Enhanced Photocatalytic activity and Chemical sensor development based on ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials for environmental safety

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Abstract

Synthesis of ternary $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterials by simple co-precipitation method and potentially applied as an efficient photocatalyst and chemical sensor has been reported. The synthesized nanomaterial was studied by XRD, SEM, EDS mapping, Photoluminescence (PL), FTIR, UV-Visible Spectroscopy. This nanocomposite exhibits enhanced efficiency in photo-catalysis in Methyl Violet 6b (MV) dye degradation. It has observed the efficiency of 97.24% under visible light and 78.98% under UV light at pH 9. Moreover, it loses only 2.61% efficiency over third time reuse. Even more, in presence of H_2O_2 , it can degrade over 98% dye within just 1 hour. PL and PLE property was also reported with the change of excitation energy and calcination temperature. The PLE shows three equidistant peaks with 20 nm intervals. For potential chemical sensor development, $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterial was deposited on a glassy carbon electrode (GCE) to give a sensor with a fast response towards selective 4-aminophenol (4-AP) in phosphate buffer phase. The sensor also exhibits good sensitivity and long-term stability, and enhanced electrochemical responses. The calibration plot is linear over the 0.1 nM to 0.01M 4-AP concentration ranges. The sensitivity and detection limit is calculated from the slope of calibration plot as $0.506329 \mu\text{Acm}^{-2}\text{nM}^{-1}$ and 0.019 nM (signal-to-noise ratio, at a SNR of 3) respectively. It is also commenced a promising future efficient photocatalyst and sensitive chemical sensor development using ternary $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterials for the potential applications of hazardous and carcinogenic toxic commercial dyes and phenolic compounds for the safety of environmental and health care fields.

Key words: Ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials; Photocatalysis; Methyl Violet dye; Photoluminescence; Chemical sensors; 4-Aminophenol; Environmental safety

Introduction

Metal oxides are one of the most significant and widely employed categories of solid catalysts, either as active phases or as supports. Metal oxides are utilized both for their acid-base and redox properties and constitute the largest family of heterogeneous catalyst system.¹⁻² Metals and metal oxides form the bulk of catalysts employed for many synthetic conversions. Suitable metals are commonly used as catalysts and their activity has been attributed to the outer electron configuration.³ Some of the mixed metal oxides are better in terms of their catalytic activity than component oxides in various reactions.^{4,5} It is well established that many characteristics of functional materials, such as composition, crystalline phase, structural and morphological features, and the surface-interface interaction properties can greatly influence the performance. Nanostructures of Boron and Boron related compounds like boron accumulated mixed oxides have lately predicted to possess exclusive properties superior to those of other one-dimensional nanomaterials, i.e., carbon nanotubes (CNTs). For example, theoretical studies projected that boron nanotubes have metallic conductivities⁶⁻⁸ and boron nitride nanotubes are insulators,⁹ whilst CNTs are either metals or semiconductors.¹⁰ To date, a variety of boron and boride compound nanostructures¹¹⁻²⁵ have been synthesized by various methods. These one-dimensional boron-related nanomaterials have great potential to go far beyond the limits of top-down manufacturing with exceptional properties.^{26, 27} Moreover, they are important for future applications in nano device fabrication. Zinc Oxide is a unique material with 3.37 eV direct band gap and 60 meV exciton binding energy making it extraordinarily expedient for material development.^{28, 29} It has been widely used in near-UV emission, gas sensors, transparent

conductor, and piezoelectric applications.³⁰⁻³³ Despite that, it is established in the literature that mixing two dissimilar oxides adds another parameter since they are liable to form new stable compound, which can lead to totally different physicochemical properties and catalytic behavior.^{34, 35}

In recent years, chemical sensing expedition has been being utilized with the metal oxide nanostructures for the detection of a wide range of chemicals such as phenyl hydrazine, ethanol, methanol, hydrazine, chloroform, dichloromethane, acetone, etc., which are not environment friendly.³⁶⁻³⁹ The sensing mechanism with metal oxides thin films utilized mainly the properties of porous film formed by the physi-sorption and chemi-sorptions methods. The chemical detection is based on the current changes of the fabrication thin films caused by the chemical components of the reacting system in aqueous medium.^{40, 41} 4-aminophenol is used in oil, lubricants and as photographic developer. It is also used as an intermediate in the production of different kinds of analgesics and antipyretic drugs. As N-acetylated form it is used as the main component of paracetamol, a drug of anti-inflammatory and analgesic capacities.⁴² 3-aminophenol is used as the marker in analysis of antibacterial drugs – sulphonamides⁴³ and 2-aminophenol is used as the precursor for indols synthesis. All isomers of aminophenols and 2,4-diaminophenol are used in dyes used in colouring of hair.⁴⁴ The presence of 4-aminophenol in urine is the marker of paracetamol and aniline influence of human organism. People of highest occupational exposure to aniline are workers employed in rubber production and processing.⁴⁵

Considering the above-mentioned factors, ternary metal oxide, $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ was utilized to develop a potential sensor for selective 4-AP at room conditions using 5% nafion as a coating agent with flat GCE. The developments of reliable and sensitive methods were used for the detection of phenolic compounds for environmental safety, protection, food quality control,

and health.^{46,47} There are several phenolic compounds have been classified as “priority pollutants” by both the United States Environmental Protection Agency (USEPA) and the European Commission. Phenolic compounds are comparatively general in waste streams of diverse large-scale processing and manufacturing where they serve as precursor materials in various industries such as coal mining, crude oil refining, paper bleaching, and production of dyes, resins, plastics, explosives, detergents, pharmaceuticals, pesticides, and herbicides.^{48, 49} In difference, few phenols of plant origin have been originated to display a broad range of attractive physiological characteristics as antioxidants, anti-inflammatories, and cardiovascular prophylactics, promoting their use as additives in some alcoholic beverages and food products.^{50,51} Recent determination methods are usually perceptive and consistent but possess limitations that increase the risk of sample loss and generation of other hazardous byproducts.⁵² Electrochemical sensing of phenolic compounds represents a promising approach that can be utilized to complement already existing methods owing to collective characteristics such as high sensitivity and selectivity, low cost, simple instrumentation and potential for miniaturization.^{53,54} Here, the ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials have significant properties such as large surface area (surface-to-volume ratio), non-toxicity, chemical stability, and high electrical conductivity; which offered high electron communication features that enhanced the direct electron communication towards the target toxic analytes. As 4-AP is highly carcinogenic and serious to health and environment, it is urgently required to fabricate a simple and reliable chemical sensor with ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials. Consequently, the 4-AP sensing properties of ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials films have been investigated and explained in term of fabrication and their typical electrochemical characteristics. The simple fabrication technique is used for the preparation of ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials on

flat GCE with conducting coating binders, which is measured by simple and reliable I-V technique. To best of our knowledge, this is the first report for sensitive detection of 4-AP with ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials using simple I-V technique in short response time.

Experimental section

Materials and methods

H_3BO_3 (Sigma Aldrich, Germany), $AlCl_3 \cdot 6H_2O$ (Sigma Aldrich, Germany), $Zn(NO_3)_2 \cdot 6H_2O$ (MERCK, India), Na_2CO_3 (AR, BDH) were purchased and used as supplied. Analytical grade of 4-amino phenol, 3-methoxy phenol, 3-chlorophenol, disodium phosphate (Na_2HPO_4), 2,4-dinitrophenol, 2-nitrophenol, 4-methoxyphenol, bisphenol A, hydrazine hydrate, phenylhydrazine, p-nitrophenol, and monosodium phosphate (NaH_2PO_4) was used and purchased from Sigma-Aldrich Company, USA. The identification of bulk crystal phase and other relevant structural information of the materials studied in this work was characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer, equipped with a graphite monochromator). The diffraction patterns were recorded in the step scan mode at 0.05 steps and at a measurement rate of 10 s/step. The diffraction patterns were registered within the 2θ angle range from 10° to 80° . The surface morphology and nano-structural characterizations were conducted using a Scanning Electron Microscope (SEM) equipped with an Energy-Dispersive X-ray Spectrometer (EDS) (JSM-7100F) linked with an EDS (Oxford) mapping device. The transmission mode Fourier transform infrared spectroscopic (FTIR) analysis of the samples was carried out using a FTIR spectrometer (Shimadzu, FTIR-8400S) with KBr as reference matrix. Photoluminescence behavior of the synthesized nanomaterial was studied by a spectrofluorophotometer (Shimadzu Corp. model RF-5301), and photocatalytic activity was observed

with the help of double beam UV-Visible spectrophotometer (UV-1800 Series, Shimadzu Corporation, Kyoto, Japan). I-V technique was executed by using Electrometer (Keithley, 6517A, Electrometer, USA) for measuring the current responses in two electrode systems for target 4-AP chemical sensor based on ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials in buffer phase at room conditions, where flat-GCE and Pt-wire was used as working and counter electrode respectively.

Synthesis of ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials:

Simple co-precipitation method was used to synthesize $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterial. This synthetic process was started by preparing 0.25 M solutions of H_3BO_3 , $AlCl_3 \cdot 6H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$ which act as sources of Boron, Aluminum, and Zinc respectively. All of them were mixed in a beaker in same volume ratio with constant stirring for 15 minutes. In this triple metal mixture 0.5 M Na_2CO_3 was added dropwise until completion of the reaction at 45 °C. The resultant mixture was stirred for a further 1 hour at 45 °C with constant stirring. After terminating the reaction, the white precipitate was separated from the solution by centrifugation, washed several times with deionized water and finally dried at 120 °C in an oven for 2 hours. The obtained white precipitate was crushed in a mortar to make it amorphous. Then the amorphous powder sample was calcined in electric muffle furnace (Gallenkamp, Korea) at 900 °C, 600°C and 450°C for three hours.⁵⁵ The calcinations converted the carbonates of the sample into their oxides.⁵⁶

Fabrication of sensor with ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials:

Phosphate buffer solution (PBS, 0.1 M, pH 7.0) was made by adding of 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 solution in 100.0 ml deionized water. GCE (surface area 0.0316 cm²) was

fabricated by ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials with ethanol and nafion as a conducting binding agent. Then it is left to dry for 1h until the film is completely uniform and dry. An electrochemical cell is constructed with ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials coated GCE as a working electrode and Pt wire is used a counter electrode. As received 4-AP chemical is diluted at different concentrations with DI water and used as a target chemical. Amount of 0.1 M PBS is kept constant in the beaker as 5.0 ml throughout the total chemical analysis. Analyte solution is arranged with various concentrations of 4-AP from 0.1 nM to 0.1 M. The ratio of current versus concentration (slope of calibration curve) is used to calculate the 4-AP sensitivity. Detection limit is evaluated from the ratio of $3N/S$ (ratio of Noise $\times$ 3 vs. Sensitivity) from the linear dynamic range of calibration curve. Electrometer is used as a constant voltage sources for I-V measurement in simple two electrode system. Amount of 0.1 M PBS was kept constant in the beaker as 5.0 mL throughout the chemical investigation. I-V response is measured with $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /nafion/GCE film.

Results and discussion:

Structural characterization of ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials

By the XRD pattern in Fig 1, Orthorhombic, Ccm21(36) B_2O_3 formation can be established as there are peaks at 2θ values (h k l) of 38.87° (2 0 0), 44.744° (2 0 1), 50.05° (2 2 1), 59.843° (2 0 2), and 62.852° (2 4 0). They correspond to the powder diffraction file (PDF) number PDF#76-0781. Hexagonal P63mc(186) ZnO can be confirmed by the peaks arising at 2θ value of 31.791° (1 0 0), 34.451° (0 0 2), 36.252° (1 0 1), 47.552° (1 0 2), 56.594° (1 1 0), 62.852° (1 0 3), 66.348° (2 0 0), 67.904° (1 1 2), and 69.05° (2 0 1) (file PDF#99-0111).²⁸ Finally, the Cubic, Fd-3m(227)Zinc-Aluminum Oxide or $Zn_6Al_2O_9(Al_2O_3 \cdot 6ZnO)$ formation is indicated by 34.451° (2 2 0), 36.252° (3 1 1), 47.552° (3 3 1), 56.594° (4 2 2), and 62.852° (5 1

1) peaks (PDF#51-0037). The particle size was calculated to be 39.3 nm. XRD data was used to determine the particle size of the synthesized nanomaterial. To do so individual contributions to peak broadening have to be considered first.

$$\beta_r \cos\theta = \frac{K\lambda}{D} + \eta \sin\theta \quad (1)$$

$\beta_r \cos\theta$ vs. $\sin\theta$ plot can provide straight line with slope $\approx$ the lattice strain, η , and an intercept equal to $K\lambda/D$. Basically, the larger the intercept, the smaller the particle size. Using $\beta_r \cos\theta$ vs. $\sin\theta$ plot (Fig. S1) the particle size and strain was calculated. The particle size 39.3 nm was obtained from the intersection of the straight line to y-axis and strain 0.08%, obtained from the slope of that line.

Fig. 1: X-Ray Diffraction pattern of ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials

Morphological and elemental analysis of ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials

Scanning Electron Microscope images in Fig. 2 (a) revealed morphology of nanomaterial, $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$. The SEM image showed an aggregation of nanoparticles with the average diameter is 78.1 nm, in the range of 62.5 ~ 125.0 nm. Fig. 2(a) and Fig. (b) showed that nanoparticle formed a complex porous nanostructure which might have high surface area, resulting perhaps the higher catalytic activity.

Fig. 2: SEM image of synthesized $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials

Furthermore, SEM-EDS was carried out to map the elemental distribution throughout the nanomaterial. As is evident, the NPs are composed of B, Al, Zn, and O with atomic percentage

of 3.95%, 17.71%, 19.42%, and 58.92% (Fig S2 and Table S1). Furthermore, SEM-EDS mapping indicated that elements were not confined in a specific space rather they were evenly distributed throughout the entire matrix (Fig S3).

Optical properties of ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials

The bands centred at 3475 cm^{-1} in FTIR spectrum of this nanomaterial can be assigned to stretching mode of H_2O absorbed from the environment.⁵⁷ The sample calcined at $900\text{ }^\circ\text{C}$ showed the stretching mode of B-O at 1529 cm^{-1} , 1429 cm^{-1} , and 1377 cm^{-1} . They are centred at 1429 cm^{-1} .⁵⁸ Zn-O band of ZnO nanoparticle appeared at 565 cm^{-1} .⁵⁹ 1029 cm^{-1} and 837 cm^{-1} peaks are due to Al-O vibrational oscillation of the molecules which matched exactly with the theoretical value calculated by DFT/B3LYP method.⁶⁰ In this spectrum there is no peaks at 873 cm^{-1} , which may indicate that there is no CO_3^{2-} left in the final sample. Similarly, absence of the $2260\text{-}2510\text{ cm}^{-1}$ peaks confirmed the absence of B-H bond. This nanomaterial is thus only oxides with little or no alien bonds (Fig. S4).

PL Study of ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials

Photoluminescence measurement was carried out in acetone. The sample was dispersed in acetone by ultra-sonication. Optical excitation was provided by a Xenon discharge lamp. PL data were taken in both 250 and 300 nm excitation energy for $900\text{ }^\circ\text{C}$, $600\text{ }^\circ\text{C}$, and $450\text{ }^\circ\text{C}$ calcined nanomaterial as shown in Fig. 3 (Table S2).

Fig. 3: PL of sample calcined at (a) 900 °C, (b) 600 °C, (c) 450 °C; and (d) PLE in 600 °C

The photoluminescence spectrum changes with the change in calcination temperature. This indicated the temperature dependent optical properties of this nanomaterial. Sample calcined at 900 °C (in Fig. 3 (a)) showed peaks at 369, 404, 412, 425, 450, 467, and 482 nm when it was excited by 250 nm wavelength. Moreover, when it was excited with 300 nm wavelength it showed peaks at 381, 404, 428, and 451 nm. A peak at 369 nm disappeared with the transition of excitation energy from 250 to 300 nm. In a similar context, when 600 °C calcined composite (Fig. 3 (b)) was excited by 250 nm light energy it emitted at 386, 404, 422, 450, 467, 482, and 492 nm and in case of 300 nm excitation, peaks were at 404, 412, 421, 450, 467, and 482 nm. Here also, the peak at 386 nm disappeared with the change in excitation

wavelength. Likewise, nanomaterial calcined at 450 °C (Fig. 3 (c)) was excited at 250 nm and observed peaks at 340, 404, 426, and 450 nm. Similarly, when excited at 300 nm wavelength, it emitted photons at 404, 426, and 450 nm. With the change of excitation wavelength 340 nm peaks diminished.

This sample was also subjected to observe photoluminescence excitation (PLE) spectra monitored at 600 nm. PLE showed an interesting characteristic. It showed peaks at 350, 370 and 390 nm and all of them are equidistant. They are 20 nm apart from one another. Deconvolution of the spectrum showed the location of the exact peak position at 343 nm (3.61 eV), 370 nm (3.35 eV) and 392 nm (3.16 eV) (Fig. 3(d)).

Applications:

(a) Photocatalytic activity of MV dye with $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials

In the UV-Visible spectrum it was clear that the synthesized nanomaterial showed plasmonic optical characteristics which lead to the assumption that it might be a good photocatalyst. To make this point and understand the efficiency and applicability of this nanomaterial, a series of photocatalytic tests were done.

In order to study the photocatalytic property, 50 mg of synthesized catalyst was added into the dye solution (1×10^{-4} M), the pH was adjusted with 0.1 M HCl or 0.1 M NaOH as required. The dye solution (100 ml) was kept in a cylindrical Pyrex beaker of 5 cm. diameter and. In order to ensure adsorption/desorption equilibrium, the solution was stirred for about 1 hour in dark, prior to the irradiation. Natural sun light was used as visible light source and an array of ultraviolet tubes (Germedical Lamp G-10T8, 10W, 362 nm) for UV light source. The reactor was set in open air in case of visible light source. 4 ml of samples were collected at regular intervals and dye solutions were separated from the photo-catalyst by centrifugation

before analysis. The change of concentration of dye solution was measured spectrophotometrically using Shimadzu-1800 double beam spectrophotometer. The photocatalytic efficiency in different pH solution was calculated using the expression (equation i)

$$\eta = (1 - C/C_0) \times 100 \quad (i)$$

where C_0 is the concentration of MV before illumination and C is the concentration after irradiation time.⁶¹ Photocatalytic activity was done under different light source to identify the optimum energy range.

According to the earlier reports^{62,63} most N-de-alkylation processes can be preceded by the formation of a nitrogen-centered radical while destruction of dye chromophore structures can be headed by the generation of a carbon-centered radical. Consistent with this, degradation of Methyl Violet should occur via two different photo-degradation pathways (destruction of the chromophore structure and N-de-methylation) due to the formation of different radicals (either a carbon-centered or nitrogen-centered radical). There is no doubt that the $\bullet\text{OH}$ attack on the dye yielded a cationic radical $\text{dye}\bullet^+$, which can then undergo hydrolysis and/or follow various deprotonation pathways.

The analysis was started by optimizing the irradiation light source. So, first of all photocatalytic efficiency was measured at a specific pH (pH-9) under Visible and UV light for an aqueous suspension of MV dye. Natural light was used as visible light source and 10W low pressure mercury lamp was used as UV light source. Fig. 4 represents the UV-Visible spectra of the photocatalytic degradation of MV dye as a function of irradiation time (a) under Visible light and (b) under UV light source. It can be seen that the maximum absorbance of MV at 570 nm gradually decreases with increasing irradiation time. As visible light has a wide range of electromagnetic radiation, it facilitated the excitation of this nanomaterial, hence showed

enlarged efficiency. The plasmonic type absorbance band assisted this process. This catalytic study showed percent efficiency of 97.24% under visible light and 78.98% under UV light source. From this data, it is obvious that our synthesized nanomaterial has vast applicability and has the potential to be a great catalyst.

Fig. 4: The graph represents the photocatalytic activity of synthesized nanomaterial at pH-9 under (a) UV and (b) Visible light; (c) and (d) are comparison of catalytic efficiency.

Influence of catalyst activator in this study was also investigated. H_2O_2 was used as catalyst activator. When this hetero-structured nanomaterial is illuminated with electromagnetic radiation with photon energy higher or equal to the band gap of ZnO, electrons in the valence band (VB) can be excited to the conduction band (CB) leaving the corresponding holes in the valence band (VB). For pure ZnO, these photo-generated electrons and holes are easy to recombine within a time scale of nanoseconds.⁶⁴ For this nanomaterial, its Fermi energy level

(E_f) is lower than the energy level of the bottom of the CB of pure ZnO so the photo-excited electrons could transfer from ZnO nanoparticles to B or Al nanoparticles. It has been proposed that a Schottky barrier formed at the interface between metal and semiconductor, while the holes can remain on the semiconductor surfaces.⁶⁵ The addition of H_2O_2 to the heterogeneous system (equation ii) increases the concentration of $\bullet OH$ radicals.

Being an electron acceptor, H_2O_2 does not only generate $\bullet OH$ radicals (equation iii) but it also inhibits the electron hole recombination process at the same time.

When the H_2O_2 concentration becomes high, the excess H_2O_2 consumes hydroxyl radicals and it performs like hydroxyl radical scavengers.⁶⁶

The similar theoretical enhancement of radical formation can be observed in our study. This process was carried out by adding 2.5 mM H_2O_2 in the reaction suspension (dye + catalyst) prior to light irradiation. The performance of the synthesized nanomaterial was boosted by the addition of the hydrogen peroxide along the catalyst for degradation. Fig. 5 showed the spectra of (a) only catalyst and (b) H_2O_2 with catalyst degradation and (d-e) are efficiency comparison. In this study one of the key point to note is that only catalyst took 240 minutes to degrade 97.24% whereas introduction of H_2O_2 only required 60 minutes to degrade 98.95% of the dye concentration. This dramatic increase in the efficiency of this catalyst can be explained by the formation of $\bullet OH$ radicals in presence of H_2O_2 .

Fig. 5: UV-Visible spectra of Visible light degradation at (a) pH-9, (b) pH-9 with H_2O_2 ; (c), and (d) are their efficiency comparison; (e) reusability of catalyst for visible light degradation at pH-

In the same pathway, another forward step of this study was achieved by taking the photocatalytic stability of the composite under consideration. One catalyst cannot be good enough if it can be used only once. To examine the applicability and reusability of our synthesized nanomaterial additional data were taken. In this study previously optimized condition was retained. First use was considered here as first photo-catalysis under pH-9. After this first use, nanomaterial particles were recovered by centrifugation of the suspension. Those recovered particles were washed with acetone and reused for further photo-catalysis. This process was repeated two more times. The result was satisfactory, gradual decrease in the absorbance of dye concentration was observed. The percent of efficiency in Fig. 5 (e) was 97.24%, 95.1%, 94.63%, and 81.92%, with a slight decrease over cycle.

(b) Detection of 4-AP with $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE by electrochemical approach

Potential application of $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ assembled onto GCE as chemical sensors (especially 4-AP analyte in buffer system) was executed for measuring and detecting target chemical. Enhancement of the $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE as chemical sensors is in the initial stage and no other reports are available. The $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE sensors have advantages such as stability in air, non-toxicity, chemical inertness, electro-chemical activity, simplicity to assemble, ease in fabrication, and chemo-safe characteristics. As in the case of 4-AP sensors, the incident of rationale is that the current response in I-V method of $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE considerably changes when aqueous phenolic analytes are adsorbed. The $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE was applied for fabrication of chemi-sensor, where 4-AP was measured as target analyte. The fabricated-surface of $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ sensor was prepared with conducting binders (5% Nafion) on the GCE surface of 4-AP chemical sensor are

anticipated having $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ on thin-film as a function of current versus potential. The resultant electrical responses of target 4-AP are investigated by simple and reliable I-V technique using $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$. The holding time of electrometer was set for 1.0 sec. A significant amplification in the current response with applied potential is noticeably confirmed. The simple and possible reaction mechanism is generalized in presence of 4-AP on $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ sensor surfaces by I-V method. In presence of $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterials, the electrons are released in presence of 4-AP by adsorbing reduced oxygen, which improved and enhanced the current responses against potential during the I-V measurement at room conditions. The $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterial was employed for the detection of 4-AP in liquid phase. I-V responses were measured with $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ coated thin-film (in two electrodes system). In experimental section, it was already outlined the 4-AP sensing protocol using the $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ modified electrode. The concentration of 4-AP was varied from 0.1 nM ~ 0.1 M by adding de-ionized water at different proportions. Here, Fig. 6(a) is represented the I-V responses for uncoated-GCE (green-dotted) and $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ (red-dotted) electrodes. In PBS system, the $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ electrode shows that the reaction is reduced slightly owing to the presence of $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ on bare-GCE surface. A considerable enhancement of current value with applied potential is demonstrated with fabricated $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ in presence of target 4-AP analyte, which is presented in Fig. 6(b). The green-dotted and red-dotted curves were indicated the response of the fabricated film after and injecting 25.0 μL 4-AM in 5.0 mL PBS solution respectively measured by fabricated $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ films. Significant increases of current are measured after injection of target component in regular interval. I-V responses to varying 4-AP concentration (0.1 nM to 0.1 M) on thin $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$

were investigated (time delaying, 1.0 sec) and presented in the Fig. 6(c). Analytical parameters (such as sensitivity, detection limit, linearity, and linear dynamic range etc) were calculated from the calibration curve (current vs. concentration), which was presented in Fig. 6(d). A wide range of 4-AP concentration was selected to study the possible detection limit (from calibration curve), which was examined in 0.1 nM to 0.1 M. The sensitivity was calculated from the calibration curve, which was close to $0.506329 \mu\text{Acm}^{-2}\mu\text{M}^{-1}$. The linear dynamic range of the $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ sensor was employed from 0.1 nM $\sim$ 0.01 M (linearly, $r^2=0.9813$), where the detection limit was calculated about 0.019 nM (ratio, $3\sigma/s$). The $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ was exhibited mesoporous behaviors, where the electrical resistance decreases under the presence of target 4-AP in PBS phase. The film resistance was decreased gradually (increasing the resultant current) upon increasing the 4-AP concentration in bulk system.

Fig. 6: I-V responses of (a) Bare and $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ coated GCE; (b) without and with 4-AP by $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE electrode; (c) concentration variation with $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE (with 4-AP at different concentrations); and (d) Calibration at +1.5 V of $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE. (Inset) Calibration of $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE with 4-AP (log-Conc. of 4-AP vs current)].

I-V characteristic of the $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ is activated as a function of 4-AP concentration at room conditions, where improved current response is observed. As obtained, the current response of the $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE electrode is increased with the increasing concentration of 4-AP, however similar phenomena for toxic chemical detection have also been

reported earlier.⁶⁷⁻⁶⁹ For a low concentration of 4-AP in liquid medium, there is a smaller surface coverage of 4-AP molecules on $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE film and hence the surface reaction proceeds steadily. By increasing the 4-AP concentration, the surface reaction is increased significantly (gradually increased the response as well) owing to large surface area contacted with 4-AP molecules. Further increase of 4-AP concentration on $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE surface (low-dimensional crystalline size and low-lattice disorder), it is exhibited a more rapid increased the current responses, due to larger surface covered by 4-AP chemical. Usually, the surface coverage of 4-AP molecules on $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE surface is reached to saturation, based on the regular enhancement of current responses.^{70, 71}

The 4-AP sensing mechanism of the $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE fabricated film is explained here. Initially, oxygen (dissolved) is chemisorbed on the $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE surfaces when the nanomaterial coated electrode is immersed in buffer-phase system. During the chemisorption, dissolved oxygen forms ionic species such as O_2^- and O^- which gain electrons from the conduction band.^{72, 73} The reaction kinetics is as follows [equations (iv) to (vi)].

The reaction between 4-AP and ionic oxygen species can take place by following (Equ. vii). The unstable (nO^-) get adsorbed onto the doped nanomaterial surfaces, which help to release free-electron onto the electrode surface in presence of 4-AP in the bulk system. So, in presence of 4-amino phenol, that chemical reaction is occurred in the buffer medium. On $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ /GCE surfaces, the analyte is oxidized and then release electrons into the conduction band, therefore decreasing the resistance (i.e., increasing the conduction current) of

the $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ film upon presence of 4-AP. So, by adsorbing unstable oxygen (nO^-) onto the doped nanomaterials, the resultant current is enhanced in presence of target analyte into the system.

Here, the reaction (equation (vii)) depends in presence of 4-amino phenol chemical in reaction medium. On $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ surfaces, the analyte is oxidized and then release electrons into the conduction band, therefore decreasing the resistance (increasing the conduction current) of the $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ film upon presence of 4-AP. To check the reproducibly, I-V response for $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ sensor was examined and presented in Fig. 7(a). After each experiment (each runs), the fabricated $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ substrate was washed thoroughly with the phosphate buffer solution and observed that the current response was not significantly decreased. Here it is observed the current loss in each reading is negligible compared to initial response of sensors using $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$. The response time was measured for the $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ fabricated sensor in the identical condition of analyte measured as repeatability and presented in Fig. 7(b), where response time was found 15 s. Interference (for selectivity) was studied for 4-AP sensor in presence other chemicals like 4-AP, 3-methoxy phenol, 3-chlorophenol, 2,4-dinitrophenol, 2-nitrophenol, 4-methoxyphenol, bisphenol A, hydrazine hydrate, phenylhydrazine, p-nitrophenol, using the $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ embedded on GCE, which is presented in Fig. 7(c). The concentrations of analytes are kept constant at $0.1\mu\text{M}$ level in PBS system. The sensitivity was retained almost same of initial sensitivity up to few days, after that the response of the fabricated $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ electrode gradually decreased. The 4-AP chemical sensor based on

$\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ is displayed good reproducibility and stability for over week and no major changes in sensor responses are found. The significant result was achieved by $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$, which can be employed as efficient electron mediators for the development of efficient chemical sensors. Actually the response time was around 15.0 sec for the fabricated $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ to reach the saturated steady-state level. The higher sensitivity of the fabricated $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ could be attributed to the excellent absorption (porous surfaces in $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{binders}/\text{GCE}$) and adsorption ability, and high catalytic-activity of the ternary metal oxides as $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterials. Due to higher specific surface area, $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterial provides a favorable nano-environment for the 4-AP detection with good quantity. The high sensitivity of $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ provides high electron communication features which enhanced the direct electron transfer between the active sites of $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ and coated-GCE. The $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ system is demonstrated a simple and reliable approach for the detection of toxic chemicals. It is also revealed that the significant access to a large group of chemicals for wide-range of ecological and environmental fields for the healthcare and environmental safety.

Fig. 7: Control experiment. (a) Repeatability of I-V responses for 4-AP in GCE coated with $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$; (b) Response time for $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ (with 4-AP); (c) Selectivity of $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ with different chemicals.

Real sample analysis with $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ sensor:

To confirm the validity of the developed sensor, the $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ was used to quantify 4-AP in industrial effluent-water (collected from the industrial effluent treatment plant, Jeddah, Saudi Arabia) and extract from the plastic bottles. The fixed amount ($\sim 25.0 \mu\text{L}$) of aqueous samples of different concentration along with the same amount of real samples were

analyzed in PBS (5.0 mL, pH 7.0) by the $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ as a working electrode. **Table 1** shows the obtained results, which demonstrated that the $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ modified sensor showed a quantitative detection of 4-AP by I-V method. Based on the results, therefore, we can conclude that the I-V method is suitable, consistent, and appropriate in real sample analyses with the ternary $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ system.

Table 1. Quantitative detection of 4-AP by I-V method using $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ modified sensor

Sample	Current (μA)				Concentration of 4-AP (nM)
	Run 1	Run 2	Run 3	Average	
Industrial water	27.5330	24.8600	23.0900	25.1610	0.11394348
Plastic bottle	29.1000	24.8790	22.9900	25.6563	0.11618648
Plastic baby bottle	23.0960	20.2582	20.7430	21.3657	0.09675617

Conclusion

In summary, an easy synthetic approach has been demonstrated for the synthesis of a ternary $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterials and its application as an efficient photo and electro catalyst. This inexpensive, facile, and easily controllable synthetic method can improve physico-chemical interaction between the nanoparticle active materials. This nanomaterial exhibits excellent efficiency in dye degradation. It has efficiency 97.24% under visible light and 78.98% in UV light at pH 9. Moreover, it loses only 2.61% efficiency over third time use. Even more, with the help of H_2O_2 it can obviously degrade over 98% only just 1 hour. It's photoluminescence property is also impressive, with the change of excitation energy and calcination temperature, PL peaks changes in intensity and shape. Moreover, the PLE shows

three equidistant peaks with 20 nm difference. In the other approach, analytical performances of 4-AP chemical sensor using $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}/\text{GCE}$ are investigated by reliable I-V method in terms of sensitivity, detection limit in short response time as well as reproducibility. This extensive research is performed in terms of preparation and characterization of ternary doped $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterials and applied for the 4-AP sensor using I-V method at room conditions. Hence, this approach is introduced a new route for efficient chemical sensor development in environmental and healthcare fields. The calibration plot was linear over a wide range of concentration (0.1 nM to 0.01M) of 4-AP. The sensitivity is $\sim 0.506 \mu\text{Acm}^{-2}\mu\text{M}^{-1}$ and the detection limit is 0.019 nM (signal-to-noise ratio, at a SNR of 3). It can be a promising sensor for the potential applications of hazardous and carcinogenic phenolic compounds in environmental field by I-V method. Here, we highlighted the analytical potential as a chemical sensor of this ternary doped $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterials and suggest avenues for further research.

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Enhanced Photocatalytic activity and Chemical sensor development based on ternary $\text{B}_2\text{O}_3\cdot\text{Zn}_6\text{Al}_2\text{O}_9\cdot\text{ZnO}$ nanomaterials for environmental safety

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Supplementary Materials

Figures

Fig. S1: $\beta_1\cos\theta$ vs. $\sin\theta$ plot from XRD patter

Fig S2. EDS of ternary $B_2O_3 \cdot Zn_6Al_2O_9 \cdot ZnO$ nanomaterials

Fig. S3: SEM-EDS mapping of (a) Boron, (b) Aluminum, (c) Zinc, (d) Oxygen, and (e) is the Overlap of all of them

Fig. S4: FTIR spectra of synthesized nanomaterial

Tables:

Table S1: EDS data representation with the atomic and mass percent elements

Element	(keV)	Mass%	Sigma	Atom%
B K	0.183	1.56	0.03	3.95
O K	0.525	34.49	0.07	58.92
Al K	1.486	17.48	0.05	17.71
Zn K	8.63	46.46	0.24	19.42
Total		100		100

Table S2: PL and PLE peaks observed with temperature variance

Calcination Temperature	Method	Observed at Wavelength/nm	Peaks Observed at Wavelength/nm
900 °C	Excitation	250	369, 404, 412, 425, 450, 467, and 482

		300	381, 404, 428, and 451
600 °C	Excitation	250	386, 404, 422, 450, 467, 482, and 492
		300	404, 412, 421, 450, 467, and 482
450 °C	Excitation	250	340, 404, 426, and 450
		300	404, 426, and 450
	Monitor	600	350, 370, and 390

Table of Content

Preparation of ternary $\text{B}_2\text{O}_3 \cdot \text{Zn}_6\text{Al}_2\text{O}_9 \cdot \text{ZnO}$ nanomaterials by simple co-precipitation method and potentially applied as an efficient photo-catalyst as well as chemical sensor has been reported, which promising the future efficient photocatalyst and sensitive chemical sensor development for the potential applications of hazardous and carcinogenic commercial dyes and phenolic compounds for the safety of environmental and health care fields