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A Comprehensive Study of Electrocatalytic Degradation of M-Tolylhydrazine with Binary Metal Oxide (Er_2O_3@NiO) Nanocomposite Modified Glassy Carbon Electrode

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Abstract: Generally, our ecosystem is continuously contaminated as a result of anthropogenic activities that form the basis of our comfort in our routine life. Thus, most scientists are engaged in the development of new technologies that can be used in environmental remediation. Herein, highly calcined binary metal oxide (Er_2O_3@NiO) semiconductor nanocomposite (*NC*) was synthesized using a classical wet chemical process with the intention to both detect and degrade the toxic chemicals in an aqueous medium using a novel electrochemical current–potential (*I–V*) approach for the first time. Optical, morphological, and structural properties of the newly synthesized semiconductor *NC* were also studied in detail using FT-IR, UV/Vis., FESEM-EDS, XPS, BET, EIS, and XRD techniques. Then, a modified glassy carbon electrode (GCE) based on the newly synthesized semiconductor nanocomposite (Er_2O_3@NiO-*NC*/Nafion/GCE) as a selective electrochemical sensor was fabricated with the help of 5% ethanolic-Nafion as the conducting polymer binder in order to both detect and electro-hydrolyze toxic chemicals in an aqueous medium. Comparative study showed that this newly developed Er_2O_3@NiO-*NC*/Nafion/GCE was found to be very selective against m-tolyl hydrazine (m-Tolyl HDZN) and to have good affinity in the presence of other interfering toxic chemicals. Analytical parameters were also studied in this approach to optimize the newly designed Er_2O_3@NiO-*NC*/Nafion/GCE as an efficient and selective m-Tolyl HDZN sensor. Its limit of detection (LOD) at an SNR of 3 was calculated as 0.066 pM over the linear dynamic range (LDR) of our target analyte concentration (0.1 pM–0.1 mM). The limit of quantification (LOQ) and sensitivity were also calculated as 0.22 pM and 14.50 $\mu A \mu M^{-1} cm^{-2}$, respectively. m-Tolyl HDZN is among the toxic chemicals in our ecosystem that have lethal effects in living beings. Therefore, this newly designed electrochemical sensor based on semiconductor nanostructure material offers, for the first time, a cost-effective technique, in addition to long-term stability, that can be used as an alternative for efficiently probing other toxic chemicals in real samples.

Keywords: binary metal oxide nanocomposite; Er_2O_3@NiO; electrocatalytic degradation; m-tolyl hydrazine detection; electrochemical method; current–potential (*I–V*) approach; glassy carbon electrode; real sample analyses

Citation: Sheikh, T.A.; Asiri, A.M.; Siddique, A.; Marwani, H.M.; Rahman, M.R.; Akhtar, M.N.; Rahman, M.M. A Comprehensive Study of Electrocatalytic Degradation of M-Tolylhydrazine with Binary Metal Oxide (Er_2O_3@NiO) Nanocomposite Modified Glassy Carbon Electrode. *Catalysts* **2023**, *13*, 905. https://doi.org/10.3390/catal13050905

Academic Editors: Tahir Muhmood and Xiaofei Yang

Received: 26 February 2023
Revised: 12 May 2023
Accepted: 16 May 2023
Published: 19 May 2023

1. Introduction

Recently, the advancement in nanoscience and nanotechnology has attained the impressive attention of many scientists owing to the significant impact of these technologies on the growth in this modern era of science. These technologies have a wide range of commercial applications in food industries [1], pharmaceutical industries [2], chemical industries [3], energy conversion and storage devices [4–6], and many other domains of life, in addition to toxic chemical sensing in our ecosystem [7–9]. Their advancement relies on the production of semiconductor nanostructure materials of different kinds of metal oxides, along with their unique morphologies at nano scales. Compared to their bulk substances, semiconductor nanostructure materials of different metal oxides have highly impressive physio-chemical properties, such as electrical, optical, mechanical, and magnetic properties, besides catalytic and thermal stability, and can be used for various purposes [10,11]. Similarly, advanced research on semiconductor nanostructure materials has also shown that doped semiconductor nanostructure metal oxides have gained popularity in the field of nanoscience as they have impressive and excellent enhanced physio-chemical properties [12–14]. Moreover, these physio-chemical properties can also be modulated according to our requirements by doping or co-doping of inner or outer transition metal oxides in different proportions into pure intrinsic semiconductor nanostructure metal oxides [15].

Recently, many researchers have focused their research on the field of advanced materials by developing different kinds of doped/undoped semiconductor nanostructure materials, with the aim of environmental remediation, for the detection, removal, and degradation of ubiquitous contaminants via different analytical approaches [16–20]. Among these various analytical approaches, different electro-analytical approaches based on doped or undoped semiconductor nanostructure materials, as well as on heteronuclear nanostructure composites, have been also reported in the literature for the detection of toxic chemicals in our ecosystem [21–23]. Subsequently, the good electron communication feature of semiconductor nanostructure materials form the basis of electrochemical sensing of toxic chemicals, in addition to their electrocatalytic degradation by advanced oxidation processes (AOPs). Although rare earth elements are not too much efficient in electrical conductivity but their electrochemical performance can be further enhanced by doping, in a very minute quantity, or mixing, in bulk with semiconductor transition metal oxides [7,24]. Thus, in this work, a binary metal oxide semiconductor nanostructure composite of erbium oxide in combination with nickel oxide (Er_2O_3@NiO) was synthesized with the intention to evaluate its electrocatalytic behavior against various toxic chemicals in an aqueous system. Results showed it to be both selective and effective against m-Tolyl HDZN. Moreover, the nanomaterials Er_2O_3 and NiO are individually thought to be multifunctional because of their prestigious physio-chemical properties [25–34], and have a wide range of applications in biomedical [34–37], chemical [38,39], thermal conductivity [40,41], pharmaceutical [42–45], sensing [15,24,46,47], electrochromic [48,49], energy storage [50–52], agri-science [53–55], and catalysis fields [56–62].

Hydrazine and its derivatives are used as raw materials that are involved in different kinds of chemical reactions during the production of final products in different domains of chemical industries, such as in the manufacture of pesticides, plant-growth regulators, dyes, paint, pharmaceuticals, and polymers [63–67]. Moreover, unprocessed effluents from these industries also contain traces of respective hydrazine compounds that are continuously contaminating our ecosystem. Our newly designed non-reported binary metal oxide(Er_2O_3@NiO) semiconductor nanocomposite (*NC*) was found to be effective against m-Tolyl HDZN, which is a derivative of hydrazine that has been declared toxic and carcinogenic in nature by the National Institute for Occupational Safety and Health (NIOISH) and the US Environmental Protection Agency (EPA) [68]. It is also known as a nephrotoxic and cynogenic chemical. It causes cancer and chronic damage to the kidney, and for this reason is known as being a nephrotoxic chemical. Similarly, it also causes hazardous effects in the liver, lungs, and central nervous system (CNS), in addition to headaches, dizziness, vomiting, and some allergic reactions in the skin, eyes, and respiratory tract if exposed to it for a long time [68–71]. So, various research techniques, such as ultra-high-performance liquid chromatography–tandem mass spectrometry [72], high-performance liquid chromatography coupled with a UV detector [73],