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Investigation of Electrical and Gas Sensing Properties of CeO_2 Nanoparticle Synthesized by Precipitation Method

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Abstract:
In the present research work, pure CeO_2 nanoparticles (NPs) were successfully synthesized using the precipitation method with cerium (III) nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$] as a precursor. The synthesized CeO_2 NPs were employed to fabricate thick films via the standard screen-printing technique, and their electrical as well as gas sensing properties were systematically studied. The prepared CeO_2 thick films exhibited a resistivity of 5939.03 Ω/m with a negative temperature coefficient of resistance (TCR) value of –0.002815 /°C, confirming their semiconducting behavior. The activation energy values were found to be 0.0546 eV in the low-temperature region (LTR) and 0.2421 eV in the high-temperature region (HTR). Gas sensing analysis revealed that the CeO_2 NPs thick films showed maximum response toward NH_3 gas, with a sensitivity of 76.95% at 120 °C for 1000 ppm concentration, along with fast response and recovery times. These results suggest that CeO_2 NPs thick films are promising candidates for efficient and selective NH_3 gas sensing applications.

Keywords- Hexahydrate, NH_3 gas, sensitivity, electrical, Gas sensing, response time.

1. INTRODUCTION:

The need for gas sensors has become increasingly important due to the rising concerns of environmental pollution, industrial safety, and human health [1]. Harmful and toxic gases such as CO, NH_3, NO_2, SO_2, CH_4, and volatile organic compounds are frequently released from industrial processes, vehicles, and domestic activities, posing serious risks to living beings and the environment even at low concentrations [1, 2]. Gas sensors provide an effective solution for real-time monitoring and detection of these hazardous gases, enabling timely preventive actions [3]. They play a vital role in industries for process control, leak detection, and ensuring workplace safety, as well as in medical diagnostics, smart homes, and environmental monitoring systems. The development of highly sensitive, selective, stable, and low-cost gas sensors is therefore essential for improving air quality management, reducing health hazards, and supporting the advancement of smart and sustainable technologies. Metal oxide-based gas sensors are among the most widely studied and commercially used gas-sensing materials due to their simple fabrication, low cost, high sensitivity, and ability to detect a wide range of toxic and combustible gases [3, 4]. These sensors typically work on the principle of change in electrical resistance when exposed to target gas molecules, which interact with the adsorbed oxygen species on the metal oxide surface. Commonly used metal oxides such as SnO_2, ZnO, TiO_2, WO_3, In_2O_3, and CeO_2 exhibit excellent semiconducting behavior, making them highly effective for gas detection. Their sensing performance strongly depends on factors such as surface area, porosity, particle size, morphology, and the operating temperature [4, 5].

Cerium oxide (CeO_2) nanoparticles also known as nanoceria, possess unique physicochemical properties such as a high oxygen storage capacity, reversible Ce^{3+}/Ce^{4+} redox behavior, excellent thermal stability, and strong catalytic activity [6, 7]. Their nanoscale dimensions provide a large surface area, high surface energy, and abundant oxygen vacancies, which enhance their reactivity and make them suitable for multifunctional applications. CeO_2 nanoparticles can be synthesized by various chemical and physical methods, including sol–gel, co-precipitation, hydrothermal, solvothermal, combustion, and green synthesis approaches, each method influencing the particle size, morphology, and defect structure. These synthesis routes allow fine control over crystallinity and surface chemistry, which are crucial for tailoring their performance in different fields [8, 9]. Owing to their remarkable redox and surface properties, CeO_2 nanoparticles find wide applications in catalysis, fuel cells, oxygen sensors, UV-blocking materials, and biomedical fields such as antioxidant, anti-inflammatory, and drug delivery agents [10, 11]. They are extensively explored in gas sensing, photocatalysis, energy storage devices, and environmental remediation due to their strong interaction with gases and pollutants. The versatile physicochemical properties of CeO_2 nanoparticles make them highly attractive for diverse scientific and technological applications [11, 12].

The main aim of the present research work is to synthesize pure CeO_2 nanoparticles (NPs) using the precipitation method with cerium (III) nitrate hexahydrate as a precursor, and to fabricate thick films through the standard screen-printing technique for investigating their electrical and gas sensing properties. The study is focused on evaluating key electrical parameters such as resistivity, temperature coefficient of resistance (TCR), and activation energy, as well as systematically analyzing the gas sensing performance of the prepared CeO_2 thick films toward different gases. Special emphasis is given to examining the sensitivity, selectivity, response and recovery times of the films for NH_3 detection, in order to establish CeO_2 NPs as potential candidates for efficient, selective, and reliable gas sensing applications.

2. EXPERIMENTAL WORK:

2.1 Synthesis of CeO_2 nanoparticles using precipitation method:

Cerium nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$] with 99.99% purity was employed as the precursor material for the synthesis of CeO_2 nanoparticles. Ammonia solution (NaOH) was used as the precipitating agent during the synthesis process to control the pH and facilitate the formation of cerium hydroxide, which upon calcination converted into CeO_2 nanoparticles. The synthesis was carried out using the precipitation method, which is simple, cost-effective, and suitable for obtaining highly pure nanoparticles. The graphical representation of the experimental workflow for the synthesis of CeO_2 nanoparticles via the precipitation route is illustrated in Figure 1 [13-15].

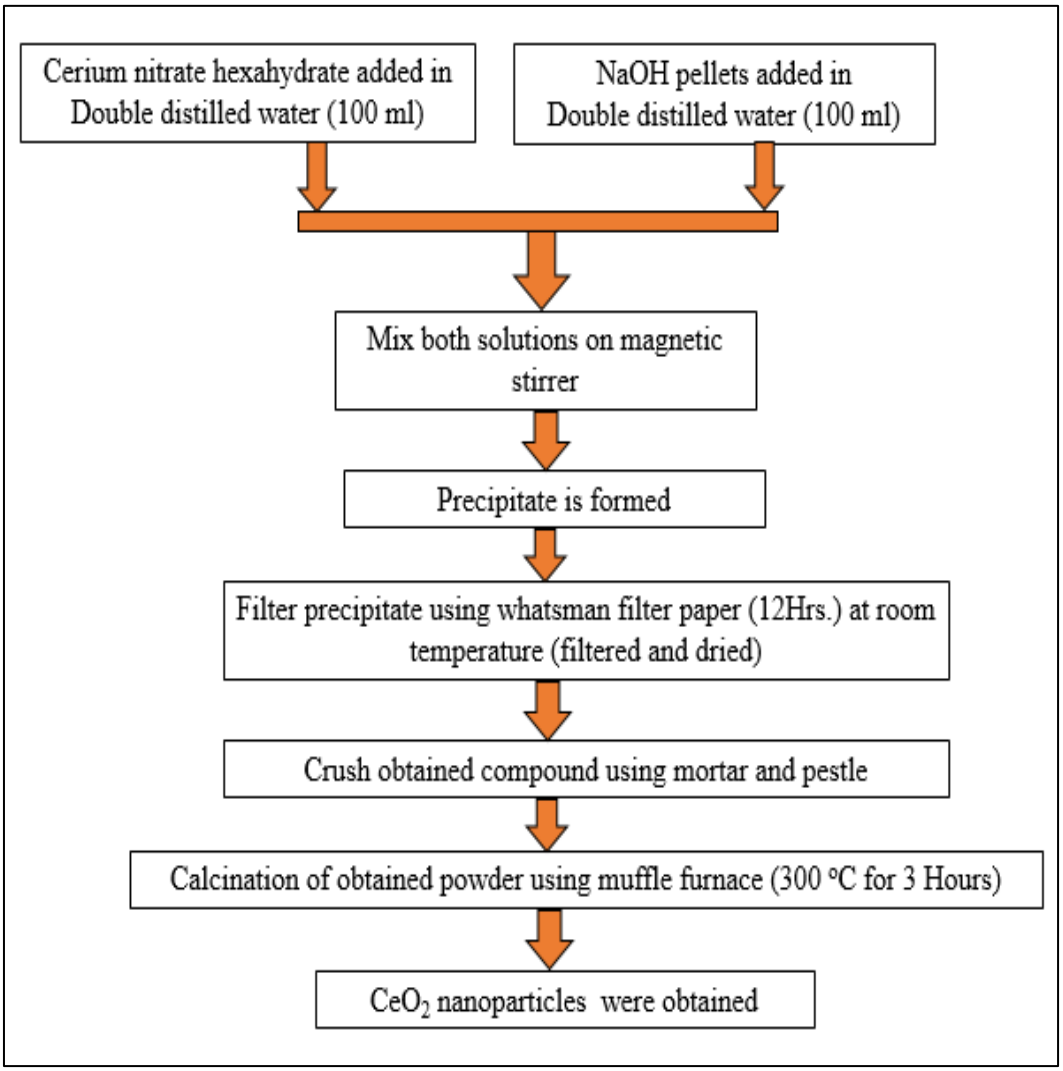

Figure 1: Synthesis steps of CeO_2 nanoparticles using precipitation method

2.2 Preparation of CeO_2 thick films using screen printing technique

The thick films of pure CeO_2 nanoparticles were prepared using the standard screen-printing technique. Initially, the synthesized CeO_2 nanopowder was mixed with an organic binders (BCA &EC) and inorganic (CeO_2 nanopowder) material to form a thixotropic paste of suitable viscosity [16]. This paste was then uniformly deposited onto pre-cleaned glass substrates using a stainless steel mesh screen, ensuring controlled thickness and uniform coating. After printing, the films were dried to remove the organic content and subsequently annealed at 200°C temperature for 2 h to improve adhesion, crystallinity, and surface morphology. The screen-printing process offers advantages such as simplicity, reproducibility, large-area deposition, and precise control over film thickness, making it highly suitable for gas sensor fabrication [16, 17] The complete procedure for the preparation of CeO_2 thick films using the screen-printing method is schematically illustrated in Figure 2.

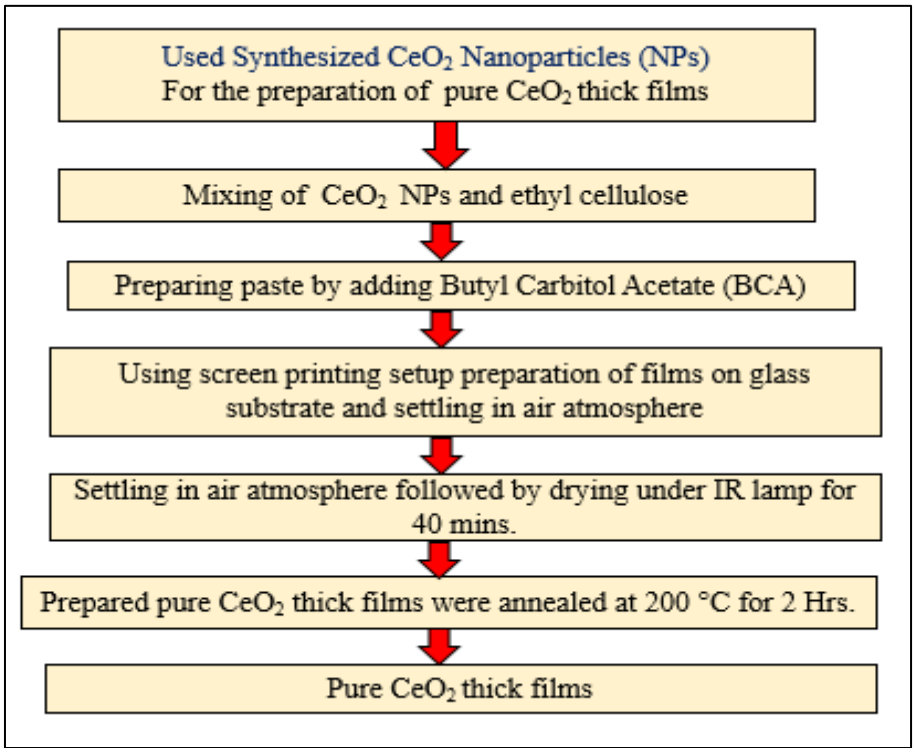

Figure 2: Steps of preparation of CeO_2 thick films using screen printing technique

2.3 Characterizations of prepared CeO_2 thick films:

2.3.1 Electrical characterizations of CeO_2 thick films:

The electrical characterization of the prepared CeO_2 thick films, key parameters such as resistivity, temperature coefficient of resistance (TCR), and activation energy in both low- and high-temperature regions were systematically investigated. These parameters are critical for understanding the semiconducting behavior and conduction mechanism of the material. The resistivity of the films was determined using Equation (1), while the TCR was calculated from the variation of resistance with temperature using Equation (2). The activation energy values corresponding to the low-temperature region (LTR) and high-temperature region (HTR) were obtained from the Arrhenius relation, as expressed in Equation (3) [16-18]. These calculations provided valuable insights into the electrical conduction and gas sensing response of the CeO_2 thick films.

$$\rho = \left(\frac{R \times b \times t}{l}\right) \Omega - m \qquad (1)$$

Where, ρ = Resistivity of prepared film, R = resistance at normal temperature, b = breadth of film, t = thickness of the film, L = length of the film.

$$TCR = \frac{1}{R_o}\left(\frac{\Delta R}{\Delta T}\right) \ /^{o} C \qquad (2)$$

Where,

ΔR = change in resistance between temperature T_1 and T_2,

ΔT = temperature difference between T_1 and T_2 and R_o = room temperature resistance of the film

$$\Delta E = Ae^{-Ea/kBT} \quad \text{eV} \qquad (3)$$

Where,

ΔE = Activation energy, T = Temperature and A = Arrhenius prefactor.

2.3.2 Gas sensing analysis of CeO_2 thick films:

The gas sensing properties of the prepared CeO_2 thick films were investigated using a static gas sensing apparatus as shown in Figure 3, in which the films served as the active sensing element. During the measurements, the electrical resistance of the films was recorded at different operating temperatures and under varying concentrations of the target gas [18, 19]. The change in resistance with respect to gas exposure was used to evaluate the sensing performance of the films. The sensitivity of the CeO_2 thick films toward the test gases was calculated using Equation (4), which relates the resistance of the sensor in air and in the presence of the target gas. This analysis enabled the determination of crucial sensing parameters such as sensitivity, selectivity, response time, and recovery time, thereby providing comprehensive insights into the gas sensing behavior of the CeO_2 films [19, 20].

$$\text{Sensitivity (\%)} = Ra\text{-}Rg/Ra \times 100 \quad (4)$$

Where,

Ra -Film resistance in air and Rg- film resistance in a gaseous atmosphere.

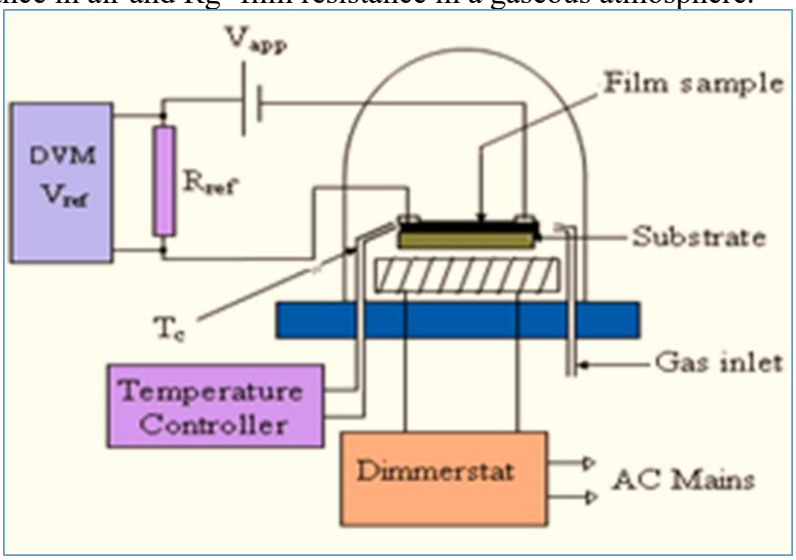

Figure 3. Schematic diagram of static gas sensing apparatus

3. RESULT AND DISCUSSION:

3.1 Electrical Characterization:

Figure 4 depicts the variation of resistance with temperature for CeO_2 thick films. It can be clearly observed that the resistance decreases continuously as the temperature increases, which is a typical characteristic of semiconducting materials. At lower temperatures, the resistance of the film is high due to limited thermal energy available for charge carriers to overcome the potential barrier [16, 17]. As the temperature increases, more charge carriers gain sufficient energy to participate in conduction, thereby reducing the resistance of the film. This negative temperature coefficient of resistance confirms the semiconducting nature of CeO_2 thick films [18].

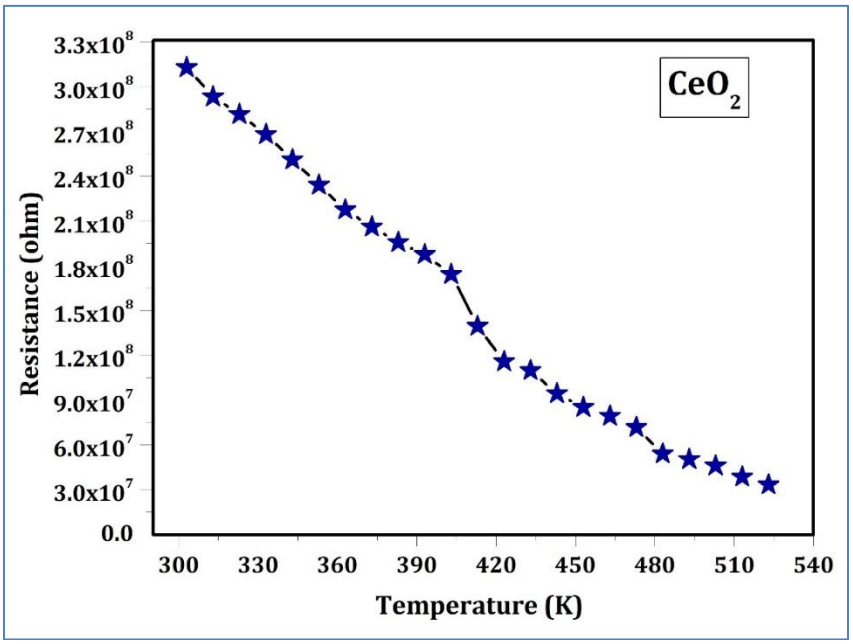

Figure 4: Resistance versus temperature of CeO_2 thick films

Figure 5 shows the Arrhenius plot of log(R) versus 1/T for CeO_2 thick films, which is commonly used to determine the activation energy of conduction. The linear regions in the plot correspond to different conduction mechanisms at low- and high-temperature regions (LTR and HTR, respectively) [18, 19]. The slope of the fitted straight lines in these regions provides the activation energy values, which were calculated to be 0.0546 eV in the LTR and 0.2421 eV in the HTR. The lower activation energy in the LTR suggests easier conduction at lower temperatures due to shallow trap states, whereas the higher activation energy in the HTR indicates the involvement of deeper trap states or increased grain boundary scattering [20, 21]. These results confirm the thermally activated conduction process in CeO_2 thick films and are in good agreement with semiconducting behavior observed in resistivity studies. The electrical outcomes of CeO_2 thick films are illustrate in Table 1.

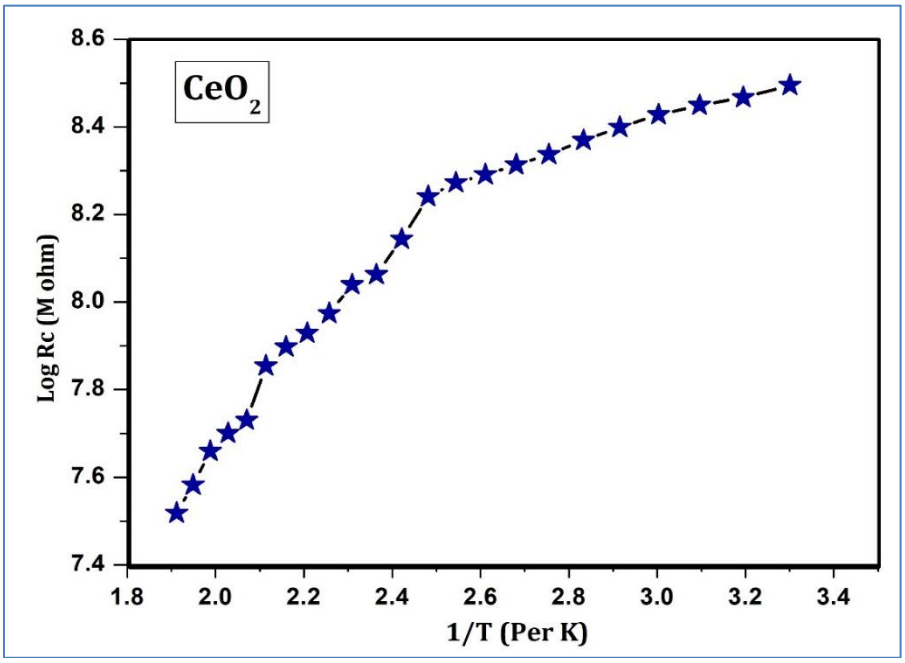

Figure 5: Arrhenius plot of CeO_2 thick films

Table-1: Electrical outcomes of CeO_2 thick films

Resistivity (Ω/m)	TCR (/°C)	Activation energy (eV)	
		LTR	HTR
5939.03	-0.002815	0.0546	0.2421

3.2 Gas sensing study of CeO_2 thick films

The gas sensing behavior of CeO_2 thick films was systematically studied with respect to operating temperature, selectivity, gas concentration, and response–recovery characteristics, as shown in Figure 6.

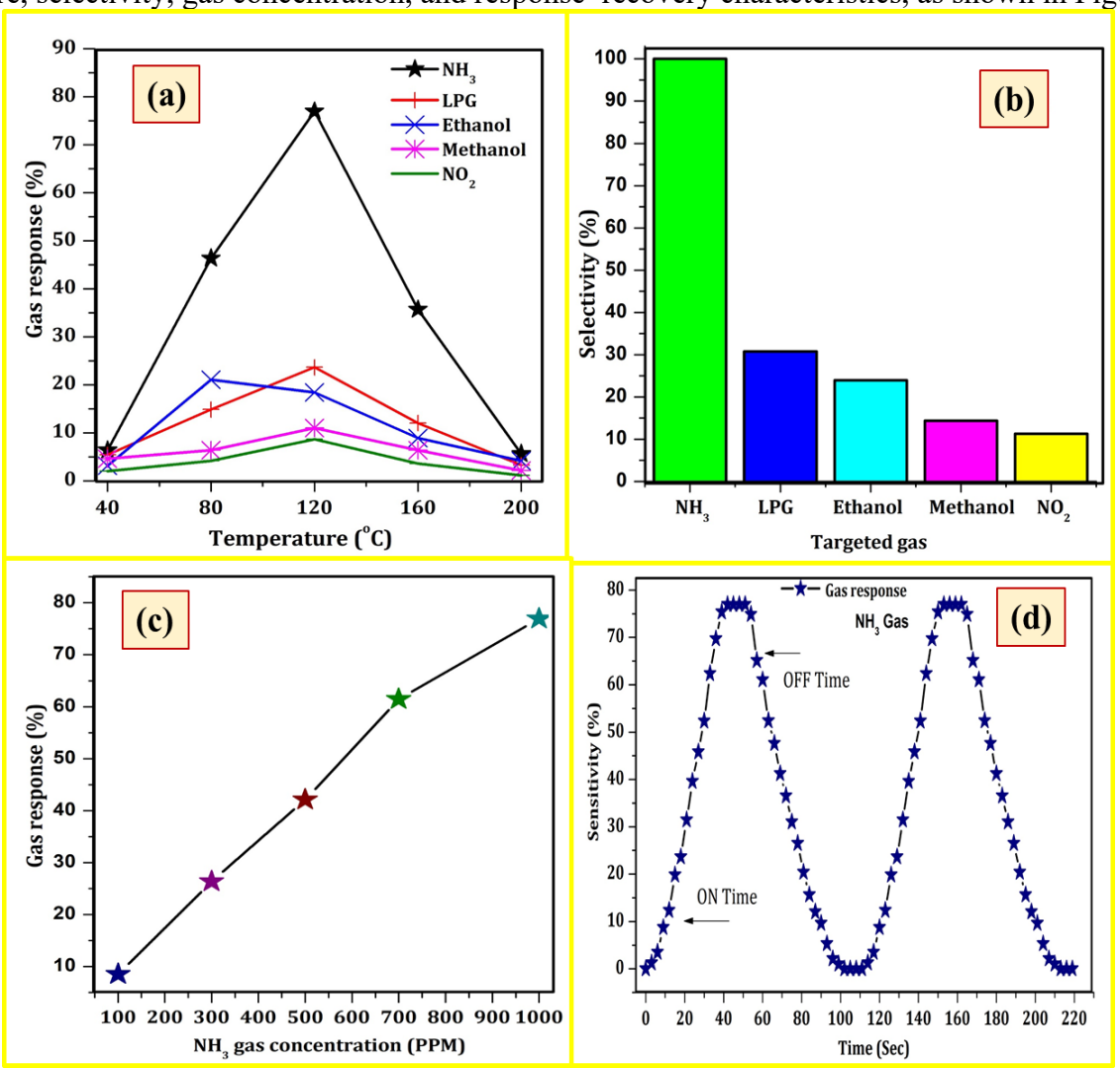

Figure 6: (a) Gas response verses operating temperature, (b) Selectivity, (c) PPM variation & (d) Response and recovery time plot of CeO_2 thick films

Figure 6 (a) illustrates the gas response of CeO_2 thick films toward different target gases such as NH_3, LPG, ethanol, methanol, and NO_2 over a temperature range of 40–200 °C. At lower operating temperatures, insufficient thermal energy restricts the surface reactions between adsorbed oxygen ions and the incoming gas molecules, leading to poor response. With an increase in temperature, surface reactions become more active due to the enhanced mobility of charge carriers and higher adsorption–desorption dynamics, thereby improving sensitivity [21, 22]. At higher temperatures (>120 °C), desorption of oxygen species occurs at a

faster rate than adsorption, reducing the availability of reactive oxygen species on the sensor surface and consequently lowering the gas response [23, 24]. The maximum sensitivity of CeO_2 thick films was found to be 76.95% toward NH_3 gas at 120 °C with a concentration of 1000 ppm, indicating that NH_3 is the most efficiently detected gas among the tested analytes. Figure 6(b) highlights the selectivity of CeO_2 thick films toward different gases. The sensor demonstrates a pronounced preference for NH_3, showing almost 100% selectivity compared to other interfering gases such as LPG, ethanol, methanol, and NO_2, which exhibit relatively low responses. High selectivity is one of the crucial requirements for practical gas sensor applications, as cross-sensitivity toward multiple gases reduces accuracy and reliability [24, 25]. The enhanced selectivity toward NH_3 can be attributed to the strong interaction between NH_3 molecules and surface-adsorbed oxygen ions on CeO_2. NH_3, being a reducing gas, reacts readily with the chemisorbed oxygen species (O^-, O_2^-, O^{2-}) on the CeO_2 surface, releasing electrons back into the conduction band of the semiconductor, thus causing a significant decrease in resistance. This strong redox interaction enhances both the magnitude and stability of the sensing response toward NH_3 compared to other gases [26, 27]. Figure 6(c) demonstrates the variation in gas response with different concentrations of NH_3 ranging from 100 ppm to 1000 ppm at the optimum operating temperature. The response increases almost linearly with increasing concentration of NH_3, which indicates that the sensor can effectively detect a broad range of NH_3 concentrations with high sensitivity. At lower concentrations (100–300 ppm), fewer NH_3 molecules interact with the surface oxygen ions, resulting in a smaller change in resistance. As the concentration increases, a larger number of NH_3 molecules participate in the surface reaction, thereby producing a greater electron release into the conduction band and enhancing the sensing response [23, 27]. At the maximum tested concentration of 1000 ppm, the response reached 76.95%, showing the ability of CeO_2 thick films to detect even high concentrations of NH_3 with remarkable efficiency. The nearly linear dependence of sensitivity on gas concentration further confirms the suitability of CeO_2 films for quantitative gas monitoring applications. Figure 6(d) presents the dynamic response curve of CeO_2 thick films toward NH_3 gas, highlighting the response and recovery times. The response time, defined as the duration required to achieve 90% of the maximum resistance change after exposure to the target gas, was found to be approximately 12 seconds, indicating rapid adsorption and surface reaction of NH_3 molecules. The recovery time, defined as the duration required to return to 90% of the baseline resistance after removal of the gas, was found to be 54 seconds. This relatively fast recovery demonstrates that NH_3 molecules desorb quickly from the CeO_2 surface once the gas is removed, enabling the sensor to regain its original state [27, 28]. The fast response and recovery characteristics are highly desirable for real-time monitoring applications, as they ensure that the sensor can detect and reset promptly in fluctuating gas environments.

CONCLUSIONS:

The pure CeO_2 nanoparticles were successfully synthesized using the precipitation method and employed to fabricate thick films via the screen-printing technique. Electrical characterization revealed a resistivity of 5939.03 Ω-m with a negative temperature coefficient of resistance (–0.002815 /°C), confirming the semiconducting nature of the films. The activation energy values were determined as 0.0546 eV in the low-temperature region and 0.2421 eV in the high-temperature region, indicating thermally activated conduction. Gas sensing investigations demonstrated that CeO_2 thick films exhibit excellent performance toward NH_3 gas, with a maximum sensitivity of 76.95% at 120 °C for 1000 ppm concentration, along with a rapid response time of 12 s and recovery time of 54 s. The films also showed good selectivity toward NH_3 compared to other gases such as LPG, ethanol, methanol, and NO_2. These findings highlight that CeO_2 thick films, owing to their stable semiconducting behavior, oxygen vacancy–driven surface activity, and efficient redox interaction with NH_3, are promising candidates for the development of low-temperature, selective, and reliable gas sensors.

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Conflict of Interest: There are no any conflict of interest.

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