Heterostructural CuO–ZnO Nanocomposites: A Highly Selective Chemical and Electrochemical NO2 Sensor

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ABSTRACT: A simple one-step chemical method is employed for the successful synthesis of CuO(50%)–ZnO(50%) nanocomposites (NCs) and investigation of their gas sensing properties. The X-ray diffraction studies revealed that these CuO–ZnO NCs display a hexagonal wurtzite-type crystal structure. The average width of 50–100 nm and length of 200–600 nm of the NCs were confirmed by transmission electron microscopic images, and the 1:1 proportion of Cu and Zn composition was confirmed by energy-dispersive spectra, i.e., CuO(50%)–ZnO(50%) NC studies. The CuO(50%)–ZnO(50%) NCs exhibit superior gas sensing performance with outstanding selectivity toward NO2 gas at a working temperature of 200 °C. Moreover, these NCs were used for the indirect evaluation of NO2 via electrochemical detection of NO2− (as NO2 converts into NO2− once it reacts with moisture, resulting into acid rain, i.e., indirect evaluation of NO2). As compared with other known modified electrodes, CuO(50%)–ZnO(50%) NCs show an apparent oxidation of NO2− with a larger peak current for a wider linear range of nitrite concentration from 20 to 100 mM. We thus demonstrate that the as-synthesized CuO(50%)–ZnO(50%) NCs act as a promising low-cost NO2 sensor and further confirm their potential toward tunable gas sensors (electrochemical and solid state) (Scheme 1).

1. INTRODUCTION

NO2 is an omnipresent species and has been closely associated with the areas of environment and food as a corrosion inhibitor and an additive. It is also an indispensable source in the generation of nitrosamines, which is exceptionally robust carcinogenic to humanoid.† Due to the toxicity of NO2, the ingestion of these ions can cause serious impact on animal and human health.‡ Acid rain results when nitrogen oxides (NOx) and sulfur oxide (SOx) are released into the atmosphere and transported by wind and air currents. NOx and SOx react with oxygen, water, and other chemicals to form nitric and sulfuric acids. Then, these chemically react with water and other materials before falling to the ground. It has been stated that NO3 can destruct the nervous system, spleen, and kidneys and has a solid correlation with high cancer levels, the ecological environment, and public health causing defective births, blue baby disorder, abortion, intrauterine growth control, and serious cancer risk,§ when its concentration is higher than 3 mg mL−1.¶ Accordingly, the determination of NO3 becomes more crucial in environmental protection and for public health due to its harmful effects. Many techniques have been developed to determine NO3 levels, such as ion chromatography,§ spectrophotometry,¶ high-performance liquid chromatography, gas chromatography–mass spectrometry,¶ capillary electrophoresis,§ and electrochemical methods.¶ However, most of these methods frequently require complicated and high-cost instrumentation. Among them, considerable attention has been given toward electrochemical methods because of their simple operation, fast response, and outstanding selectivity. In recent years, tunable electrochemical sensing based on various electrocatalytic systems has attracted great attention because of its high sensitivity, rapid and controlled response, and ease in operation.¶¶ Furthermore, electrochemical sensors are especially more suitable for detecting NOx and further conversion in real time. The reduction process of NOx is quite complicated and involves a sequence of in-between products.¶¶ At present, a variety of electrocatalytic materials have been reported for the construction of NOx sensors, such as carbon, metal/metal oxide nanostructures, etc.¶¶ Among the various electrocatalysts used for NOx...
Scheme 1. Synthesis of CuO−ZnO NCs by a Chemical Approach for Electrochemical and Chemical NO2 Determination and Conversion Studies

A mixture of p−n composite nanomaterials has been synthesized for gas sensors such as NiO/SnO2,26 Co3O4/ZnO,27 NiO/WO3,28 CuO/ZnO,29 CuO/TiO2,30 NiO/ZnO31a etc. It reflects that a substrate with enough conductivity and chemical stability is required to make certain the formation of valid p−n-type junctions.

Here, CuO−ZnO nanocomposites (NCs) were prepared via a single-step easy chemical synthesis method and their NO2 gas sensing properties were observed, which is one of the works exploring the response with sensing time. In the synthesis method prepared 1:1 proportion of ZnO with CuO shows a comparatively low sensing time and temperature. The response time lied within 6 s, for 5 ppm NO2 gas concentration. However, the recovery time was relatively short. Thus, a method with a superior gas response, a relatively lower working operating temperature, and a shorter response time could be attained by CuO(50%)−ZnO(50%) NC flakelike architecture. Compared to separate gas sensing result reported31 in CuO and ZnO were not too good so we have synthesized CuO−ZnO NCs for gas sensing applications because these composites are short band gap, easily prepared by a one-step synthesis method, and are nontoxic, environmentally friendly, abundant in nature, and cost-effective.31

The current study shows a facile chemical method, which was effectively used for the synthesis of CuO(50%)−ZnO(50%) NCs having low cost and straight approach of depositing dissimilar kinds of metals directly into a composite form (Scheme 1). The arrangement and morphology of as-synthesized NCs were studied by diverse characterization techniques, and their gas sensing properties were analytically investigated at different working temperatures from 100 to 250 °C using NO2, SO2, H2S, CO, MeOH, and Cl2 gases, respectively. The studies herein propose that the CuO(50%)−ZnO(50%) NCs are extremely selective and sensitive toward NO2 gas as compared to other gases. Other gas sensor parameters such as temperature needy response, reproducibility, selectivity, response/recovery, and immovability of CuO−ZnO NCs were also systematically studied and investigated. In the present work, we observed nanoflakes of CuO−ZnO, which are hitherto unattempted (a new
morphology of this composite). These flakes can more easily adsorb to NO₂ gas molecules, resulting in better performance with excellent stability. The as-obtained CuO—ZnO NCs had a permeable configuration with relatively high precise surface region. It was create that the CuO(50%)—ZnO(50%) nanoflakes inborn the morphology of originator while frequent pores were formed later than the annealing. So extend the gas sensing concert of this morphology. Yang et al. studied the CuO—ZnO heterostructure for NO₂ gas sensing at 350 °C working temperature. Jin and co-workers studied CuO—ZnO NCs for NO₂ gas sensing at a working temperature of 300 °C. Novelty of our material is, as per previous report solid state gas sensing result is 100 ppm exposing NO₂ gas sensing at 200 °C for 73% response as compare to better above reported NO₂ sensing result as well as shown excellent in room temperature (RT) electrochemical sensing at high current density and lower detection limit of nitrate sensing.

2. RESULT AND DISCUSSION

2.1. Structural and Compositional Revelation. X-ray diffraction (XRD) shown in Figure 1a demonstrates the characteristic peaks of CuO(50%)—ZnO(50%) NCs, the peaks at 2θ values corresponding to the crystal planes of 110, 002, 101, 102, 110, 103, 200, 112, 021, 201, 004, and 202. The 2θ value indices of the nanocomposite were observed as for 31, 34, 35, 36, 38, 47, 48, 56, 58, 61, 62, 66, and 68°, respectively. The bar which is indicated in the Miller indices had shown the negative direction of the plane, which is in good accordance with earlier information on a like system. The XRD peaks are in superior conformity with the reported diffraction pattern of CuO with a monoclinic structure (JCPDS card # 00-041-0254). Similarly, diffraction peaks for ZnO having a hexagonal structure match well with the reported XRD pattern (JCPDS card # 01-079-0206). Figure 1b shows the energy-dispersive X-ray analysis (EDAX) results, confirming that O, Cu, and Zn are present in prepared CuO(50%)—ZnO(50%) NCs. Both the XRD and EDAX evidence the successful synthesis of CuO(50%)—ZnO(50%).

The morphological studies of CuO—ZnO NCs were carried out by TEM analysis. The large-scale homogeneous features of NCs are shown in Figure 1c (low magnification) and Figure 1d (high magnification). The CuO(50%)—ZnO(50%) NCs consisting of the characteristic flakelike NCs of width about 50—100 nm and length of a few micrometers are in good agreement with earlier reports. TEM images show that the surface of ZnO is covered by CuO nanoparticles (NPs). Also, the exposed ZnO flakes are shown in the TEM image (Figure 1c).

The thermogravimetric analysis (TGA) profile is shown in Figure 2a. CuO(50%)—ZnO(50%) NCs reveal thermal stability, and to investigate the amount of PVP present, TGA shows the three major steps observed for weight losses of the CuO(50%)—ZnO(50%) NCs. In the first stage, weight losses (M₁) of 0.66% for CuO—ZnO occur in the range of 22—108 °C, and the process starts with the loss of bound water. The second step of weight loss takes place from 108 to 233 °C corresponding to the mass loss (M₂) of 1.29% for CuO(50%)—ZnO(50%) NCs, which is related to the decomposition of PVP (structure-directing agent). At higher temperatures however, additional decomposition steps take place. The third step of weight loss (M₃) taking place from 233 to 376 °C indicates the weight loss of 1.79% for CuO—ZnO, which is attributed to the complete conversion to the crystalline form. Figure 2b shows typical N₂ adsorption—desorption isotherms of CuO(50%)—ZnO(50%) NCs. To calculate the porosity of the CuO(50%)—ZnO(50%) NCs, we have recorded N₂ adsorption—desorption curves of the dehydrated material at a relative pressure of 0—1 bar at 77 K. The amount of N₂ absorbed on the metal oxide is found to be ~135 cm³ g⁻¹ on P/P₀ of 0.98, and this could be due to the porous structure of CuO—ZnO, which is probably developed due to the nanodimensions. The isotherm appears to be of nearly type IV in nature, characteristic for solids containing both micro- and mesopores. The specific surface area using Brunauer—Emmett—Teller (BET) analysis, average pore radius, and total pore volume were calculated to be 67.6 m² g⁻¹, 6.1 nm, and 0.206 cc g⁻¹, respectively. The UV—visible

Figure 1. (a) PXRD of CuO—ZnO NCs confirms the monoclinic and hexagonal structure formation. (b) Energy-dispersive X-ray of CuO—ZnO NCs. (c) Transmission electron microscopy (TEM) image of CuO—ZnO NC-based flakes having large-scale distribution and (d) TEM image of a single flake of CuO—ZnO NCs having dimensions 50—100 nm.

Figure 2. (a) Representative TGA curve shows the different weight losses as a consequence of volatile contamination, moisture, and PVP molecules bound on the surface; (b) N₂ adsorption—desorption isotherm for CuO—ZnO NCs.
spectra of CuO(50%–ZnO(50%) NC samples were recorded. CuO(50%)–ZnO(50%) NCs exhibit a UV band at 3.17 eV, whereas CuO(50%)–ZnO(50%) NCs show a UV spectral band with significant assimilation in the visible region. The accredited arrangement of extra defects at the interface of CuO with ZnO is of specific significance for the gas sensing purpose [Supporting Information (SI)].

Chemical states and surface compositions of Cu and Zn present in the nanomaterials were examined by the X-ray photoelectron spectroscopy (XPS) survey of the CuO(50%)–ZnO(50%) NCs as shown in Figure 3a. The outcome shows the presence of the elements like O, Zn, C, and Cu in the CuO(50%)–ZnO(50%) NCs. The peak at 285.35 eV is attributed to the carbon that lingers in small quantities after blazing exposed the PVP at 500 °C. The CuO(50%)–ZnO(50%) NCs are shown in Figure 3b. The Zn 2p peaks centered at 1022.7 and 1045.8 eV (ZnO) are assigned to Zn 2p3/2 and Zn 2p1/2, respectively. These peaks are the same as those of Zn2+ in hexagonal wurtzite ZnO.35 The Zn 2p peaks are seen to be shifted to slightly higher binding energies for the CuO(50%)–ZnO(50%) NC material of 1021.96 eV (Zn 2p3/2) and 1045.04 eV (Zn 2p1/2). The O 1s peak shows high resolutions (Figure 3c) of several partly cover mechanism. The peak fitted with characteristic Gaussian functions and determined to peaks (1), (2), and (3) with binding energies of 529.9, 530.50, and 531.62 eV for ZnO NCs, correspondingly. Peak (2) may be correlated to O2− ions in the lattice. Peak (1) may be attributed to the O2− ions adsorbed on the surface of films, whereas peak (3) may be attributed to the O2−, O−, and OH− ions in oxygen-lacking regions. In the case of the CuO(50%)–ZnO(50%) NCs, the O 1s peaks (1)–(3) are observed to be shifted to somewhat higher binding energies of 529.9, 530.50, and 531.62 eV, respectively.35 The Zn 2p peaks seen at 1021.96 eV (Zn 2p3/2) and 1045.04 eV (Zn 2p1/2) binding energies move to faintly superior energies in the composite CuO(50%)–ZnO(50%) sample.

In brief, the shift to higher binding energies of Zn 2p in the CuO(50%)–ZnO(50%) NC sample can be attributed generally to the interaction between CuO and ZnO nanomaterials, while that of O 1s obviously is attributed to changes in the O2 environment at the surface owing to CuO glaze. Change in the surface O2 species in the samples was also confirmed by calculating the ratio of the areas under the curves of [peak (1) + peak (3)] and peak (2). The ratio is 0.76 for the CuO(50%)–ZnO(50%) NC samples, representing an increase in the quantity of engrossed O2 species in the CuO(50%)–ZnO(50%) NCs. On the other hand, this addition is not the main cause for the development in NO2 gas sensing recital, converse below. The Cu 2p spectra show a high-resolution peak in Figure 3d. The peak at 934.65 eV is attributed to Cu 2p3/2, while the peak at 954.76 eV is attributed to Cu 2p1/2.
demonstrating the existence of CuO nanoparticles among the +2 oxidation state of Cu. In addition, the peaks of Cu 2p\(_{3/2}\) and Cu 2p\(_{1/2}\) were experimental peaks 954.11 eV (S\(_{2}\)) and 963.23 eV (S\(_{2}\)), correspondingly, attributed to a moderately full d-orbital (3d\(^6\) in the case of Cu\(^{2+}\)). The XPS and XRD results sturdily support the arrangement of CuO with Cu(II) on the ZnO surface.\(^{35}\)

### 2.2. Gas Sensing Studies.

The selectivity study of the CuO(50%)–ZnO(50%) NC sensor was conducted on hazardous gases H\(_2\)S, NO\(_2\), CO, SO\(_2\), CH\(_3\)OH, and Cl\(_2\), each at a concentration of 100 ppm, and the observed results are shown in Figure 4a. The selectivity study clearly indicates that the CuO(50%)–ZnO(50%) NC sensor is more reactive toward the NO\(_2\) gas than to the other gases, viz., H\(_2\)S, CO, SO\(_2\), CH\(_3\)OH, and Cl\(_2\). Such a higher response (73%) observed for NO\(_2\) strength to the higher rate of interface take place NC sensor surface area and NO\(_2\) gas molecules as evaluate to additional tested gases (Figure 4a). All gas sensing response curves for analyte selectivity are shown in detail in the Supporting Information. The highest response of the CuO(50%)–ZnO(50%) NC sensor to NO\(_2\) is confirmed by calculating the selectivity coefficient (K). The selectivity coefficient (K) of NO\(_2\) gas with respect to other gases is projected using the following equation, and obtained values are listed in Table 1.\(^{36}\)

\[K = \frac{S_a}{S_b}\]  

(1)

**Table 1. Analyte Gas Coefficient, "K", Values of the CuO(50%)–ZnO(50%) Nanocomposite Sensor by NO\(_2\) as a Target Gas**

| test gas | CO | H\(_2\)S | SO\(_2\) | Cl\(_2\) | CH\(_3\)OH |
|----------|----|---------|---------|--------|-----------|
| K values | 14.6 | 5.61 | 36.5 | 48.66 | 29.2 |

Here, \(S_a\) represents the sensor responses (\(R_a/R_0\)) to NO\(_2\) gas and \(S_b\) represents the sensor response to other test gases. The superior K value for a selective gas of the CuO(50%)–ZnO(50%) NC sensor shows enhanced ability to find out the objective gases from the other test gases.\(^{36}\)

The working temperature is measured since it is a vital feature during the gas sensing study, which influences the adsorption/desorption procedure of oxygen ions on the top of the sensor outer surface. Surface metal-oxide-based sensors absorb oxygen from air and form O\(^{2-}\), O\(^{-}\), and O\(^{0}\) species.\(^{37}\)

The surface negative charges produce a superior surface potential barrier, which results in a high electrical resistance.\(^{38}\)

The sensor oxidizes NO\(_2\) gas, and the NO\(_2\) gas molecules exert a pull on the electrons from sensor nanomaterials, which can be denoted to their towering electron attraction.\(^{39}\) These processes lead to the transfer of electrons from the sensor materials to the surface of NO\(_2\) forming the species NO\(_2^-\) (from NO\(_2\)) and NO\(^-\) (from NO). The process takes electrons from the conduction band or the donor level of the material, which results in reduction in the electron bulkiness, thereby increasing the hole transporter density at the surface of the sensor. The increased concentration of the hole carriers results in lowering of the resistance of the semiconductor film. In addition, it results in a thinner space charge layer and consequently reduction in the potential barricade at the grain restrictions, causing reduction in the resistance of the sensor.\(^{39}\)

The scheme can be expressed as follows:

\[O_2 \leftrightarrow O_2^- \leftrightarrow O^- \leftrightarrow O^{2-}\]  

(2)

\[NO_2 + e^- \rightarrow NO_2^- / NO + e^- \rightarrow NO^+\]  

(3)

\[NO_2 + O^- \rightarrow NO_2^- / NO + O^- \rightarrow NO_2^-\]  

(4)

Frequently, the response of metal oxide [CuO(50%)–ZnO(50%)]-based gas sensors is quite high in the temperature range 100–250 °C, in which oxygen has O\(^{2-}\) nature. The optimization of working temperature for the CuO(50%)–ZnO(50%) NC gas sensor (predetermined 100 ppm NO\(_2\) gas) is shown in Figure 4b. The CuO(50%)–ZnO(50%) NC gas sensor shows a maximum response rate of 73% at an operating temperature of 200 °C in the presence of 100 ppm NO\(_2\) gas (Figure 4b). Herein, the response (\(R_a/R_0\)) of CuO(50%)–ZnO(50%) NC sensing is smaller at lower working temperatures (less than 200 °C) owing to the small rate of reactions, which might be owing to the inferior rate of dispersal of gas molecules. Although the speed of these reactions becomes corresponding on mediator 200 °C, since the result of CuO(50%)–ZnO(50%) NC sensor achieved its highest response rate. Consequently, an additional study is carried out at 200 °C as an optimized sensor temperature. See the gas sensing response curve at all temperatures (100–250 °C) in the Supporting Information (SI).

The dynamic response (\(R_a/R_0\)) curve of the CuO(50%)–ZnO(50%) NC sensor toward a range of concentrations (5–100 ppm) of targeted NO\(_2\) gas at 200 °C is revealed in Figure 4c, which displays the response of sensor (designed with eq 5) established to be rising with the concentration of NO\(_2\). The response arc of the CuO(50%)–ZnO(50%) NC sensor toward 5 ppm NO\(_2\) is shown in Figure 4c. The highest response (\(R_a/R_0\)) of 73% to 100 ppm NO\(_2\) along with ~8% to 5 ppm NO\(_2\) at a working temperature of 200 °C is detected. At inferior concentrations, NO\(_2\) gas molecules cover a smaller surface of the CuO(50%)–ZnO(50%) NC sensor and, as a consequence, lessen the surface acquaintances, consequently leading to a smaller response value. Besides, at high concentration, NO\(_2\) covers a larger CuO(50%)–ZnO(50%) NC surface, resulting in a higher response (\(R_a/R_0\)) value due to the greater surface interactions; at various NO\(_2\) gas concentrations of 5–100 ppm, the response percent is shown in the calibration curve (Supporting Information). The design of variation in response and renewal times as a role of diverse NO\(_2\) gas concentration ranging from 5 toward 100 ppm on 200 °C be given in Figure 4d. Response and renewal times are significant parameters in analyzing a gas sensor. Response and renewal times and recovery time are the times to achieve a 90% resistance change when the gas is injected into the chamber. They mainly depend on the quickness of adsorption and desorption, respectively.

The response time of the CuO–ZnO thin film to NO\(_2\) gas as a function of the NO\(_2\) gas concentration is shown in Figure 4d. It shows the recovery time of the CuO thin film to NO\(_2\) gas as a function of the NO\(_2\) gas loading. In this study, the response time and recovery time are defined as the times to achieve a 90% change in resistance upon exposure to NO\(_2\) and air, respectively. Regarding the effect of the working temperature on the sensing speed of the CuO–ZnO film, the fastest response and recovery were observed at 200 °C. In addition, the sensor showed the shortest sensing time (sum of the response time and recovery time) at 200 °C. However, the response and recovery times showed little dependence on the NO\(_2\) concentration. The dependence of the response time and recovery time of the sensors on the working temperature could
also be explained in a similar manner to the response transients. Different oxygen ion species form at different temperatures after the adsorption of oxygen molecules at the sensor surfaces, and the reaction rate of NO$_2$ with O$^-$ at 200 °C might be stronger than that of O$_2$ at 100 °C or O$^{2-}$ at 300 °C, leading to the fastest sensing at 200 °C. As shown in the figure, the CuO–ZnO thin films synthesized in this study showed shorter sensing time toward NO$_2$.\cite{39}

Response and recovery profiles (Figure 4d) show that the response time and recovery time differ inversely from all others with respect to different concentrations of NO$_2$ gas. The response time of the CuO(50%–ZnO(50%) NC sensor is set up to be decreasing from 13 to 5 s, while the renewal time increases from 60 to 280 s with increasing NO$_2$ gas concentration from 5 to 100 ppm. Such a falling in response time on increasing NO$_2$ gas concentration may be owing to big accessibility of available sites on the sensor surface for gas adsorption. However, the increase in recovery time may be caused by gas type which is left following later than the gas communication in the decrease in desorption speed and therefore recovery time increase as NO$_2$ gas concentration also increases.\cite{40}

The gas response ($R_g/R_a$) in expression of change in electrical resistance values of CuO(50%–ZnO(50%) NCs to 100 ppm NO$_2$ gas sensor is shown in Figure 5a. The gas response reproducibility and reversibility are mainly considered as crucial factors of sensors, and the uniformity of the sensor is chiefly reliant on such parameters. Reproducibility and reversibility tests of the CuO(50%–ZnO(50%) NC sensor are shown in Figure 5b,c, respectively. Figure 5c indicates the response ($R_g/R_a$) reversibility of the CuO(50%–ZnO(50%) NC sensor toward 40, 80, and 60 ppm NO$_2$ gas concentration. The stability response of the CuO–ZnO NC sensor is shown to be decreased from 73 to 54% (after 20 days) with 73% constancy (Supporting Information).

2.3. NO$_2$ Gas Sensing Mechanism. Experimentally, it is observed that when oxidizing NO$_2$ gas is exposed to the CuO(50%–ZnO(50%) NC sensor, it shows rapid reduction in the resistance ($R_g/R_a$), which indicates the p-type activities of CuO, and therefore charge transport basically occurs during CuO. This modification in the resistance values is owing to the adsorption of the gas molecules on the surface of the NC layer. When NO$_2$ gas molecules cooperate with the p electron network of CuO have set ZnO nanoparticles capture from CuO sequence results in reduce the resistance. The preliminary resistance is noticed when NO$_2$ gas is turned off and new air is introduced into the cavity. This can be made clear on the basis of planned schematic energy band diagram shown in Scheme 2a–c. For drawing the energy band diagram, the experimentally calculated values of the band gap energies have been used. Scheme 2a shows the energy band diagram of individual CuO and ZnO, representing that the Fermi level ($E_F$) of p-type CuO is close to the valence band ($E_v$), whereas in n-ZnO, the Fermi level is close to the conduction band ($E_c$). Accordingly, all sensing measurements of CuO(50%–ZnO(50%) NCs show high sensor response ($R_g/R_a$), and this enhancement in the response can be due to the interfacial depletion layer of p–n-type CuO–ZnO NCs connecting the surface of CuO and ZnO nanoparticles. Fascinatingly, the adsorption of ionized oxygen at surfaces of the ZnO–CuO NCs controls the flow of electron (Scheme 2b). The revealing of CuO(50%–ZnO(50%) NCs to NO$_2$ gas sensor will reason the captured electrons to free into the fabric. These free electrons use the holes in CuO and also lead to excess electrons in ZnO, resulting into decrease in the width of the depletion film. Due to the survival of p–n hybrid CuO(50%–ZnO(50%) NCs, the consumed holes in CuO would supplement rapidly from the electron depletion film at the interface of NCs. Through this electron transfer process, the holes in the CuO(50%–ZnO(50%) NCs migrate to CuO across the heterocontact interface and the electrons move into their interfacial conduction band, which in turn increase the charge carrier concentration as well as decrease its resistivity.\cite{41}

Figure 5. (a) Plot of change in electrical resistance for 100 ppm oxidizing NO$_2$ gas with time, (b) reproducibility of NO$_2$ at 200 °C operating temperature, and (c) reversibility of the CuO–ZnO NC sensor.
The n-type ZnO NPs form a CuO barrier layer with the matrix, leading to the formation of the depletion layer and is schematically shown in Scheme 2. Interestingly, the surface NO$_2$ gas molecules when come in contact with CuO(50%)--ZnO(50%) NCs affect the width and decrease the depletion layer, which results in a further decrease in the resistance, which is schematically shown in Scheme 2c. Furthermore, they increase the conductivity of the CuO(50%)--ZnO(50%) NC-based sensor material. The space charge region in CuO decreases the adsorption of NO$_2$ gas species (by reduction of electrons), which further produces high conductivity. The n-type ZnO form a CuO barrier layer with the matrix, leading to the formation of the depletion layer and is schematically shown in Scheme 2. Interestingly, the surface NO$_2$ gas molecules when come in contact with CuO(50%)--ZnO(50%) NCs affect the width and decrease the depletion layer, which results in a further decrease in the resistance, which is schematically shown in Scheme 2c. Furthermore, they increase the conductivity of the CuO(50%)--ZnO(50%) NC-based sensor material. The space charge region in CuO decreases the adsorption of NO$_2$ gas species (by reduction of electrons), which further produces high conductivity. Therefore, the inflection of the space charge region at the boundary of CuO with ZnO NPs gives better response toward the NO$_2$ gas sensor. The enhanced performance of CuO(50%)--ZnO(50%) NCs is attributed to their unique p–n-type heterostructure. In Scheme 2c, a p–n heterojunction is formed, and also, the energy band bends with the depletion layer to form a uniform Fermi level ($E_f$) in the thermal equilibrium state (Scheme 2c).

The construction of n–p-type composites between n-type ZnO and p-type CuO, where electrons move from n-type ZnO to p-type CuO while the holes transfer conversely from CuO to ZnO until the system obtains equalization at the Fermi level, results in the formation of a hole depletion layer that promotes the quantity of the chemisorbed oxygen species.$^{42}$ Scheme 2d shows the systematic representation of the electron–hole transfer mechanism, and it can be calculated that the barrier heights of the conduction band [$\Delta E_c = E_{c2} - E_{c1}$] and the valence band [$\Delta E_v = (E_{v1} - E_{v2}) - \Delta E_c$] at the p–n junction are 0.75 and 0.72 eV, respectively.$^{42}$ Table 1 shows the performance of the as-prepared CuO(50%)--ZnO(50%) NCs and some reported metal-oxide-based nanocomposites of NO$_2$ gas sensors from the literature (see in the Supporting Information).

### 2.4. Electrochemical Sensing of Nitrate by CuO(50%)--ZnO(50%)-Based Electrodes

Electrochemical measurements were performed on CHI-660E by modified glassy carbon (GC) with CuO(50%)--ZnO(50%) NCs, and Pt foil and saturated calomel electrode (SCE) are counter and reference electrodes, correspondingly. As shown in Figure 6a, the overlay linear sweep voltammetry (LSV) response for GC (i), CuO(50%)--ZnO(50%)/GC NPs (ii) in 0.5 M KOH solution and the LSV for CuO--ZnO/GC NPs, (iii) 30 mM NO$_3^-$ in 0.5 M KOH at scan rate of 50 mV s$^{-1}$ to connect the potential range of surface CuO(50%)--ZnO(50%) oxidation and NO$_3^-$ oxidation reactions. The superimposed LSV in 0.5 M KOH for GC (i) and GC--ZnO (ii) NP electrodes reflects that there is no any peak in the absence of NO$_3^-$, though a new important oxidation peak is obtained at +0.80 V versus rotating cylinder electrode in the presence of 30 mM NO$_3^-$ corresponding to electrocatalytic oxidation of NO$_3^-$ to NO$_2^-$ with comparable report systems.$^{43}$ Furthermore, no representative anodic peak is initiated in the anodic sweep on GC in the presence of NO$_2^-$ ions, which reflects its inability toward oxidation of NO$_2^-$.$^{43}$ These observations demonstrate significantly the electrochemical ability of CuO(50%)--ZnO(50%) NCs toward NO$_3^-$ determination, which also further provides an indirect link for NO$_2^-$ oxidation in an aqueous system. Further, the influence of the increase in concentration of NO$_3^-$ on the electrocatalytic oxidation potential and peak current of the CuO--ZnO NP electrode in 0.5 M KOH is also demonstrated. In Figure 6b, the oxidation potential and peak current at an onset potential of 0.80 V versus SCE demonstrate a linear response with an increase in NO$_3^-$ ion concentration in the range of 20–50 mM; moreover, this linear range is broader than that of the reported method.$^{44}$ Also, the influence of the scan rate on the electrocatalytic oxidation peak potential ($E_{pa}$) and peak current for NO$_3^-$ on the CuO(50%)--ZnO(50%)/glassy carbon electrode (GCE) at 0.5 mM was studied using LSV. The Figure 6c current values were found to be improved with an increase in scan rate starting from 10 to 100 mV s$^{-1}$. The linear relationship connecting the anodic peak currents with the square root of the scan rate in Figure 6d indicates that NO$_3^-$ oxidation is a diffusion-controlled reaction.

### 2.5. Electrochemical Impedance Spectroscopic and Chronoamperometric (Current Stability) Measurements

The electrocatalytic activities of as-synthesized CuO(50%)--ZnO(50%) NCs were further studied using electrochemical impedance spectroscopy (EIS). The EIS is used to assess the charge transfer resistance of the materials. Figure 7a demonstrates the Nyquist plots of as-synthesized CuO(50%)--ZnO(50%) NCs, and the semicircle shows small
diameter in the plot, indicating the minor resistance at the electrified interface. As an outcome, the charge transfer resistance ($R_{ct}$) of NaNO$_2$ at 30 mM is found to be $\sim 520 \, \Omega$. In general, among all of the customized electrocatalysts, CuO(50%$)$−ZnO(50%) has a minor $R_{ct}$ value, which indicates that the electron transfer kinetic reaction rate in the presence of NaNO$_2$ is extra rapid than in the absence of NaNO$_2$. The estimated $R_{ct}$ standards are 520 and 25 000 $\Omega$, which result due to the presence and absence of CuO−ZnO, respectively.

As a result, the fabricated CuO−ZnO of EIS observations is calculated since a superior validation and shows small semicircle to improve the catalytic activity of CuO−ZnO in presence of NaNO$_2$ and CuO nanowall based Cu substrate based electrocatalytic systems. The modified CuO−ZnO/GCE electrochemical sensor shows a smaller semicircle in the Nyquist plot (Figure 7a), indicating that it exhibits excellent electrochemical nitrate sensing property compared to CuO−ZnO/GCE in 0.5 M KOH; without nitrate, the resistance of the electrochemically modified sensor rapidly decreases in the presence of 30 mM NO$_2^-$ ions in a 0.5 M KOH solution of electrolyte. Figure 7b shows immovability curves of CuO(50%$)$−ZnO(50%) NCs toward a practical onset potential of 0.6 V versus SCE for 8000 s in the solution containing 20 mM NaNO$_2$ into 0.5 M KOH electrolytic solution. Here, the electrode retains its initial response for 20 mM NaNO$_2$. The current decline is significantly slower in the entire experiment range, which demonstrates its outstanding survival capacity toward NO$_2^-$ to NO$_3^-$ electrocatalytic oxidation. Table S2 relationship of investigative recital of diverse electrochemical sensors used for nitrate (NO$_3^-$) discovers (see the Supporting Information).

3. CONCLUSIONS

We have successfully prepared novel and stable CuO−ZnO NCs and characterized them using different microscopic and spectroscopic techniques. Their gas sensing activities were further studied toward various target gas molecules. On the basis of the gas sensing study, it is discovered that the CuO(50%$)$−ZnO(50%) NC sensor is proficient in detecting extremely low concentrations (near about 5 ppm of NO$_2$ gas) of NO$_2$ at a working temperature of 200 °C. Moreover, this NC-based sensing system is capable through the quick response/recovery times, outstanding repeatability, and stability in NO$_2$ response. The CuO(50%$)$−ZnO(50%) NC sensor displays the highest response rate of 73%, on coming in contact with 100 ppm NO$_2$ gas. More significantly, the CuO−ZnO NCs also demonstrated an excellent electrocatalytic...
activity toward detection followed by oxidative conversion of nitrate with a wide concentration range (20–50 mM) and lower detection limit (~1 μM) with higher sensitivity. The modified electrode offered an appreciable repeatability and reproducibility. Moreover, the fabricated electrode selectively detected the nitrate in the presence of intrusive ions. Moreover, the developed sensor electrode showed good stability. Therefore, the present low-cost CuO(50%–ZnO(50%) NC system can be used as an excellent nanoelectrode-based system for the electrochemical detection of nitrate. This sensor electrode can be used potentially for the precise detection of nitrate into food and industrial samples.

4. EXPERIMENTAL SECTION

4.1. Chemicals. Zinc acetate, copper acetate, sodium nitrate (extra pure), acetone, alcohol, ethylene glycol, and poly(vinylpyrrolidone) (PVP) were purchased from Sigma-Aldrich; poly(vinyl alcohol) (PVA), 2-propanol, sodium hydroxide, ammonia, and NaOH were of analytical grade and were purchased from S. D. Fine Chem, India; and deionized (DI) water (DW) was used for chemical and electrochemical reactions.

4.2. Synthesis of CuO–ZnO Nanoparticles and Characterization Techniques. The synthesized CuO(50%–ZnO(50%) NCs (in Scheme 3) were expensive when prepared by the chemical emulsion method. In a 250 mL round-bottom flask, analytical-grade 0.01 mM Cu(Ac)₂ and Zn(Ac)₂, as a source of “Cu” and “Zn” were added, purchased from Sigma-Aldrich; these chemicals were stirred in DI water; further, 0.01 M poly(vinylpyrrolidone) (PVP, Sigma-Aldrich) was added to the reaction mixture; and then, the mixture was stirred vigorously at RT for 30 min to make a homogeneous solution of Cu acetate, Zn acetate, and PVP. This mixture was transferred into an oil bath, and 5 M solution of NaOH was added dropwise into it up to the pH 10 and refluxed to 80 °C for 8 h to obtain a brownish-black precipitate. The as-synthesized NCs were washed a number of times using DW and methanol to eliminate the excess impurities and dried at 80 °C for 1 h in an oven. The synthesized NC powder was then transferred into an alumina boat, calcined further at 500 °C for 2 h, and consequently cooled to RT (Scheme 3).

For preparing a thin film, CuO–ZnO NC powder was transferred to a poly(vinyl alcohol) (PVA) solution as a binder and constantly stirred for 12 h to get a dispersion of solution. The prepared uniform dispersion of solution of CuO–ZnO was drop-casted on a glass substrate using the doctor blade method, and the prepared film was dried in an air atmosphere. This film was then heated at 400 °C for 2 h to remove the PVA binder and then used for the gas sensing application.

4.3. Characterization Techniques. Here, crystallinity and surface morphology of the CuO(50%–ZnO(50%) nanocomposites were studied by X-ray diffraction (XRD; model: Ultima IV Rigaku, Cu Kα source) and TEM (model: JEOL), respectively. Moreover, the CuO–ZnO nanocomposites were further analyzed through energy-dispersive spectroscopy. The porosity and surface area were determined through the BET method at a Quantachrome Auto sorbiQ instrument.

4.4. Gas Sensing Measurement. The CuO(50%–ZnO(50%) nanocomposite gas sensing properties were calculated with the assist of a routine fabricated two-probe gas sensor unit. To study the response (Rg/Ra) to different poisonous gases, the change in the electrical resistance value of the CuO(50%–ZnO(50%) NC-based sensing substrate was measured and confirmed by a programmable electrometer (model: Keithley 6514), which connects NCs with a two-probe gas sensor arrangement. A pair of Ag electrodes (0.1 mm thick and 1 cm long) was deposited on the top of NC materials, with assist of a paintbrush, for electrical contacts. The CuO(50%–ZnO(50%) materials for gas response [S (%)] were promising, which can be ascertained by the following equation:

\[ S(\%) = \frac{R_a - R_g}{R_a} \times 100 \] (5)

where R_a and R_g are the electrical resistance standards of CuO(50%–ZnO(50%) NCs in the presence of targeted gases and air, respectively (Figures 8 and 9).
4.5. Preparation of CuO–ZnO Modified Electrode.

Electrochemical NO₂ sensing studies were carried out on an electrochemical setup, CH-Instruments (CHI-660E), using a conventional three-electrode system. In this setup, a 3 mm diameter modified glassy carbon electrode (GCE), a saturated calomel electrode (SCE) as a reference electrode, and a Pt wire as a counter electrode were used. First, prior to cleaning of the GC electrode with polished by alumina powder sequential use 1.0, 0.3, and 0.05 μm, respectively, and washing with all electrodes distilled water and methanol, ready to use for electrochemical study. The CuO–ZnO catalyst was prepared in 2-propanol and for modified electrocatalyst drop cast on GCE and continuation to the electrochemical studies.

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**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01382.

Comparison of performance of the as-synthesized CuO–ZnO NCs with some representative compositions from the literature (Table S1); calibration curve of NO₂ gas sensing at 5–100 ppm (Figure S1); stability plot of CuO–ZnO NCs (Figure S2); UV–vis absorption spectra of pure and CuO–ZnO nanocomposites and the inset plot graph of the band gap of CuO–ZnO nanocomposites (Figure S3); correlation of analytical performance of different electrochemical sensors for nitrite (NO₂⁻) detection (Table S2); change in resistance of sensor on exposure of 100 ppm NO₂ gas at different operating temperatures (Figure S4); selectivity study of the sensor (Figure S5) (PDF)

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**Notes**

The authors declare no competing financial interest.

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