectrum of the g-C₃N₄ shown in Figure 3F can be fitted into three peaks at 397.8 to 406.3 eV, corresponding to pyridine and pyrrole-like N

and then, a peak emerged at 285 to 294.2 eV, which also corresponds to C 1s in the g- $C_3N_4/ZnFe_2O_4$ [42, 43]. It suggests that through sonochemical treating $ZnFe_2O_4$ could be combined with g- C_3N_4 , which promoted the formation of bimetal oxide on the surface of the nanocomposite electrocatalyst. According to previous XPS literatures, the existence of bimetal oxide in nanocomposite is used to electrochemical activities of the material.





Figure 4. CVs at bare electrode (a), $g-C_3N_4$ modified electrode (b) and $ZnFe_2O_4/g-C_3N_4$ modified electrode (c) in presence of 150 µM NTP at 50 mVs⁻¹ (pH 5.0; phosphate buffer; N₂). (B) CVs obtained at $ZnFe_2O_4/C_3N_4$ modified GCE in pH 5.0 phosphate buffer (with nitrogen gas) with different concentrations of NTP and inset diagram is cathodic peak current/µA and [NTP]/µM.



Figure 5. Electrochemical reduction mechanism of 4-nitrophenol (NTP) based on $ZnFe_2O_4/g-C_3N_4$ composite modified GCE in pH 5.0 (phosphate buffer; N₂; 50 mV/s).

Figure 4A is explore, the CV analysis for unmodified electrode (a), $g-C_3N_4/GCE$ (b) and $ZnFe_2O_4/g-C_3N_4/GCE$ (c) (0.1 M; phosphate buffer; pH 5.0) containing 150 μ M of NTP. The potential range was applied between 0.1 V and -0.8 V and the scan rate is 50 mV per second. $ZnFe_2O_4/g-C_3N_4$ modified GCE offered more advantageous to NTP electrochemical reduction due to the properties of electrocatalytic ability and fast electron transfer. It's based on electrochemical ability of $ZnFe_2O_4$ and graphitic carbon nitride sheets. Furthermore, the electrochemical mechanism of the NTP is given in Figure 5 [44-46] and it's clearly explained 4-nitropheonl is converted into 4-hydroxyminopheonl by $ZnFe_2O_4/g-C_3N_4$ electrocatalyst. The electrochemical reduction current is obtained at $ZnFe_2O_4/g-C_3N_4/GCE$ and it's higher than that obtained at unmodified electrode (a) and $g-C_3N_4$ modified GCE (b). In addition, the overpotential also reduced at $ZnFe_2O_4/g-C_3N_4$ modified GCE compare to unmodified GCE. Therefore, the improved electrocatalytic ability of $ZnFe_2O_4/g-C_3N_4$ can be manifested and it has excellent electro-catalytic activity based on graphitic carbon nitride. Figure 4B, presented the

CVs obtained at $ZnFe_2O_4/g-C_3N_4$ modified GCE in 0.1 M phosphate buffer (pH 5.0; 50 mV/s) containing various concentrations of NTP (with nitrogen gas 15 seconds). A cathodic peak current was linearly increased as the concentration of NTP increased (**inset to Figure 4B**).



Figure 6. (A) CVs obtained at $ZnFe_2O_4/C_3N_4$ modified GCE in pH 5.0 phosphate buffer with different scan rate (20 to 240 mV/S) of NTP, the inset is the linear relationship between cathodic peak current and square root of the scan rate.

The electrochemical current responses were increased linearly with concentrations of NTP chemical, which is reveal for the anti-fouling potential of the $ZnFe_2O_4/g-C_3N_4$ modifier. Further, the calibration plot is good linearity (inset). The electrochemical effect of the scan rate (kinetic analysis) toward electro-catalytic NTP reduction was studied by $ZnFe_2O_4/g-C_3N_4$ at different scan rates (20 to 240 mV/s; Figure 6A). Moreover, the plot between the cathodic peak current of NTP and the square root of the scan rate which is applied and its exhibits good linearity. Therefore, these results are suggesting a diffusion-controlled process based on surface of $ZnFe_2O_4/g-C_3N_4$ modified glassy carbon electrode (Figure 6B). Then, the influence of electrolyte was checked (pH) on $ZnFe_2O_4/C_3N_4$ modified electrode towards 100 µM NTP chemical at 0.1 M phosphate buffer (Figure 7A). The pH of electrolyte is changes and the peak current with

potential (V; Ag/AgCl) of NTP cathodic peaks is also changed due to properties of $ZnFe_2O_4/C_3N_4$. The reduction peak current increases as the pH increases from 3 to 5 and reached maxima at pH 5.0 (Figure 7B). For pH 7 and 11, the cathodic peak current progressively decreases. Thus, the reduction of NTP is more favorable at pH 5.0 (phosphate buffer) based on $ZnFe_2O_4/C_3N_4$ modified GCE at 50 mV/s.



Figure 7. (A) CVs are carried out in (pH range: 3.0 to 11.0) phosphate buffer containing (100 μ M) NTP at ZnFe₂O₄/C₃N₄ modified GCE (50 mV/s; 0.1 M PB). (B) Plot is peak current/ μ A and different pH (3.0 to 11.0).

3.3. Amperometric determination towards NTP chemical

Figure 8A displayed, the amperometric (i-t) analysis of $ZnFe_2O_4/C_3N_4$ modified (RDE) rotating electrode (rotation speed=1100 RPM) with injections of NTP into phosphate buffer (pH 5.0) at a regular intervals of 50 seconds. Moreover, the electrode operational potential (E_{app}) is – 0.58 V (Ag/AgCl). Furthermore, well–defined and fast responses of NTP were obtained and steady–state current was reached within six seconds. The electrochemical sensor and amperometric working range is 0.015–724.17 μ M (Figure 8B) and limit of detection (LOD) is calculated as 4.17 nM. In addition, the electrochemical sensitivity of the work was calculated to

1.68 μ A μ M⁻¹ cm⁻². Further, the electrochemical sensor parameters are superior over existing ZnFe₂O₄/C₃N₄ incorporated and modified (RDE) electrodes (**Table 1**). Mainly, the detection limit is attained very lower at ZnFe₂O₄/C₃N₄ film modified electrode has surpassed that of many previous electrochemical (NTP) and other sensors.



Figure 8. (A) Amperometric responses obtained at $ZnFe_2O_4/C_3N_4/GCE$ after successive injection of NP (4-nitrophenol; NTP); (B) The plots of amperometric responses current vs NTP concentration/. Base solution: pH 7.0 PB (Applied potential: -0.58 V).

Table 1. Comparison of electro-analytical parameters obtained at $ZnFe_2O_4/C_3N_4$ film modified rotation disc electrode (RDE) towards NTP with previous reports.

Modified Flectrode	Limit of	Linear	Pof
Mounieu Electroue	detection/µM	range/µM	Kei.
Au NPs/ªGCE	8.0	10–100	[47]
^b GO sheets	0.02	0.1–120	[48]
°MWCNTs/Nafion	0.04	0.1–10	[49]

		Journal Pre-proofs		
Gı	aphene sheets/Nafion/dSPCE	0.6	10–620	[50]
^e r(GOS–Au NPs	0.01	0.05–2	[51]
Ag	g NPs/chitosan	0.07	0.07–2.0	[52]
ſM	IMIPs/Au/AuE ^g	0.1	0.1–140	[53]
^h D	TD/Ag NPs/ ⁱ CPE	0.25	1.0–100	[54]
jH	A NPs	0.60	1.0-300	[55]
Zr	Fe ₂ O ₄ /g-C ₃ N ₄ /GCE	4.07	0.015-724.17	This work

^aGCE= Glassy-carbon electrode, ^bGOS= Graphene oxide sheets, ^cMWCNTs= Multiwall carbon nanotubes, ^dSPCE= Screen-printed carbon electrode, ^erGOS= Reduced graphene oxide sheets, ^fMMIPs= Molecularly imprinted polymers, ^gAuE= gold electrode, ^hDTD= trioxadiazacyclonanodecine–dione, ⁱCPE= Carbon-paste electrode, ^jHA NPs= Hydroxyapatite nanoparticles.

The selectivity (anti-interference ability) of the modified sensor was examined by performing experiments in presence of likely interfering agents. **Figure S1 (A)** showed the amperometric response of the modified electrode towards 50 μ M of NTP, and 0.5 mM of ascorbic acid (AA), catechol (CT), serotonin (ST), histamine (His), metronidazole (MTZ), zinc ion (Zn), hydroquinone (HQ), Tryptophan (TRP), acetaminophen (AC), potassium (K⁺) and lysine (Lys). Besides, the modified electrode has quickly responded to NTP at ZnFe₂O₄/g-C₃N₄ in pH 5.0 (phosphate buffer; N₂ gas). However, it was insensitive (maybe no peak) to the other species (biomolecules, drugs and metal ions). Therefore, ZnFe₂O₄/g-C₃N₄ modified electrode high recognizes to detect NTP in phosphate buffer.

3.4. Durability, Reproducibility and Reproducibility of ZnFe₂O₄/g-C₃N₄ modified electrode

In order to examine, the durability of the ZnFe₂O₄ and g-C₃N₄ modified electrochemical sensor. The sensor performance of the ZnFe₂O₄/g-C₃N₄ modified electrode was monitored every day towards 100 μ M NTP at phosphate buffer (pH 7.0; 0.1 M), and then the modified electrode was stored at 5°C. Similar experiments were studied and the sensor performance was retained 95.62% after 30 days, compare to initial sensor response. Therefore, ZnFe₂O₄/g-C₃N₄ modified sensor has the excellent durability property (Figure S1B). Moreover, repeatability analysis was performed using one electrode and 10 repeated measurements based on ZnFe₂O₄/g-C₃N₄ film modified electrode and the R.S.D of the 10 repeated measurements is 3.41% (Figure S2A). Finally, the reproducibility experiments were tested using five individual ZnFe₂O₄/g-C₃N₄ modified electrodes and data were recorded by CV method in phosphate buffer (pH 5.0; N₂ gas) containing 100 μ M NTP. The R.S.D of the five measurements at five modified electrodes was 3.29% (Figure S2B). According to those results, the electrochemical sensor and ZnFe₂O₄/g-C₃N₄ modified electrode exhibited acceptable range of stability, repeatability and reproducibility.

3.5. Real time analysis of ATP at ZnFe₂O₄/g-C₃N₄ modified electrode

The practical analysis of the ZnFe₂O₄/g-C₃N₄ fabricated sensor was analyzed in different water samples. Drinking water collected from National Taipei University of Technology, Taiwan and river water collared form near river (New Taipei City). These samples were analyzed directly and then known amounts of NTP were spiked into water samples (drinking water and river water) and amperometric analysis was tested by optimized electrochemical experimental conditions (like Figure 8 experiment). The electrochemical sensor performance was calculated using standard addition method (SAM) and data are given in **Table 2.** Therefore, the ZnFe₂O₄/g-C₃N₄ modified electrode (carbon based) has high potential to be used in practical applications.

	Added	Found	Recovery	*RSD
Water Samples	(µM)	(µM)	(%)	(%)
	10	9.83	98.30	3.51
Drinking water	20	19.84	99.20	2.62
	50	49.74	99.48	3.26
	10	9.74	97.4	3.21
River Water	20	19.68	98.40	3.22
	50	48.19	96.38	3.71

Table 2. Electrochemical determination of NTP in water samples based on $ZnFe_2O_4/g$ -C₃N₄/GCE. *Relative standard deviation (RSD) of n=3 experiments.

4. Conclusions

In this work, a facile and robust sonochemical and solvothermal synthetical routes were developed to prepare a nano-ball like $ZnFe_2O_4$ particles decorated graphitic carbon nitride nanocomposite. The chemical structures and shape of the nanomaterials were confirmed by morphological (TEM), elemental (EDS), spectral (XPS) and electrochemical methods (CV and amperometric). The $ZnFe_2O_4/g-C_3N_4$ film modified electrode (carbon based) shown excellent electrocatalytic performances by amperometric method. It was demonstrated which showed wide working range (0.015–724.17 μ M) and low detection limit (4.07 nM). The electrochemical detection at nanomolar range is revealed and its good sensitivity in the quantification of NTP.

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Research Highlights

- ZnFe₂O₄ nanoparticles covered with graphic carbon nitride sheets were synthesized through a green based sonochemical method.
- > The electro-catalytic activity of the proposed hybrid electro-catalyst was investigated.
- The hybrid electro-catalyst has express nanomolar limit of detection in phosphate buffer (pH 7.0).
- The hybrid electro-catalyst showed a superior electrochemical performance (wide linear range and high sensitivity).
- Such a unique electro-catalyst was successfully applied real sample analysis in water samples.

CRediT authorship contribution statement

Sathishkumar Chinnapaiyan: Data processing, Methodology, Formal analysis, Writing - original draft. Tse-Wei Chen: Methodology, Formal analysis, Revision work. Shen-Ming

Chen: Project administration, Resources, Supervision. Zeid Abdullah Alothman^c, Mohammad Ajmal Ali: Administration, Resources, Supervision, Funding acquisition. Saikh Mohammad Wabaidur: Resources, Methodology, Fahad Al-Hemaid: Visualization, Methodology, Shih-Yi Lee: Formal analysis, Supervision, Funding acquisition, Wen-Han Chang: Visualization, Methodology.

國立台北科技大學

DEPARTMENT OF CHEMICAL ENGINEERING AND BIOTECHNOLOGY

NATIONAL TAIPEI UNIVERSITY OF TECHNOLOGY

No. 1, Section 3, Chung-Hsiao East Road

Taipei - 106, Taiwan, Republic of China

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Yours, Sathishkumar Chinnapaiyan and other authors National Taipei University of Technology Taiwan-106.