



Sensitive detection of urea based on Dy₂O₃-Co₃O₄@ZrO₂ nanocomposite by electrochemical approach for environmental assessment

Muhammad Zeeshan Rafiq^{a,1}, Amna Siddique^{a,1}, Muhammad Fazle Rabbee^{b,1},
Shehzada Muhammad Sajid Jillani^c, Jehan Y. Al-Humaidi^d, Aqsa Dildar^a,
Muhammad Tariq Qamar^e, Syed Kamran Haider^f, Muhammad Nadeem Akhtar^a, M.A. Fazal^g,
Muhammad Ahmad Khan^h, Mohammad Mizanur Rahman Khan^{i,*}, Tahir Ali Sheikh^{a,*},
Mohammed M. Rahman^{j,k,*}

^a Institute of Chemistry, Faculty of Chemical & Biological Sciences, The Islamia University of Bahawalpur, Baghdad-ul-Jadeed Campus, Bahawalpur-63100, Pakistan

^b Department of Biotechnology, Yeungnam University, Gyeongsan 38541, South Korea

^c Interdisciplinary Research Center for Membranes and Water Security, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

^d Department of Chemistry, College of Science, Princess Nourah bint Abdulrahman University, P.O. BOX 84428, Riyadh 11671, Saudi Arabia

^e Department of Chemistry, Forman Christian College (A Chartered University), Ferozpur Road Lahore, Lahore-54000, Pakistan

^f School of Chemical Engineering, University of Ulsan, 93 Daehak-ro, Nam-gu, Ulsan 44610, Republic of Korea

^g Department of Mechanical and Materials Engineering, University of Jeddah, Kingdom of Saudi Arabia, Saudi Arabia

^h Department of Chemistry, University of Nebraska, Lincoln, 68588, Nebraska, USA

ⁱ Research Center for Green Energy Systems, Department of Mechanical Engineering, Gachon University-1342, Seongnam-daero, Sujeong-gu, Seongnam-si, Gyeonggi-do, Republic of Korea 13120

^j Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

^k Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah 21589, Saudi Arabia

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ABSTRACT

This approach involved the wet chemical synthesis of Dy₂O₃-Co₃O₄@ZrO₂ nanocomposite (NC) for detecting as well as electrochemically hydrolyzing the hazardous substances in an aqueous solution. A comprehensive examination of the resultant material was carried out using advanced analytical techniques encompassing UV-DRS, FTIR, I-V, powder XRD, FESEM equipped with EDS, DPV, and HR-TEM, in addition to BET analysis, to investigate its optical, structural, elemental and morphological properties. After that, a novel electrochemical probe with high selectivity and sensitivity was tailored for urea, among other interfering chemicals, by modifying glassy carbon electrode (GCE) by applying a thin layer of Dy₂O₃-Co₃O₄@ZrO₂ NC. Within the modification of GCE, 5 % ethanolic nafion served as a conductive adhesive binder. Through a comparative analysis, it was found that our newly developed Dy₂O₃-Co₃O₄@ZrO₂-NC/Nafion/GCE was exceptionally sensitive towards urea and had long-term stability along with good affinity with it even in the presence of numerous interfering species. The slope of calibration curve was used to determine the key analytical parameters, such as sensitivity, limit of detection (LOD) and limit of quantification (LOQ), so as to optimize the above stipulated newly develop electrochemical probe. The analytical parameters, including LOD at signal-to-noise ratio (S/N) over 3, LOQ and sensitivity were found to be 0.0491 nM, 0.164 nM, and 19.47 $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$, respectively, across linear dynamic range (LDR) ranging urea concentrations from 1.0 nM to 10.0 mM with r^2 value as 0.9680. As a result, this study also sheds light on cost-effectiveness and long-term stability of newly fabricated electrochemical probe, selective only for urea, in addition to its efficiency. Moreover, this study gives us an idea to effectively interrogate the various toxic chemicals in real samples by using a novel electrochemical, I-V, approach based on reported / non-reported different kind of semiconductor nanocomposite modified GCEs as selective electrochemical probes.

* Corresponding authors.

E-mail addresses: mmrkhan@gachon.ac.kr (M. Mizanur Rahman Khan), tahir.ali@iub.edu.pk (T.A. Sheikh), mmrahman@kau.edu.sa (M.M. Rahman).

¹ These authors equally contributed in this study.

1. Introduction

Generally, nanoscience is the emerging field of modern sciences in the twenty-first century of this world because of its amazing advances and applications in the pharmaceutical [1], biological [2], and chemical sectors [3]. The synthesis of semiconductor nano-structured materials with different morphology in terms of distinct size, shape, and structure is essential for further development in the field of nanoscience / technology. Because of their small size, semiconductor nano-structured materials of metal oxides have majestic physicochemical properties, namely, amplified electrical, magnetic, mechanical, thermal, and catalytic properties.[4,5] Due to extensive applications, nanoscience has captured the attention of researchers [6]. Similarly, studies have been reported regarding the detection of toxic substances and biomolecules using semiconductor nano-material. [7–10]. Furthermore, in light of recent research, doped nanomaterials of metal oxides are of greater fame and interest as compared to un-doped nanomaterials because of their ability to detect harmful substances and function as semiconductors [11–13]. From the periodic table, we can see that the doping of rare earth elements into semiconductor transition metal oxide have excellent physicochemical properties than pristine nano-structured metal oxide. Some doped nano-structured materials / composite have also been reported in the literature with good electrical, magnetic, mechanical, thermal, and catalytic properties [14,15].

In this approach, a semiconductor nano-structured composite of metal oxides ($\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$) was synthesized by a wet chemical process for the detection of toxic chemicals in an aqueous medium. Zirconium, a group IV transition metal, is considered as most accessible and cost-effective because of its abundance in our earth's crust [16,17]. As zirconium (IV) has a density of about 2.8 g/cm and a low toxic concentration of about $[\text{LD}_{50}(\text{ZrCl}_4, \text{oral rat}) = 1688 \text{ mg kg}^{-1}]$, it is an extraordinarily helpful for the synthesis of nanoparticles [18]. Zirconia (ZrO_2) is a noteworthy compound that provides refinement to the nanocomposite's grains when used as a doping agent [16,19]. It has excellent significant stability, chemical inertness and microbial resistance in addition to low thermal conductivity [20–22]. Some studies have also been reported with its admirable catalytic application and its well-known exceptional catalytic performance based on the oxygen vacancies present on its surface [23,24]. Similarly, cobalt oxide (Co_3O_4) is also considered to be very crucial in light of its unique commercial applications like chemical sensing [25], gas sensing [26–29], catalysis [30], energy storage [31], drug delivery, magnetic resonance imaging (MRI), and medication delivery [32]. Likewise, dysprosium oxide (Dy_2O_3) has commercial applications in capacitors, glass, lasers, and optical imaging [33]. Moreover, Dy_2O_3 has also captured the attention because of thermal stability and electron transfer feature in addition to potential applications in bio-medical sector [34,35] such as drug screening, distribution of medicinal applications, and cancer research [36,37]. In combined form these materials resulted in a nanocomposite with enhanced physicochemical activity compared to their intrinsic forms, optimizing sensitivity, selectivity, and stability for electrochemical sensing in an aqueous system.

Due to rapid urbanization as well as industrialization, along with innovation in technology in present-day science, several unwanted hazardous chemicals are being discharged into our surrounding and continuously contaminating it. Ever-present pollutants also known as ubiquitous contaminants have toxic effects on our ecosystem [38–40]. Herein, the synthesized doped semiconductor nanomaterial $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ was synthesized with aim to detect the toxic chemicals as an environmental remediation. The newly synthesized material was found to be selective and sensitive only for urea among the various hazardous chemicals in an aqueous system. Urea's wide-ranging applications extend to numerous industries, such as the pharmaceutical, fertilizer, cosmetics, and plastic sectors [41]. No doubt urea is less toxic but urea itself and its derivatives at high concentration considered as toxic for living beings and has toxic effects on lungs, kidneys, and liver

[42,43]. The high volume of wastewater containing urea released by industries and living beings is becoming an alarming concern for our ecosystem [44]. The rise in urea concentration within domestic water waste is due to urine secreted by humans and animals [45].

Several methods / techniques have been applied for the detection of urea that might include UV-Visible spectrophotometer [46], high-performance liquid chromatography [47,48], fluorescence [48,49], LC-MS [50,51], electrophoresis [52], gas chromatography-electron capture detector (GC-ECD) [53], gas chromatography [54], electrochemical approach [55,56]. As all the above-mentioned techniques are entirely complex and costly, it has become essential to devise an economical, innovative, proficient, and reasonable approach for the identification of urea. In this method, $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ was fabricated on GCE as a highly effective and precise electrochemical probe for the detection of urea using the I-V technique for the very first time.

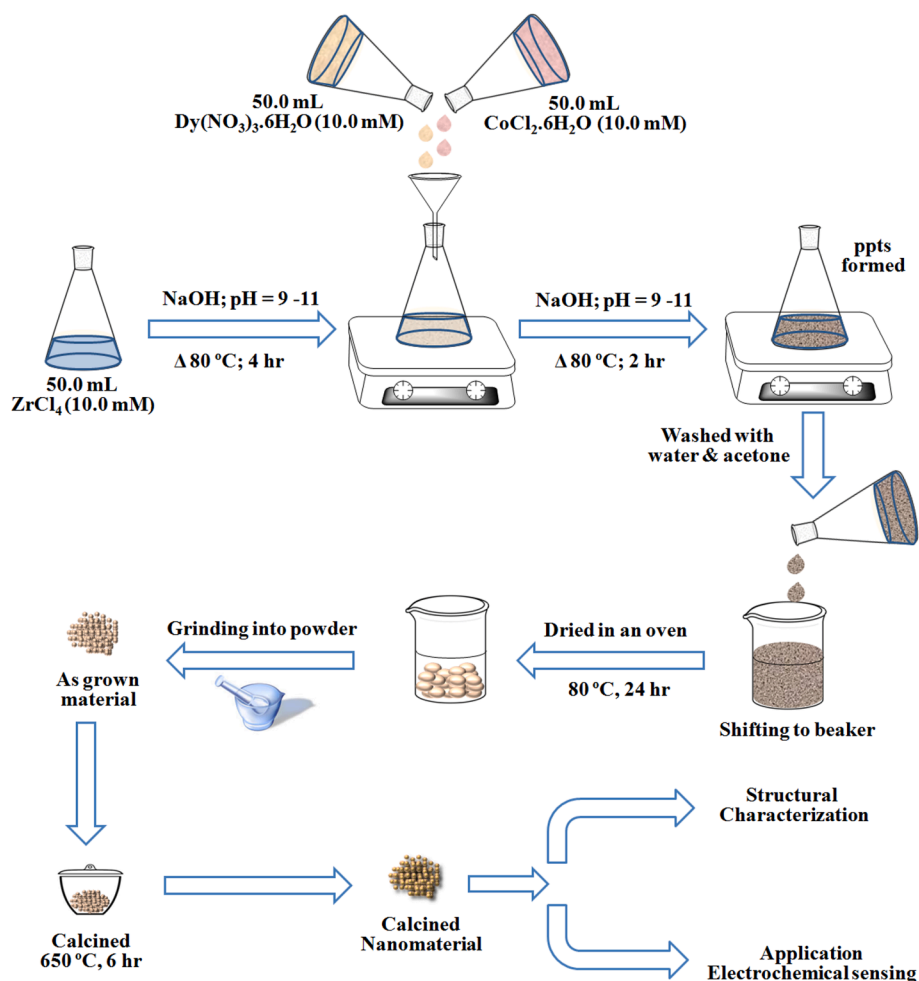
2. Experimental Section

2.1. Materials and Methods

All the chemicals that have been used in this work were purchased from Sigma-Aldrich Company and were of analytical grade. The precursor chemicals such as dysprosium nitrate hexahydrate, zirconium tetrachloride, cobalt chloride dihydrate, and sodium hydroxide were sourced with a purity of at least 99.9 %, so no purification steps were carried out before their use. Similarly, solvents and other reagents that have also been used in this work were also of analytical grade and required no further purification before their use. The optical characterization and structural analysis of our newly synthesized $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NCs were performed using a Thermo Scientific NICOLET iS50 FTIR spectrometer (Madison, WI, USA), and a Thermo Scientific 300 UV/Visible spectrophotometer. The crystallinity of the sample was determined via powder X-ray diffraction using a Thermo Scientific Diffractometer (ARL X'TRA XRD). The comprehensive analysis of the sample's structural morphology and elemental composition was carried out using FESEM equipped with EDS. The BET analysis was conducted using Quantachrome: Autosorb (ASIQCU01000-6, USA) to determine the surface area of the newly developed material. The Keithley electrometer (6517A, USA) was employed for the qualitative and quantitative detection of urea employing an innovative electro-chemical, I-V method, against applied voltage (0.0 V – +1.5 V). Herein, a two-electrode system was set up, consisting of a Pt wire as the reference/counter electrode and a modified GCE as the working electrode.

2.2. Synthesis of ternary metal oxide ($\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$) nanocomposite

The synthesis of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ semiconductor nanocomposite was achieved through an incredibly conventional simple solution method at alkaline pH. In this process, 50.0 mL of 10 mM ZrCl_4 solution was agitated for 15 min. in a 250.0 mL Erlenmeyer flask, followed by drop wise addition of NaOH in order to shift the pH towards alkalinity. The reaction flask was then heated and stirred continuously on an electric hot plate for 4 h at 80 °C. In addition to the above precursor solution, equimolar (10.0 mM) solutions of $\text{Dy}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2\cdot 2\text{H}_2\text{O}$ were added in a 1:1 ratio by volume (50.0 mL each) and subjected to stirring for an additional 2 h at 80.0 °C. The pH of the reaction medium was maintained within the range of 9 to 11 by using NaOH. After 2 h of being stirred, the resulting precipitates from well-agitated solution were obtained at the end of reaction. The resulting precipitates were filtered and then subjected to washing with plenty of water and then acetone followed by heating at 80 °C in an oven for a duration of 24 h to remove the all moisture content from the sample. After that, the final product was homogenized by grinding and then calcined at 650 °C for 6 h constantly in muffle furnace (Barnstead Thermolyne, 6000 Furnace, USA), as seen in Scheme 1. Similarly,



Scheme 1. Synthesis of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ nanocomposite by simple solution method.

synthesis of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ has also been ascribed in the form of chemical reactions in electronic supplementary material, ESM-2.2.

Sodium hydroxide plays a crucial role in maintaining the pH of the reaction medium towards alkalinity by donating OH^- ions to the solution and hydrolyzing reactant precursors into their corresponding hydroxides. When the concentration of precursor ions, including Zr^{4+} , Dy^{3+} and Co^{2+} along with OH^- reaches its optimum level, the nucleation of their hydroxides begins to precipitate. According to Ostwald ripening theory, the $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ nanocrystals went through self and mutual accumulation, followed by van der Waal forces. Consequently, the re-aggregation of these crystals resulted in the synthesis of a $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NC, Fig. S1. Following the synthesis of the nanocomposite, its structural, morphological, and optical characteristics were analyzed via sophisticated analytical techniques/methods like UV-Visible spectroscopy, powdered X-ray diffraction (XRD), fourier-transform infrared spectroscopy (FTIR), FESEM, EDS, HR-TEM, and BET. At the end, the synthesized nanocomposite was employed in sensing of urea using a simple and reliable electrochemical (I-V) method for the first time.

2.3. Fabrication of GCE as selective electrochemical urea probe

Our newly prepared nanocomposite was used for the fabrication of GCE using a very simple and easy-to-use protocol. Before fabrication, a highly precise methodology was considered for the GCE washing process. GCE was initially treated with acetone for 10 min., followed by extensive washing with distilled water and ethanol and then dried at $80\text{ }^\circ\text{C}$ for 15 min. in an oven. After washing, the $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$

nanocomposite was transformed into a slurry by blending it with ethanol. This slurry was then coated onto the GCE with a 5 % ethanolic Nafion solution as a conductive adhesive binder. Ultimately, a completely dried and smoothly coated $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$ was finally achieved by drying it at normal condition for around 20 min., as depicted in Fig. S2. So, to measure the (I-V) response, an electrochemical cell was constructed using Pt-wire as a reference electrode and $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$ as a working electrode. Keithley electrometer (6517A, USA) was applied as a steady voltage source to measure the current response in a simple bi-electrode system. After that, equimolar (0.2 M) solutions of Na_2HPO_4 (39.0 mL) and NaH_2PO_4 (61.0 mL) were mixed in a 100.0 mL measuring cylinder, resulting in a phosphate buffer (PB) with a pH of 7.00. The volume of PB (0.2 M) remained the same in the 10.0 mL beaker during the whole procedure. The stock solution (0.1 M) of different concentrations (0.01 nM ~ 0.1 M) of urea was prepared using the dilution method in deionized water (DI). The various concentrations served as analytes of interest. With the aim of maximizing the efficiency of newly developed electrochemical probe for selective urea detection, a number of analytical parameters, such as limit of quantification (LOQ), limit of detection (LOD), coefficient of correlation (r) / r^2 square value and sensitivity were calculated by the calibration curve's slope. Its sensitivity was found to be $19.47\text{ }\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$ and calculated using the relation sensitivity = slope of calibration curve / surface area of GCE.

3. Results and Discussions

The newly synthesized non-reported ternary metal oxide ($\text{Dy}_2\text{O}_3\text{-}$

$\text{Co}_3\text{O}_4@\text{ZrO}_2$ semiconductor nanocomposite was subjected to DRS, FTIR, FESEM, EDS, BET, HR-TEM, and powdered-XRD analysis to determine its morphological, structural and optical properties.

3.1. Optical characterization of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4@\text{ZrO}_2$ nanocomposite

FTIR analysis was performed to identify the functional groups and FTIR spectrum was recorded from 400 cm^{-1} to 4000 cm^{-1} . In Fig. 1, as grown, two broad peaks at 465 cm^{-1} and 1120 cm^{-1} are assumed to be mixed peaks of all metal oxides (zirconium oxide, dysprosium oxide and cobalt oxide). A characteristic peak attributed to M–O–M is typically observed with in the spectral range of 800 cm^{-1} – 1280 cm^{-1} . Usually, zirconium oxide shows a peak at 1120 cm^{-1} which corresponds to the bending vibration of hydroxyl groups that are bound to zirconium oxide [57,58]. Similarly, dysprosium oxide shows a bending vibration ranging from 550 cm^{-1} to 590 cm^{-1} and cobalt oxide shows a range of 510 cm^{-1} to 660 cm^{-1} . In the literature, it has been reported that dysprosium oxide shows the peaks at 590 cm^{-1} , 553 cm^{-1} and 559 cm^{-1} [33,59,60] as well as cobalt oxide shows the peaks at 511 cm^{-1} , 566 cm^{-1} and 663 cm^{-1} [25,61]. The broad band at 3440 cm^{-1} and the peak at 1638 cm^{-1} are allocated to O–H stretching and the bending vibration arising from surface absorbed water. The O–H group gets eliminated because of calcination at high temperature [61]. After calcination, the bands at 3440 cm^{-1} and 1638 cm^{-1} disappeared owing to the high temperature and a new peak appeared at 1100 cm^{-1} , which is assumed to be the mixed peak of all metal oxides as stipulated above.

Similarly, the optical characteristics of ternary metal oxide ($\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4@\text{ZrO}_2$) semiconductor nanocomposite were also measured over a wavelength range of 250 nm to 1200 nm using UV–Vis diffuse reflectance spectroscopy and the percentage reflectance peaks were found to be at $\lambda_{\text{max}} = 480.2\text{ nm}$ and 1033.3 nm , Fig. 2(a). Moreover, band gap energy was also calculated by using the Kubelka-Munk function and it was found to be 2.68 eV , Fig. 2(b). Kubelka-Munk equation (Eq. ix) and Tauc equation (Eq. x) are two widely recognized formulas that can accurately determine the band-gap energy (E_g) by using the percentage reflectance.

E_g refers to the band gap energy while $h\nu$ represents the photon energy. The factor “n” can undertake several possible values, depending on the type of inter-electron band transition, half ($1/2$) for direct and 2 for indirect transitions.

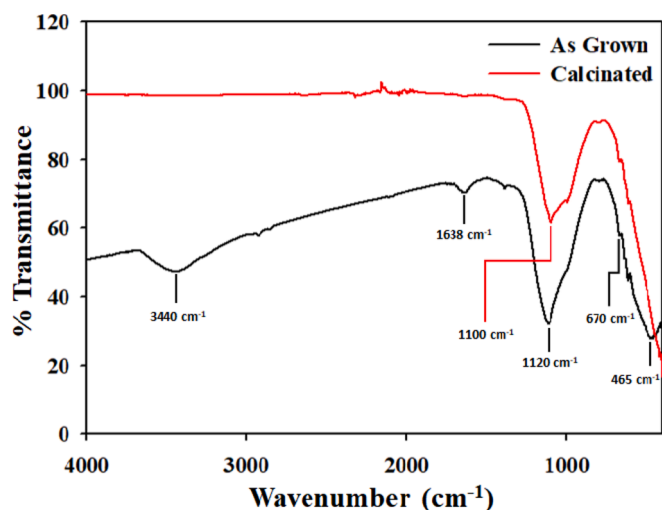


Fig. 1. FTIR spectrum of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4@\text{ZrO}_2$ nanocomposite before and after calcination.

3.2. Structural, morphological & elemental analysis of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4@\text{ZrO}_2$ nanocomposite

A nitrogen adsorption / desorption isotherm, generally known as BET (Brunauer-Emmett-Teller) analysis was also conducted to determine the specific active surface area of our nanocomposite at a cryogenic temperature of 77.0 K by using a highly accurate instrument called Quantachrome: Autosorb (ASIQCU01000-6, USA). For this purpose, multi-point adsorption data obtained from linear N_2 adsorption isotherms and a plot of relative pressure against nitrogen gas adsorption, Fig. 3, were employed to determine the specific active surface area (S_{BET}), pore width and pore volume. The values were found to be $19.903\text{ m}^2/\text{g}$, 17.296 nm and 0.074 cc/g So, this extensive investigation showed that our NC have an exceptionally highly specific active surface area (S_{BET}) which ensures the presence of textural pores with definite pore capacity & pore width in highly ordered mesoporous structure of semiconductor nanocomposite. Moreover, the precise control of the alkaline medium during the reduction of precursor reactants led to the development of porosity [62]. Thus, morphological and textural studies of our newly synthesized NC reveal promising properties for enhancing electro-catalytic performance in chemical sensing applications.

Similarly, the structural and morphological composition of our newly synthesized NC was also observed by FESEM equipped with EDS mapping and images, from low to high resolution, along with EDS mapping were recorded so as to study the elemental characteristics of our material, Fig. 4(a-c). It was observed that $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4@\text{ZrO}_2$ NC has a definite structural feature with large surface area, accompanied homogeneous elemental distribution all over the surface, Fig. 4(d-h). Furthermore, the EDS peaks of corresponding structural elements of our composite (O, Co, Zr and Dy) are also outlined in EDS spectra in percentage by weights of 57.36 %, 8.44 %, 33.76 % and 0.44 %, respectively, Fig. 4(i). Consequently, from the EDS analysis, it can also be noticed that no other peak associated with any impurity is present in EDS spectra which has also been confirmed by EDS mapping. So this analysis enlighten us that our composite synthesized by simple solution method contains only O, Co, Zr and Dy.

The XRD analysis was also performed so as to determine the crystallinity as well as phase purity of the composite. The crystallinity of a metal oxide may be accessed by its metal oxygen framework and found to be 86.49 %. The analysis was performed at 2θ degree in the range of 10° – 70° . Fig. 5, shows the diffraction planes of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4@\text{ZrO}_2$ NC. The diffraction angles positioned at 2θ values of 29.71° , 34.63° , 49.61° and 59.22° were assumed to be of ZrO_2 and were also precisely aligned with their corresponding crystal planes designated as (003), (012), (104) and (113), respectively (ICDD card: 00–037-0031) [63,64]. Similarly, peaks positioned at 29.25° , 47.54° and 56.59° were correspond to diffraction planes designated as (002), (110) and (112), respectively, and were closely align with the values documented in the literature for Dy_2O_3 (ICDD card: 00–018-0475) [65]. Moreover, peaks positioned at 18.99° , 36.84° , 38.54° and 65.23° were correspond to Co_3O_4 (ICDD card: 01–074-2120) with their crystal planes denoted as (111), (311), (222) and (440), respectively [66,67]. The peak appear at 33.153° correspond to (020) is assumed to be the mixed peak of dysprosium and cobalt oxide (ICDD card: 01–073-1197) [68]. So, all the above stipulated reflection planes were well matched with literature reports and confirmed that our synthesized material encompassing all the precursor elements (Zr, Dy & Co). Moreover, the average crystallite size was also calculated by the following Scherrer equation, and it was found to be 16.38 nm :

$$D = \frac{K\lambda}{(\beta \cos \theta)}$$

Where D is the crystallites size, K is the Scherrer constant having value 0.94, λ represents X-ray wavelength, θ denotes the diffraction angle and β is full-width half maximum (FWHM).

High resolution transmission electron microscopy (HR-TEM)

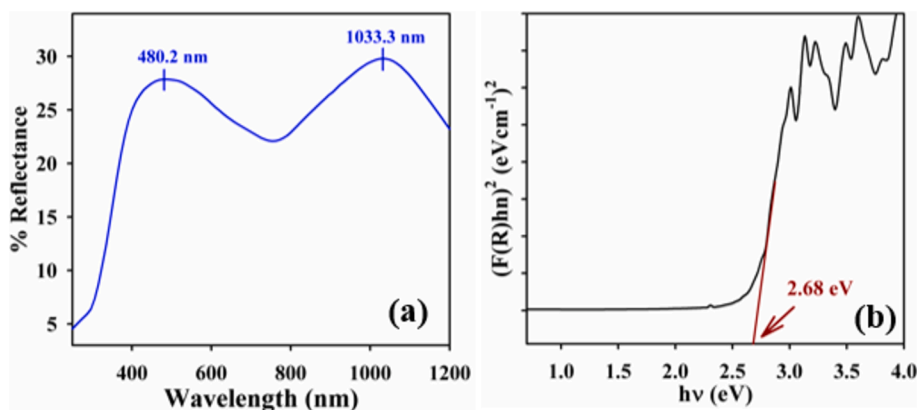


Fig. 2. (a) UV-Vis DRS spectrum of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ nanocomposite; (b) Tauc plot for band gap energy.

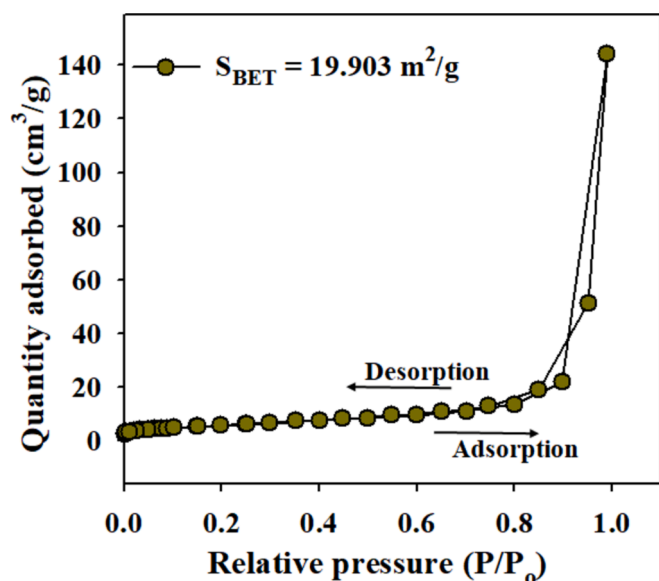


Fig. 3. Brunauer-Emmett-Teller (BET) surface area analysis of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ nanocomposite.

analysis was also performed to further investigate the surface morphology of our composite material. Moreover, HR-TEM images, Fig. 6(a-d), also enlighten us that all metal oxides are evenly distributed as well as intermixed with each other in our newly synthesized NC. Lattice fringes accompanied by interplanar distances within the range of 0.282 nm can be clearly depicted in Fig. 6(e). Similarly, mixed lattice fringes can also be observed easily in Fig. 6(e) which confirms that our material is composite of all metal oxides correspond to reaction precursors. The selected area electron diffraction (SAED) pattern, Fig. (f), also affirms the coexistence of all metal oxides (Zr_2O_3 , Dy_2O_3 and Co_3O_4) within our newly synthesized semiconductor nano-structured composite, aligning closely with the ICDD cards outcomes of XRD results.

3.3. Applications: Urea detection employing an electrochemical I-V approach

Herein, $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NC was applied to detect toxic chemicals qualitatively and quantitatively in an aqueous system using an electrochemical I-V approach through a Keithley electrometer (6517A, USA) based on its modified GCE as selective electro-chemical probe. It was found that, along with number of toxic chemicals, this recently synthesized $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NC modified GCE was found to be

exceptionally selective and sensitive only for urea. Furthermore, this study has also reveals that this newly modified GCE has remarkable benefits such as a large surface area, good I-V responses, non-toxic nature, as well as its bio-safety, stability and non-toxic characteristics.

Firstly, to determine the sensitivity of our recently synthesized non-reported NC, the current response of both bare and coated GCE was monitored by immersing it in 0.2 M PBS with a neutral pH of 7 over an applied potential (0.0 V – +1.5 V), Fig. 7(a). The findings demonstrated that GCE modified with $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NC exhibited an enhanced current response just because of its high electronic communication feature between the surface of GCE and active surface area of coated material. After positive current response, the modified GCE was applied against the urea for its qualitative as well as quantitative determination. Consequently, a significant shift was also noticed in positive current response of fabricated GCE in the presence of urea, particularly concerning the applied potential during I-V measurement just before and after the introduction of 25.0 μL of 0.1 μM urea solution in 5.0 ml PB, as shown in Fig. 7(b). So, this increased current response of modified GCE upon exposure to urea was due to the adequate absorption capability of our target analyte, accompanied by its smaller size, porosity and greater surface area as have been depicted in BET analysis Fig. 3.

Moreover, a selectivity test was also conducted in the company of different toxic chemicals, including 4-Aminophenol (4-AP), Ethanol, Hydrazine, 2-Nitrophenol (2-NP), Bisphenol A (BPA), Creatine, Citric Acid, Nitrate, and 4-Nitrophenol (4-NP) to confirm its specificity towards our target analyte, urea. Regardless of being subjected to a variety of toxic chemicals, our newly synthesized $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NC was found to be incredibly sensitive and selective only for urea, as it exhibits a high current response against the urea, as shown in Fig. 8(a). Throughout this examination, each toxic chemical was uniformly taken at a concentration of 0.1 μM with a corresponding volume of 25.0 μL .

Additionally, an interference effect of above stipulated chemicals towards our newly modified GCE in the presence of urea was also investigated in the form of statistical approach. From this approach it was observed that our newly modified GCE has remarkable affinity for urea at +1.3 V with no significant variation in current response as compared to other toxic chemicals under investigation, as shown in Fig. 8(b) and Table 1. In this investigation, concentration as well as volume of each chemicals was taken as same as for selectivity test and current response of urea was assumed as 100 % in comparison with other toxic chemicals under investigation.

3.4. Proposed mechanism for trace detection of urea

A proposed pathway for an ultrasensitive detection of urea based on $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NC as an electrochemical probe selective only for urea by employing an I-V approach is shown in Scheme 2. Scheme 2(a) exhibits the current response of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NC without our

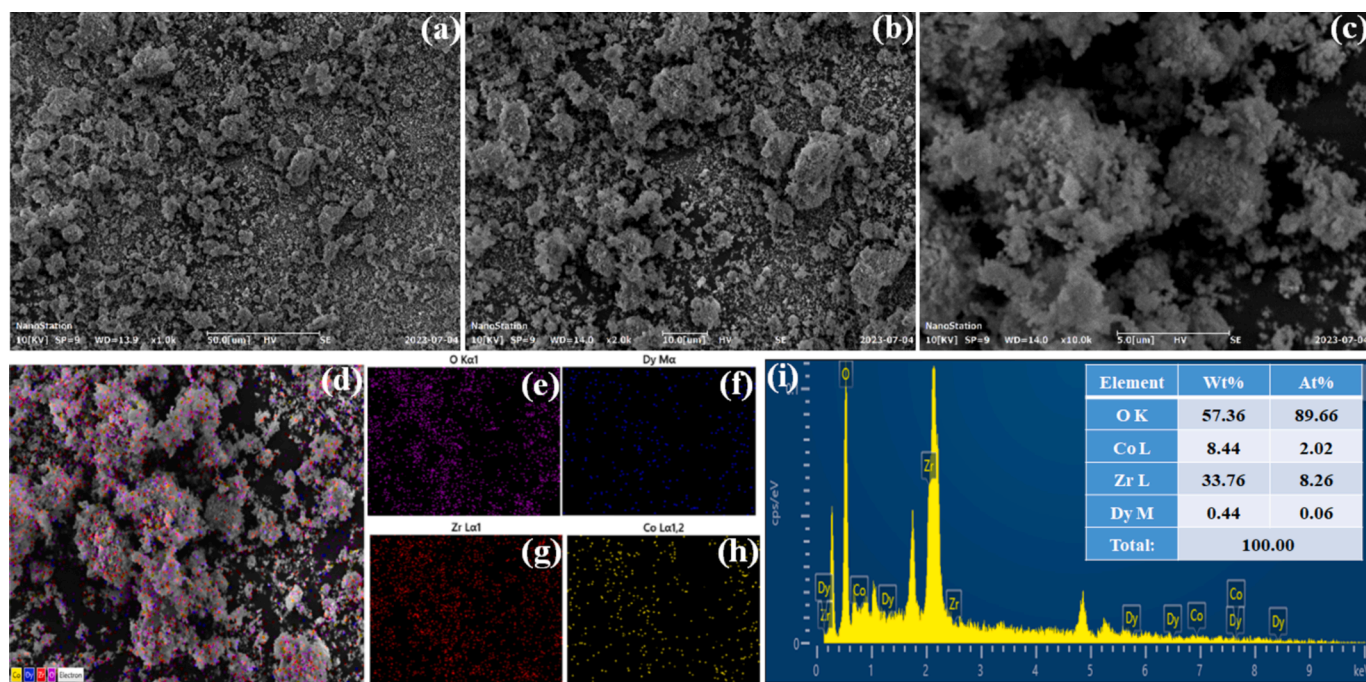


Fig. 4. SEM-EDS mapping of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ nanocomposite; (a-c) SEM Images from low to high resolution; (d) EDS elemental mapping of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$; (e) oxygen; (f) dysprosium; (g) zirconium; (h) cobalt; (i) EDS spectrum along with elemental composition.

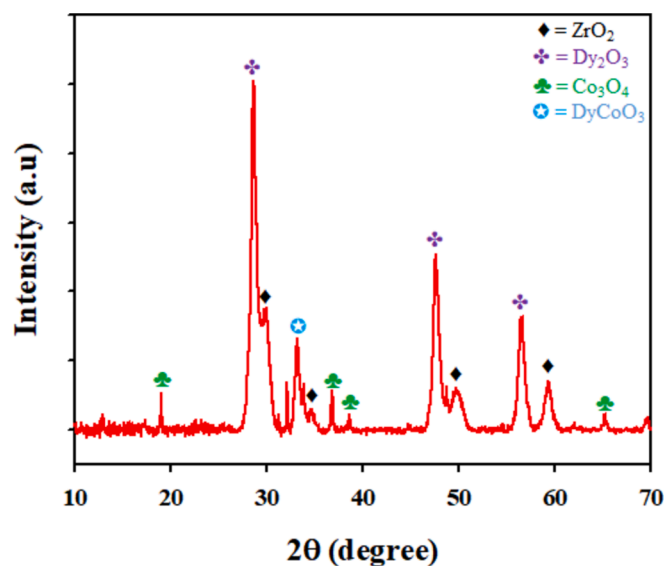


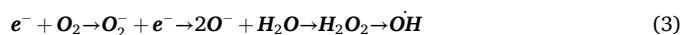
Fig. 5. XRD pattern of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ nanocomposite.

target analyte, urea, while Scheme 2(b) demonstrates a comparison study of responses obtained from coated GCE with and without urea.

It is suggested that the detection of urea is reliant on the electrochemical oxidation or reduction of newly fabricated $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NC coated onto the smooth surface of GCE. When this newly modified GCE is immersed in phosphate buffer, the dissolved oxygen chemisorbed onto porous surface of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NC. This chemisorbed oxygen is converted into its ionic species, namely superoxide (O_2^-) and peroxide (O^-) by gaining electrons from their conduction bands and results in substantial increase in I-V response of newly coated GCE [69,70].



The aforementioned reactions do not come to an end here; instead, they keep going, resulting in excessive generation of free hydroxyl radicals owing to surface-absorbed water [71]. An overall reaction is as follow:



The excess hydroxyl radical in our system converts the amino group of urea into nitroso group, followed by the formation of nitroformamide (NH_2CONO_2) with the release of NO_2^- . After that, NO_2^- is further converted into *NO_2 in conjunction with the production of electrons. This influx of electrons led to a further augmentation of current response during the I-V measurement of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$ under suitable conditions. Similarly, nitroformamide is further converted into carbamic acid by the action of excessive hydroxyl radical in the system and yielding NH_4^+ as well as HCO_3^- as end products, scheme 2, and same have been reported in the literature [44,72,73]. The aforementioned reactions occurred in large quantity on the porous surface of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ nanocomposite. So, adsorbed oxygen on porous surface of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ nanocomposite make it sensitive towards urea and electro-catalytically degrades it. So, rate at which urea oxidize is proportional to the amount of adsorbed oxygen, greater the amount of adsorbed oxygen on porous surface of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ nanocomposite greater its oxidizing capacity toward urea.

3.5. Optimization of newly designed electrochemical urea probe

To optimize the efficacy of our newly designed $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2$ NC as selective electrochemical probe only for urea, various analytical factors, including linear dynamic range (LDR), limit of detection (LOD), limit of quantification (LOQ), sensitivity and coefficient of correlation (r) / r^2 square value, were evaluated from the slope of calibration curve plotted from the concentration variation plot. With this intention, various concentrations of urea, ranging from 1.0 nM – 1.0 M (full concentration ranges), were examined to evaluate the I-V responses against each concentration in an aqueous solution of pH = 7.2. Consequently, a

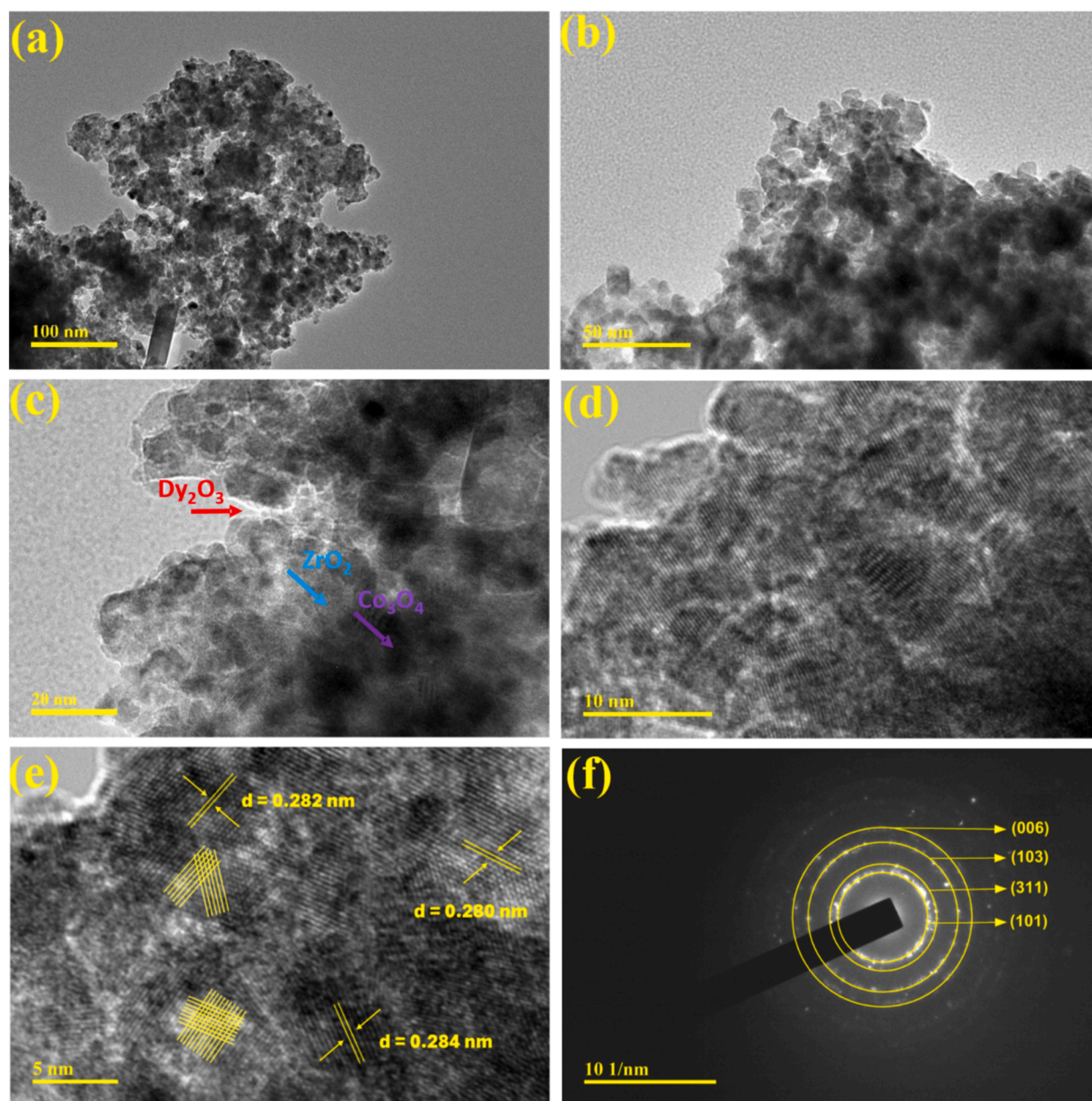


Fig. 6. HRTEM images and SAED pattern of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{ZrO}_2$ nanocomposite: (a–b) TEM images of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{ZrO}_2$ nanocomposite from low to high magnification; (c–e) HR-TEM images showing Lattice fringes along with an inter planar distances in the range of 0.282 nm; (f) selected area electron diffraction (SAED) pattern.

consistent and measurable increase in current response under optimized conditions, from lower to higher values, was observed as a function of urea concentration Fig. 9(a). Afterwards, a calibration curve at a potential of +1.2 V, Fig. 9(b), was precisely plotted from urea concentration variation plot to determine the various analytical parameters mentioned above. Thus, the results for LOD at S/N of 3 over a LDR of 1.0 nM – 10.0 mM was determined to be 0.049 nM in addition to LOQ 0.164 nM. Moreover, the values for sensitivity and coefficient of correlation (r) / r^2 square were found to be $19.47 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$ and $0.9838 / 0.9680$, respectively. Additionally, differential pulse voltammetry (DPV) was also analyzed with the $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{ZrO}_2$ nanocomposite modified electrode in the identical conditions with the 0.1 V/s scan rate. Concentration variation and calibration results are presented in the Fig. 9(c) and Fig. 9(d). Analytical parameters are found as LOD (0.046 nM), LDR (1.0 nM – 10.0 mM), LOQ (0.153 nM), and sensitivity ($18.09 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$).

Herein, the current response of modified GCE against the applied potential (0.0 – +1.5 V), in the presence of 25.0 μL of 0.1 μM urea in 5.0 mL of PBS of different pH was also observed and found to be maximum at pH = 7.2. The enhanced performance of the modified electrode at pH = 7.2 was due to several factors. At this neutral pH, the electrochemical environment is assumed to be optimal for the $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{ZrO}_2$ nanocomposite's catalytic activity. Specifically, at this pH, the electrochemical properties of the nanocomposite, including its charge transfer kinetics and stability, is considered as maximized, resulting in better performance compared to other pH levels. While, current responses under both, acidic and basic, conditions were observed comparatively low as compared to neutral pH, Fig. 10(a). Additionally, the response time of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{ZrO}_2\text{-NC/Nafion/GCE}$ was also examined with regard to urea sensing. It was observed that a saturated steady state is achieved in just only 8 to 15 sec., as illustrated in inset of Fig. 10(b) and (c).

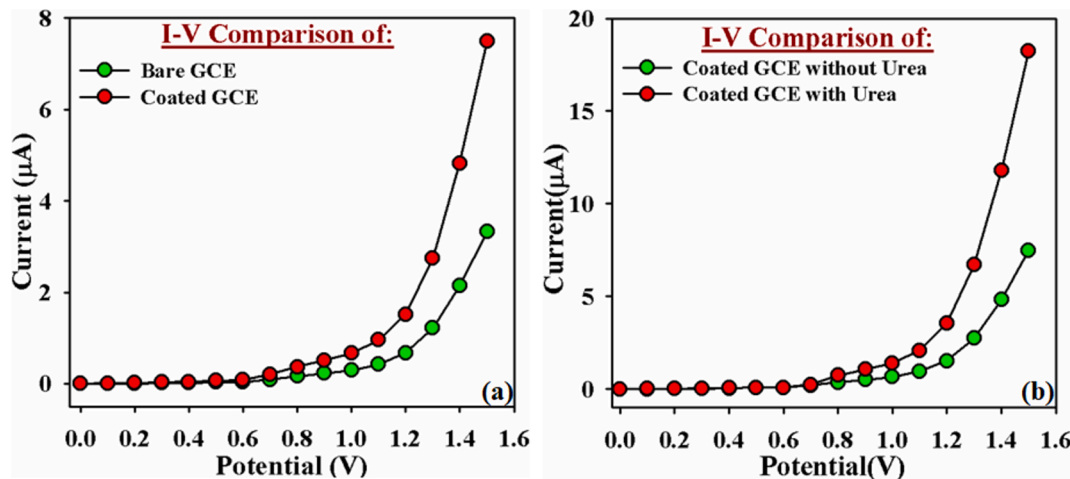


Fig. 7. Comparison of I-V responses of modified GCE; (a) I-V comparison of bare and coated (modified) GCE; (b) I-V comparison of coated GCE with and without urea.

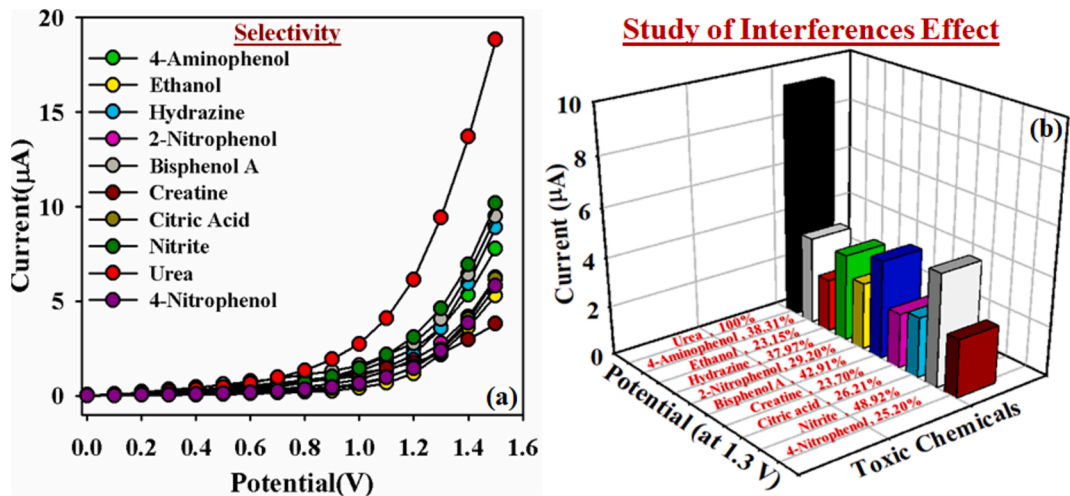


Fig. 8. Selectivity and interference study: (a) Selectivity test of modified GCE with various toxic chemicals and showing maximum response with urea; (b) Study of interference effect of various toxic chemicals towards $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$ in the company of urea at +1.3 V.

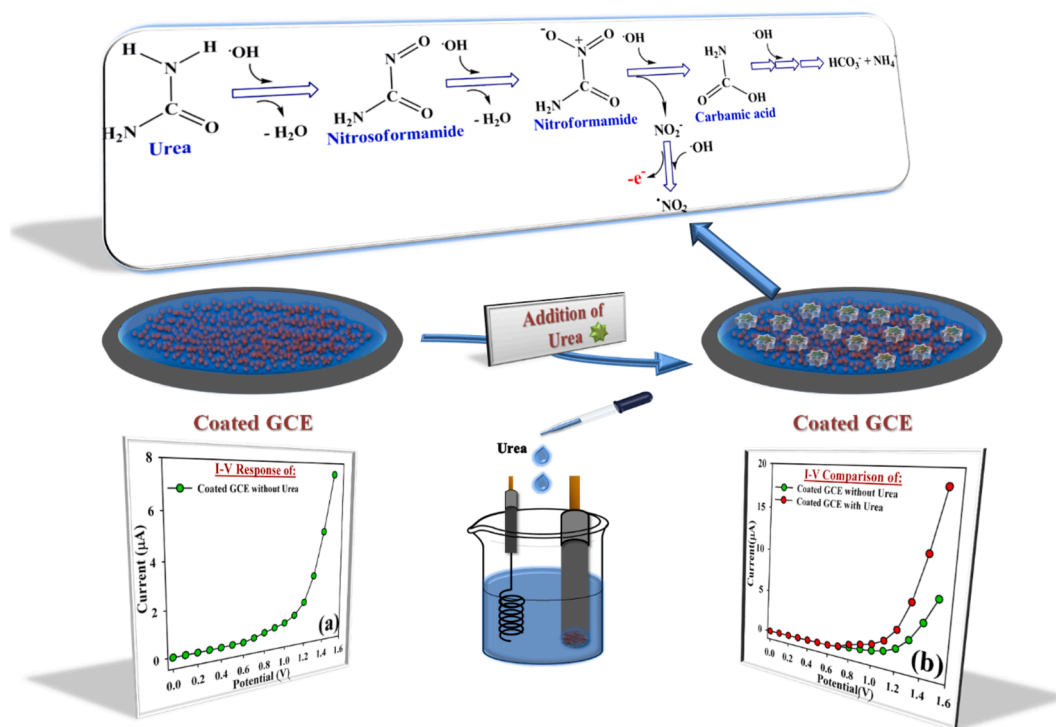
Table 1
Interference Effect of various toxic chemicals on $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$.

Toxic Chemicals	Observed Current (μA)				Interference effect (%)	SD (n = 3)	RSD (%) (n = 3)
	R1	R2	R3	(μ) at 95 % CL			
Urea	9.402	9.385	9.413	9.400 ± 0.03	100.00	0.013	0.15
4-Aminophenol	3.615	3.589	3.600	3.601 ± 0.03	38.31	0.013	0.36
Ethanol	2.170	2.173	2.185	2.176 ± 0.01	23.15	0.007	0.36
Hydrazine	3.587	3.558	3.563	3.569 ± 0.04	37.97	0.015	0.44
2-Nitrophenol	2.735	2.742	2.757	2.745 ± 0.03	29.20	0.011	0.41
Bisphenol A	4.095	4.001	4.006	4.034 ± 0.13	42.91	0.053	1.31
Creatine	2.238	2.230	2.216	2.228 ± 0.03	23.70	0.011	0.50
Citric acid	2.468	2.459	2.466	2.464 ± 0.01	26.21	0.004	0.19
Nitrite	4.592	4.602	4.604	4.599 ± 0.01	48.92	0.006	0.14
4-nitrophenol	2.369	2.367	2.371	2.369 ± 0.00	25.20	0.002	0.08

“Interference effect of urea is consider to be 100 %; R = reading; μ = mean; CL = confidence limit; SD = standard deviation; and RSD = relative standard deviation.”.

Furthermore, to validate the reliability and accuracy of the I-V approach as well as $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$ as selective electrochemical probe for urea, the repeatability and stability tests were also conducted under standard conditions, specifically at 0.1 μM concentration of urea. During the repeatability test, the current response was measured repeatedly, with nine to ten consecutive readings at fixed intervals of 20 min. So, this test showed strong repeatability without any

significant change in current reponse, Fig. 11(a). Moreover, to ensure stability, the I-V response of modified GCE towards urea was also observed for 15 to 16 days and found to be stable and repeatable with no electrode fouling or erosion, Fig. 11(b). It's important to mention here that all these experiments regarding to stability as well as repeatability were performed under the same conditions upto 16 days by using the same electrode after washing with DI water for each run.



Scheme 2. Proposed mechanism for electrochemical detection & hydrolyzing the urea in an aqueous system with graphical representation in comparison.

So, in contrast to other analytical techniques reported in literature, the newly designed $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$, as an efficient electrochemical probe sensitive to urea, showed rapid response time, exceptional accuracy, and long-term stability in addition to its excellent adsorption as well as absorption behaviour, and electrocatalytic capability. Furthermore, the increased surface area and reduced dimensions of the porous nanocomposite, as has also been demonstrated in BET analysis, are responsible for providing a conductive nano-environment for urea detection electrochemically, along with its efficient electronic communication features. An extensive review of literature confirms that this novel I-V approach utilizing $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$ is highly effective and sensitive towards urea, comprising both qualitative and quantitative dimensions, exhibiting a low detection limit, a short response/reaction time, and being convenient to use in contrast to different analytical techniques [48,74–85], as outlined in the following tabular format (Table 2).

3.6. Real sample Analysis

Spike samples that have been collected from different sources were analyzed using the $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$ sensor probe for validation (Table 3). Actual samples were obtained from industrial effluents and bodies of water that were known to contain urea. In order to preserve stability throughout analysis, samples were filtered to eliminate any particulate matter and kept at 4.0°C . Samples were allowed to come to room temperature prior to analysis. To evaluate the accuracy of the modified electrode in terms of urea recovery, a standard urea solution was subsequently introduced into a known volume of each sample. The use of a conventional addition approach involves the use of electrochemical analysis (DPV). The real sample analysis findings were obtained and are shown in Table 3, which shows that the $\text{Au Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$ probe was successfully used to detect and analyze urea in various ambient spike samples. The sensor demonstrated dependability and good performance, suggesting that a fabricated electrode may be used to validate it in a real-world setting using a spike sample.

4. Conclusion

Within the context of this study, a highly efficient electrochemical probe incorporating $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{ NC}$ was fabricated with the intention of investigating its electrocatalytic performance against harmful chemicals. After comprehensive structural characterization of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{ NC}$, an innovative electrochemical approach utilizing I-V analysis was effectively practiced for the first time to investigate as well as an electro-hydrolyze the harmful chemical substances in an aqueous solution using $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{ NC}$ modified GCE as selective electrochemical probe. This newly modified GCE exhibited remarkable specificity exclusively for urea in the presence of other interferences, with an impressively low detection limit of 0.049 nM and a sensitivity of $19.47\text{ }\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$. So, this innovative approach has proven to be simple, proficient, and cost-effective in comparison to other highly sophisticated analytical techniques. Additionally, it also unveils an innovative strategy for the fabrication of advanced electrochemical probes based on semiconductor nano-structured materials for detecting various toxic chemicals beyond their electrocatalytic degradation by employing I-V approach. Moreover, these novel electrochemical, I-V, approach hold tremendous potential for precise and selective detection of harmful chemical substances across various sectors such as health care and environmental conservation on a broad scale.

CRediT authorship contribution statement

Muhammad Zeeshan Rafiq: Writing – review & editing, Methodology, Investigation, Formal analysis. **Amna Siddique:** Writing – review & editing, Methodology, Investigation, Data curation. **Muhammad Fazle Rabbee:** Writing – review & editing, Validation, Resources, Methodology, Data curation. **Shehzada Muhammad Sajid Jillani:** Writing – review & editing, Visualization, Validation, Resources, Investigation. **Jehan Y. Al-Humaidi:** Writing – review & editing, Methodology, Funding acquisition, Formal analysis. **Aqsa Dildar:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Muhammad Tariq Qamar:** Writing – review & editing, Validation, Resources, Methodology, Investigation. **Syed**

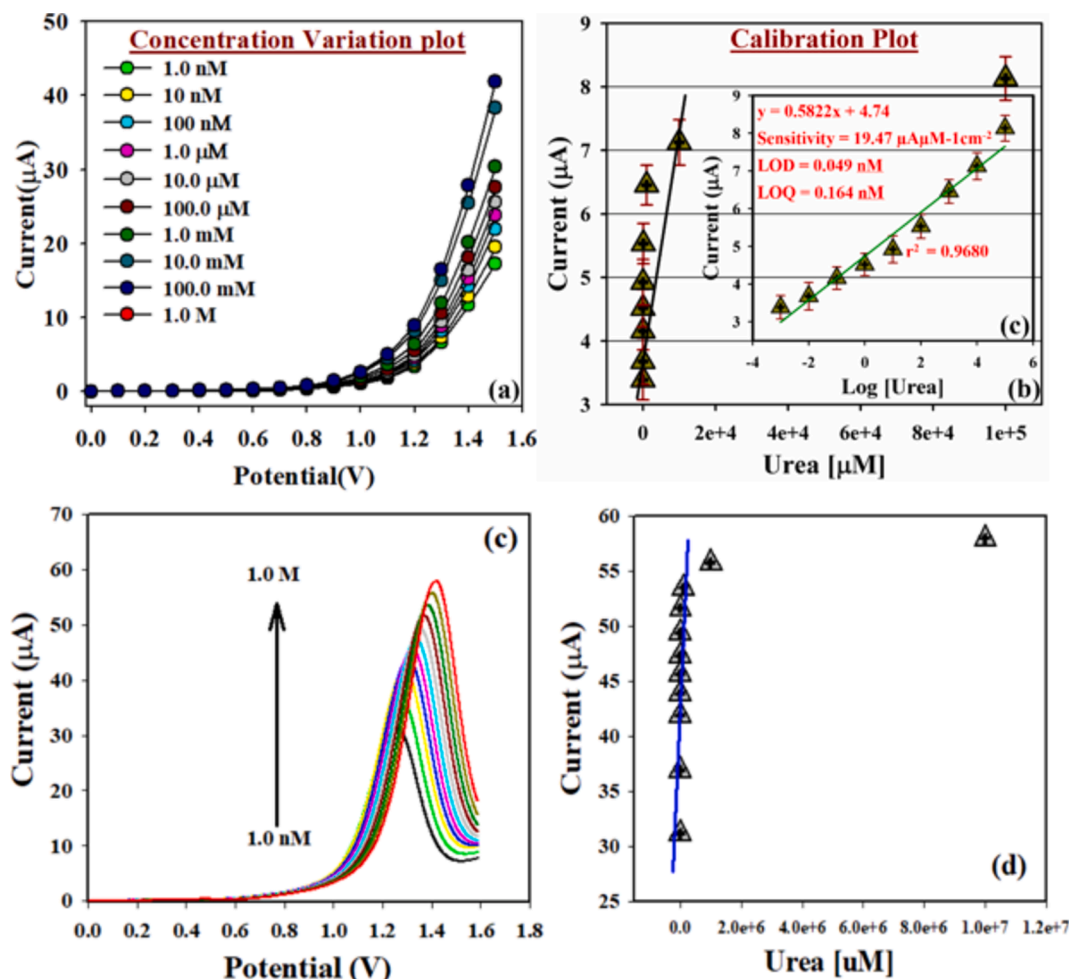


Fig. 9. Optimization of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$ as selective electrochemical urea probe: (a) Concentration variation plot of Urea; (b) Calibration plot of Urea at +1.2; (c) Concentration variation of urea by DPV (Scan rate: 0.1 V/s; Concentration range: 1.0 nM – 1.0 M); and (d) Calibration plot.

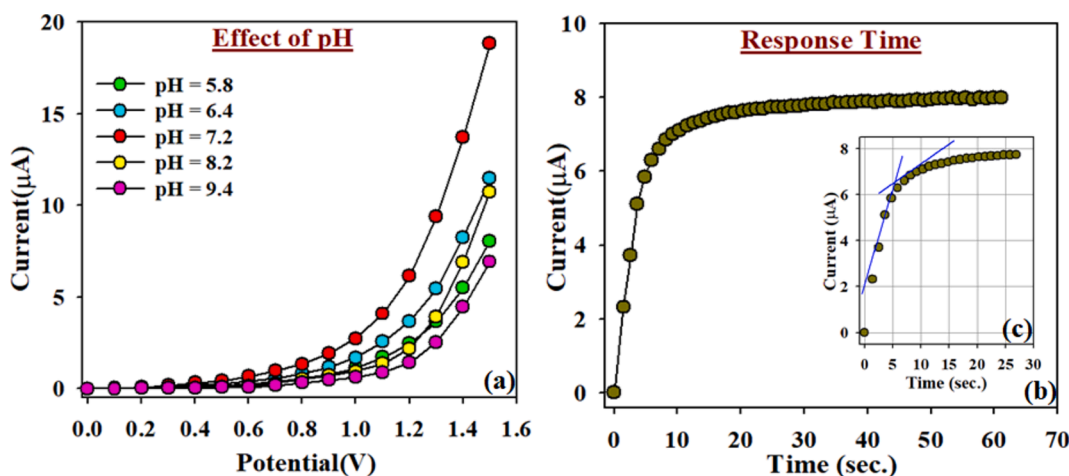


Fig. 10. Effect of pH and response time: (a) Effect of pH on the performance of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$; (b) & (c) Response time plot (time Vs current) of $\text{Dy}_2\text{O}_3\text{-Co}_3\text{O}_4\text{@ZrO}_2\text{-NC/Nafion/GCE}$ against urea.

Kamran Haider: Writing – review & editing, Resources, Investigation, Funding acquisition, Formal analysis. **Muhammad Nadeem Akhtar:** Writing – review & editing, Methodology, Investigation. **M.A. Fazal:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Muhammad Ahmad Khan:** Writing – review & editing, Software,

Methodology, Formal analysis. **Mohammad Mizanur Rahman Khan:** Writing – review & editing, Resources, Methodology, Investigation, Data curation. **Tahir Ali Sheikh:** Writing – original draft, Resources, Methodology, Formal analysis. **Mohammed M. Rahman:** Writing – review & editing, Visualization, Supervision, Formal analysis, Conceptualization.

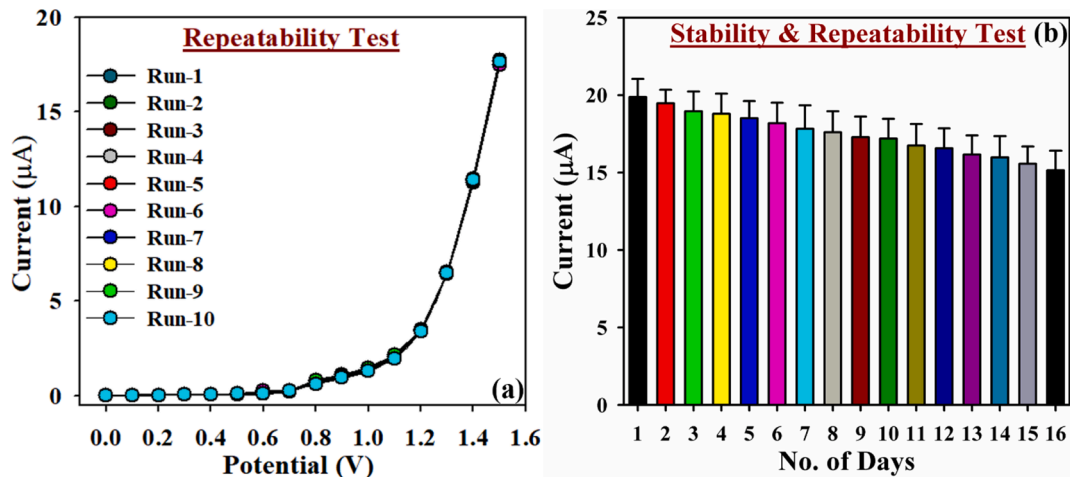


Fig. 11. Repeatability and Stability Test: Conc. and volume of urea was taken as 0.1 µM and 25.0 µL; (a) Repeatability test; (b) Stability test up to 16 days.

Table 2
Comparison of proposed I-V method with previously reported analytical methods for the detection of urea.

Methods / Materials	Sensitivity	LDR	LOD	LOQ	Ref
HPLC	—	—	50 nM	250 nM	[48]
Sol-gel calorimeter	—	0.04–16.5 mM	1660 nM	8320 nM	[74]
Reflectance spectrophotometric / SiO ₂ Nps	—	50–500 mM	10 × 10 ⁶ nM	—	[75]
UV/Vis spectrophotometric/Calcium alginate microsphere	0.09 pH units min ⁻¹	0.017–10 mM	17 × 10 ³ nM	—	[76]
Cyclic voltammetry/ZnO nanorod on Ag/glass electrode	41.64 µA mM ⁻¹ cm ⁻²	0.001–24.0 mM	10 × 10 ³ nM	—	[77]
Cyclic voltammetry /Gold ink@AuMNs	31 nAmM ⁻¹	0.05–2.5 mM	2800 nM	—	[78]
Voltammetry/MIP@ISFET	18.4 mVM ⁻¹	0.1–100 mM	10 ⁵ nM	—	[79]
Voltammetry/SnO ₂ :F@EGFET	109 ± 3 mM pUrea ⁻¹	1.0–7.94 mM	—	—	[80]
CV-SWV /modified polypyrrole-graphene oxide nanocomposite electrode	—	5 × 10 ⁻⁴ –30 × 10 ⁻⁴ mM	270 nM	—	[81]
DPV/Reticulated nickel hydroxide	—	0.1–50 mM	100 nM	—	[82]
Amperometry, impedimetric /Polypyrrole-coated Pt-electrode	1.11 µAµM ⁻¹	0.08–1.44 mM	40 × 10 ³ –50 × 10 ³ nM	—	[83]
Amperometry/ Polyester@AuNP	7.48 nAmM ⁻¹	0.01–35 mM	10 × 10 ³ nM	—	[84]
Photoluminescence /CdSe/ZnS core-shell QD's	—	0.01–100 Mm	10 ³ nM	—	[85]
I-V method Dy ₂ O ₃ -Co ₃ O ₄ @ZrO ₂ -NC/Nafion/GCE	19.47 µAµM ⁻¹ cm ⁻²	1.0 nM–10.0 mM	0.049 nM	0.164 nM	Present work

LDR = Linear Dynamic Range; LOD = Limit of Detection; LOQ = Limit of Quantification; CV = Cyclic voltammetry; CV-SWV = Cyclic voltammetry-square-wave voltammetry; DPV = differential pulse voltammetry; GCE = Graphene carbon electrode; NPs = nanoparticles; MN'S = microneedles; MIPs = Molecularly imprinted polymers; ISFET = Ion-sensitive field effect transistor; EGFET = Extended Gate Field Effect Transistor; QD's = Quantum dots; I-V method = Current-voltage method.

Table 3
Analyzing actual environmental samples with DPV and a conventional addition procedure utilizing a Dy₂O₃-Co₃O₄@ZrO₂-NC/Nafion/GCE sensor probe.

Real samples	Added urea conc. (µM)	Measured urea conc. ^a by Dy ₂ O ₃ -Co ₃ O ₄ @ZrO ₂ -NC (µM)			Average recovery ^b (%)	RSD ^c (%) (n = 3)
		R1	R2	R3		
Industrial effluents	30.00	31.07	32.18	29.85	103.44	3.76
Sea water	30.00	30.68	32.01	30.13	103.13	3.12
Lake water	30.00	30.51	29.06	29.10	98.50	2.79

^a Calculations using Dy₂O₃-Co₃O₄@ZrO₂-NC /GCE were averaged across 3 repetitions (n = 3).
^b Measurement or calculation of urea concentration. (Unit: µM).
^c Accuracy in 3 replicated measurements (R1, R2, and R3) is represented by their relative standard deviation value.

Declaration of competing interest

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.

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Data availability

Data will be made available on request.

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