

Environmental carbonaceous aerosols conversion into methanol using a zinc-decorated ZnO nanocage

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HIGHLIGHTS

- The environment is full of toxic gases which are harmful to humans.
- To study materials and suggest for the development of sensors to detect these toxic gases.
- Zinc doped zinc oxide nanocage sensor detect and activate carbon dioxide gas.
- Activated carbon dioxide is successfully converted into methanol.
- Zn-doped ZnO nanocatalyst can be used for the environmental cleaning of toxic gases.

ABSTRACT

The environmental aerosols in major South Asian cities were characterized using Aerosol Robotic Network datasets. Various types of aerosols were identified and classified. Industrial urban/vehicle emissions and biomass-burning carbonaceous aerosols dominated during the winter, whereas dust aerosols dominated during the summer and pre-monsoon seasons, respectively. Moreover, mixed aerosol types existed throughout the year. An attempt has been made to detect carbonaceous aerosol CO₂ using Zn-decorated ZnO nanocages, which can be converted into CH₃OH and H₂O using H₂ molecules. The adsorption of Zn on the nanocage of ZnO reduced the bandwidth to 2.18 eV from 4.05 eV, with an increase in the room temperature sensitivity and a sensing response of −49.38 % and −91.9 %, respectively. The emergence of intermediate states near the Fermi level narrowed the bandgap. The negative electronegativity and electron affinity suggest the polar nature, high reactivity, and softness of the Zn-decorated ZnO CO₂ complexes. Furthermore, a minimal recovery time of 2.249×10^{-11} s was noticed at room temperature, highlighting the remarkable catalytic efficiency of the ZnO–Zn/CO₂ system compared to previously published Ag-decorated ZnO nanocages. An increase in temperature has minimal effects on the sensing response, while the recovery time decreased notably. This research was conducted within the context of density functional theory.

1. Introduction

The negative impacts of environmental aerosols on living organisms and on disrupting seasonal variations and rainfall have gained increasing attention in South Asia [1]. Atmospheric aerosols are generated and emitted through natural and anthropogenic events, such as soil erosion, combustion, agricultural processes (nitrogenous emissions, tillage operations, fertilizers, and pesticides), construction,

urbanization, transportation, biomass burning, and industrialization [2]. Among these, the rapid growth of industry, urbanization, and vehicle transportation significantly increases the emission of environmental aerosols, which has a negative impact on living organisms [3]. As environmental aerosols emerge from different sources, they possess different shapes, sizes, and elemental compositions; therefore, their classification includes dust, biomass burning, urban/industrial, and mixed aerosols. These particles can be classified based on their size,

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Fig. 1. Environmental study area map of the South Asian countries.

sources of generation and transportation, and impacts on the climate [4]. Dust and carbon-containing environmental aerosols absorb shorter wavelength radiation [4,5], affecting the global climate [6]. Higher concentrations of atmospheric aerosols contribute to cloud strength and prolong the life of clouds [7]. These environmental aerosol particles are generated directly from different sources and enter the atmosphere owing to incomplete combustion. Consequently, fossil fuels, such as CO_x , SO_x , NO_x , and hydrocarbons [8], remain in the earth's atmosphere in various forms.

Climate change occurs because of rising of CO_2 levels [9]. The amount of CO_2 produced has doubled since the 1950s, reaching 445 parts per million by 2021 [10]. Excess CO_2 concentrations of more than 40,000 ppm can lead to respiratory infections, pulmonary disorders, cardiac conditions, and lung cancer [11]. In 2022, anthropogenic activities were responsible for approximately 33.8 billion tons of annual CO_2 emissions [12]. The conversion of carbonaceous aerosols, such as CO_2 , into valuable chemical stocks provides a solution to minimize their negative impact. Over the past two decades, scientists have begun developing heterogeneous catalysts for the conversion of CO_2 to methanol as a byproduct. This product, methanol, can be employed as a fuel in fuel cells to generate electricity as well as a feedstock for the synthesis of other chemicals [13].

ZnO, an n-type metal oxide, has a hexagonal structure ($a = b = 3.250 \text{ \AA}$ and $c = 5.206 \text{ \AA}$) with a bandwidth of 3.37 eV and a large surface area, thereby garnering the attention of researchers for its application in catalysis and gas sensors [14,15]. They can be synthesized in various forms, including nanowires, nanotubes, nanoribbons, and nanoparticles. The concept of nanocages based on a Buckyball (C_{60}) [16] has opened a new era of round-structured semiconductors.

As the climatic effects of each environmental type of aerosol differ from one another [17,18], it is necessary to classify and understand their impacts on the climate. Various clustering algorithms have been used for aerosol-type detection and measurement [17,19]. Numerous studies have explored aerosol optical depth (AOD) and the Angstrom exponent (AE) clustering technique [20].

Globally, limited research has been conducted on clustering techniques in South Asia [17,21]. Russell et al. utilized the extinction Angstrom exponent and adversarial autoencoder clustering methods to distinguish different aerosol types. Tiwari et al. classified major aerosols using the AOD versus AE clustering technique over the Indo-Gangetic Plain (IGP) in different seasons [22]. The characterization of environmental aerosols over the South Asian region and the sensing and

conversion of secondary aerosols, i.e., CO_2 gas, into beneficial byproducts are still limited.

For the first time, we conducted a comprehensive study on the characterization of environmental aerosol types using the cluster technique and retrieved Aerosol Robotic Network (AERONET) datasets for the period 2006–2014 from the most polluted selected cities in South Asia, namely, Karachi and Lahore (Pakistan), Jaipur and Kanpur (India), Dhaka (Bangladesh), and Kathmandu (Nepal). The classification was conducted by examining various aerosol properties, such as AOD and AE, to determine the dominant aerosol types. Additionally, a density functional theory (DFT)-based approach was adopted for the sensing and conversion of secondary aerosol CO_2 to methanol using ZnO-Zn-decorated nanocages. The nanocage was designed with the formula $(\text{XY})_n$, where $n = 12$, X = metallic element, and Y = nonmetallic elements [23]. The $(\text{XY})_{12}$ nanocage forms an octahedron with eight hexagonal and six tetragonal faces [24]. ZnO nanocages are widely used in solar cells, optical sensitizers, sensors, photocatalysts, quantum devices, hydrogen storage, and biomedical nanomaterials because of their semiconductor, piezoelectric, and pyroelectric properties [25]. The low toxicity, high thermal stability, excellent chemical stability, biocompatibility, large specific surface area, high electron mobility, and excellent electrical characteristics of these materials render them superior [26]. In its pristine form, ZnO nanocages interact poorly with numerous gases, limiting their effectiveness as sensors [27]. Several modifications, including chemical functionalization, defect formation, and impurity addition, have been employed to address this problem. Among these techniques, surface decoration is widely used to increase metal oxide sensitivity [28,29]. In particular, surface decoration with noble metals decreases the resistance of pure nanomaterials while improving their sensing, catalytic, and optoelectronic properties. Furthermore, transition metal decoration increases free electron concentration, resulting strong hybridization with gas species, ultimately boosting the conductivity and gas adsorption capacity of the nanomaterial [30]. The wide range of radiation absorption [31] and the large surface-to-volume ratio [32] of ZnO nanomaterials highlight their ability to perform environmental remediation, thereby serving as excellent substrates for pollutant elimination [33].

2. Instrumentation and methodology

2.1. Study area

South Asia (25.0°N , 76.4°E) covers the countries of Pakistan, Afghanistan, India, Bhutan, Nepal, the Maldives, Sri Lanka, and Bangladesh from east to west with ground-based AERONET stations. South Asia covers approximately 5.1 million km^2 with 1.749 billion inhabitants [34]. The myriad of environmental aerosols in this region not only influences South Asia but also affects the global environment. Therefore, the sources and types of the environmental aerosols should be traced [35].

Karachi (24.8°N , 67.0°E) is a populous Pakistani city situated 8 m above sea level with an arid and semiarid climate, dry/warm winters, and hot/humid summers [4]. Lahore (31.5°N , 74.3°E) is Pakistan's second largest commercial zone at 210 m above sea level and has a semiarid climate characterized by hot summers, cool winters, and intense fog in January [4], covering an area of 404 km^2 . Jaipur (26.9°N , 75.8°E) is a semiarid Indian city that is situated 431 m above sea level and experiences hot summers, pleasant winters, and heavy monsoon rains [4]. Kanpur (26.5°N , 80.3°E) is a densely populated city in the middle of the IGP 142 m above sea level that experiences scorching long summers, winters with severe fog, and dust storms before the monsoon. In this region, aerosols are generated mostly by both natural and anthropogenic operations with significant seasonal fluctuations [36]. Kathmandu (27.7°N , 85.3°E) is Nepal's capital and is nestled in the Himalayas. Its height is 1100–2700 m above sea level and it experiences mildly cold nights, a winter temperature of approximately 10°C , and a

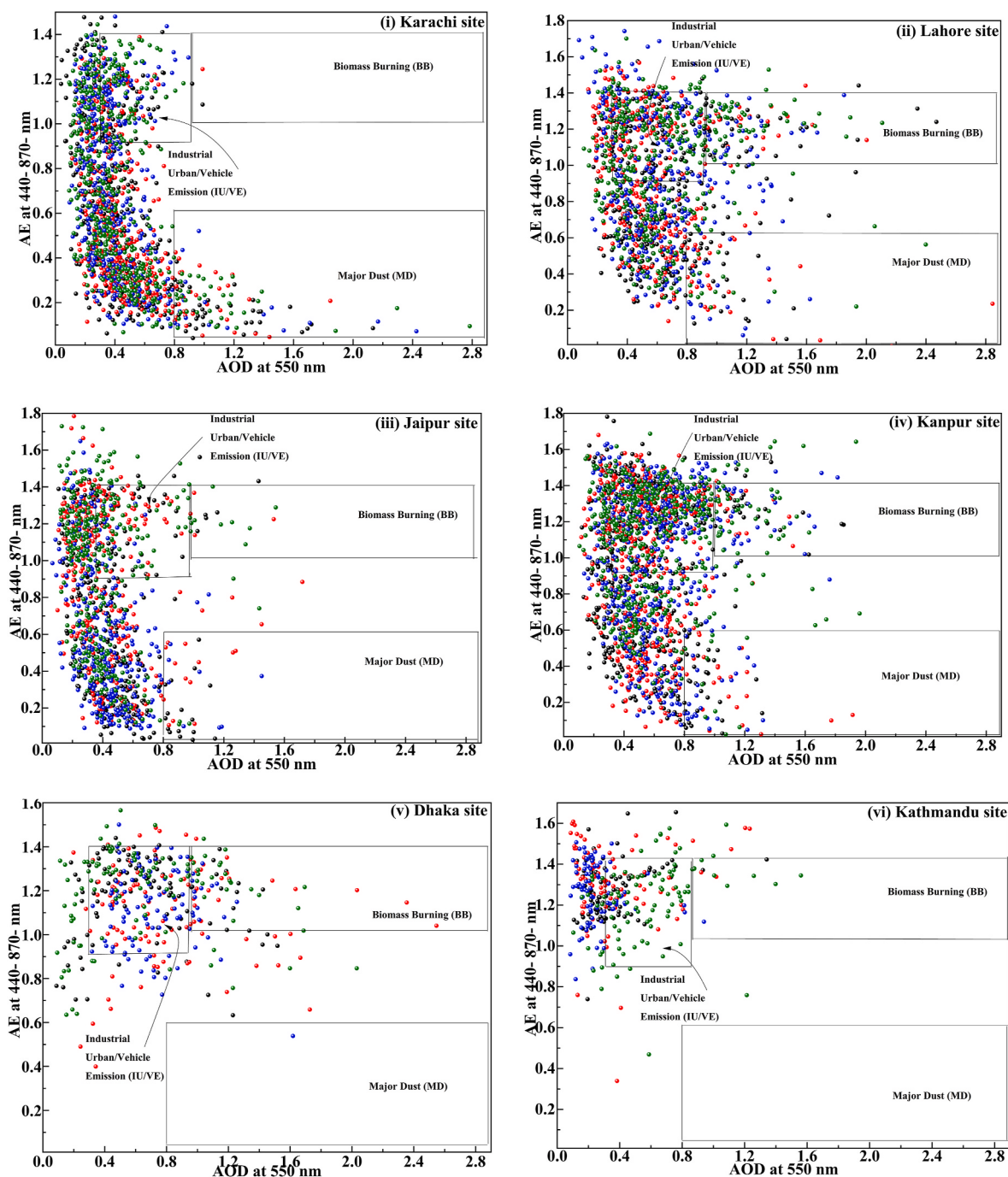


Fig. 2. Different types of environmental aerosols, i.e., industrial urban vehicles, biomass and major dust over the selected cities of South Asia: (i) Karachi, (ii) Lahore, (iii) Jaipur, (iv) Kanpur, (v) Dhaka, and (vi) Kathmandu. Red, blue, and green colors are used for visibility of the figure only. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

summer temperature of 28–30 °C. It has an approximate population of 1.6 million people within its area of 685 km² [37]. Dhaka (23.8°N, 90.4°E), the capital of Bangladesh, has a population of more than 9 million people. It is a major transportation center that features high environmental aerosol emissions from natural and unnatural sources and is surrounded by four rivers covering an area of 305 km². It experiences a tropical climate with four distinct seasons [38]. Fig. 1 demonstrates the study area map.

2.2. Instrumentation

AERONET is a remote-sensing device that operates on the ground

and provides information on aerosol parameters at wavelengths of 340, 380, 440, 500, 670, 870, 940, and 1020 nm [39]. For longer (440 nm) and shorter wavelengths, the AERONET AODs have uncertainties on the order of ± 0.01 and ± 0.02 , respectively [40]. The measurement errors were approximately 10 % and 35%–100 % for small and large particles, respectively [40]. Globally, 400 AERONET points have been installed. Its data exist in three formats: Level 1 for unscreened data, Level 1.5 for cloud-screened data [41], and Level 2.0 for precise data [40]. The data are published at www.aeronet.gsfc.nasa.gov; both direct and indirect inversion products are freely accessible.

In this study, we retrieved Level 2.0 AOD and AE data parameters from direct versions for the period 2006–2014 to characterize the

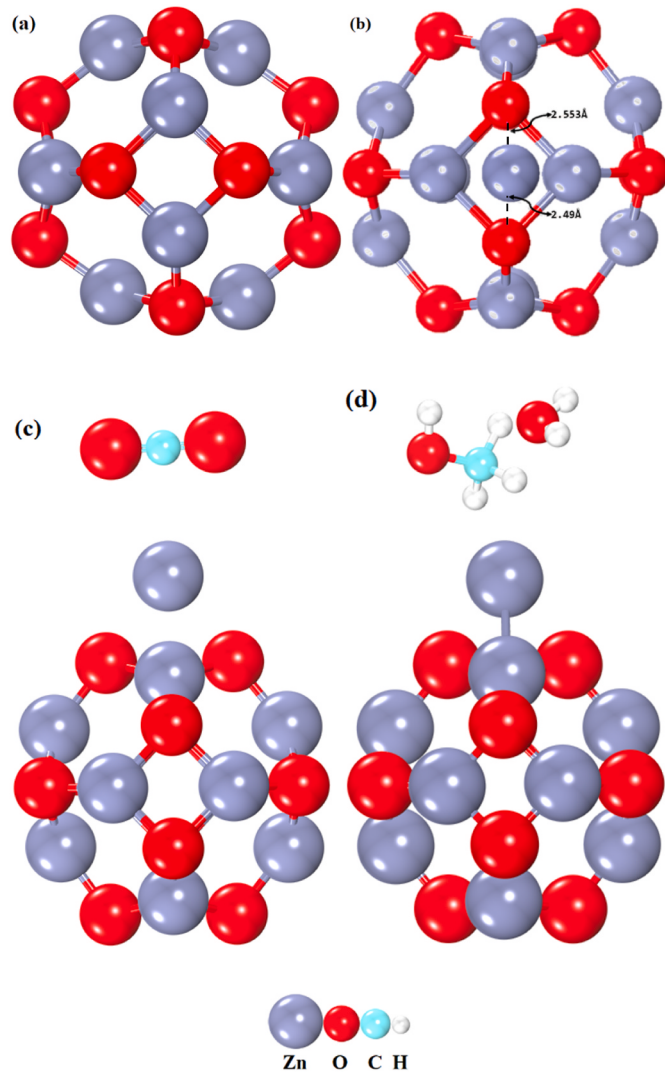


Fig. 3. (a) Pristine ZnO, (b) Zn-ZnO top view, (c) CO₂ gas complex interaction with the Zn-ZnO nanocage, and (d) Methanol (CH₃OH) + water (H₂O) as byproduct.

Table 1
Threshold values for the aerosol classification using cluster methodology based on several studies.

Location	AOD	AE	Aerosol Type	References
South Asia	0.8–2.9	0.01–0.6	Major Dust (MD)	current study
	0.3–0.9	0.9–1.4	Industrial Urban (IU)/VE	
Nanjing	0.9–2.9	1–1.4	Biomass Burning (BB)	Kumar et al. (2018) [55]
	<0.2	1.0 >	Clean continental	
	<0.2	<0.6	Marine	
	>0.3	1.0 >	Biomass Burning/Urban	
	0.5 >	<0.7	Desert Dust	
Varanasi	0.7 >	<0.6	Mostly Dust (MD)	Tiwari et al. (2015) [22].
	0.3–0.7	<0.9	Polluted continental (PC)	
	0.3–1.0	0.9 >	Anthropogenic Aerosol	
	1.0 >	1.0 >	Biomass Burning (BB)	

Table 2

Bandgap energy (E_{gap} , eV), adsorption energy (E_{ads} , eV), and sensitivity (S, %) of the pristine ZnO nanocage, Zn-decorated ZnO nanocage, and complex compositions of the ZnO nanocage.

System	E_{ads}	E_{lumo}	E_{homo}	E_{gap}	ΔE_{g} (%)	sensitivity (%)
ZnO	–	1.92	–2.13	4.05	–	–
ZnO/CO ₂	–	1.28	–2.85	4.13	–	–
ZnO–Zn	–0.85	0.89	–1.29	2.18	46	–
ZnO–Zn/CO ₂	–0.14	1.01	–1.04	2.05	50	–49.38
ZnO–Zn/CO ₂ + 3H ₂	–0.081	0.77	–1.10	1.87	55	–

various types of environmental aerosols over selected cities in South Asia.

2.3. Computational techniques and description

DFT studies of the Zn-decorated ZnO nanocage were conducted using the HYBRID DFT + U technique within the Spanish initiative electronic simulations with thousands of atoms (SIESTA) [42,43]. Initially, a ZnO nanocage with 12 atoms per element was modeled and optimized using a $3 \times 3 \times 1$ k-point grid. Similarly, a cutoff energy of 200 Ry and a $6 \times 6 \times 6$ k-point grid were employed for optoelectronic properties calculation [44]. In the conjugate gradient approximation method, an atomic force and self-consistency field of 10^{-6} eV and 0.002 eV/Å, respectively, were utilized to achieve tight convergence. The bandgap energy is underestimated by the generalized gradient approximation (GGA) [45] and overestimated by the errors in local density (LDA), whereas HYBRID DFT misinterprets the Coulombic interaction in the d orbital in addition to the higher energy states applied to transition metals [46]. For the transition metals, a HYBRID DFT (75 % GGA and 25 % LDA) with a Hubbard parameter ($U = 11$) [47] was employed to accurately calculate the properties. All the geometries were optimized using GGA with exchange correlation by the authors, specifically the revised Perdew Burke Ernzerhof [48]. For each atom of the ZnO nanocage, double zeta potential and pseudoatomic orbital basis set were utilized [42].

3. Results and discussion

This study aimed to characterize aerosol types over selected cities in South Asia from 2006 to 2014 using their properties retrieved from AERONET based on an advanced clustering technique. Aerosol properties, such as AOD and AE, can be clustered to classify aerosols. Additionally, this study focused on the sensing and catalytic hydrogenation of carbonaceous aerosols, such as CO₂ gas activated into methanol and H₂O molecules, on the decorated surface of a ZnO–Zn nanocage and investigated the impact of these aerosols on the optoelectronic properties of the nanocluster.

3.1. Clustering analysis

It is a tool used to categorize environmental aerosols into several classes/types to extract various aerosol properties using direct and indirect AERONET data [19]. Environmental aerosols were classified by analyzing the scatter plots of AOD and AE [18]. In Jaipur, five major aerosols, namely, desert dust, biomass burning, maritime, and mixed aerosol types, were characterized by AOD versus AE clustering analysis based on the AERONET data [49].

3.1.1. AOD and AE

The AOD measures the amount of light absorption depending on the size, shape, and expansion of the aerosol concentration. Moreover, AE indicates the aerosol size [50]. The analysis of the variations in the relationship between AOD and AE provides a potential approach for categorizing and evaluating the impact of different factors on particulate

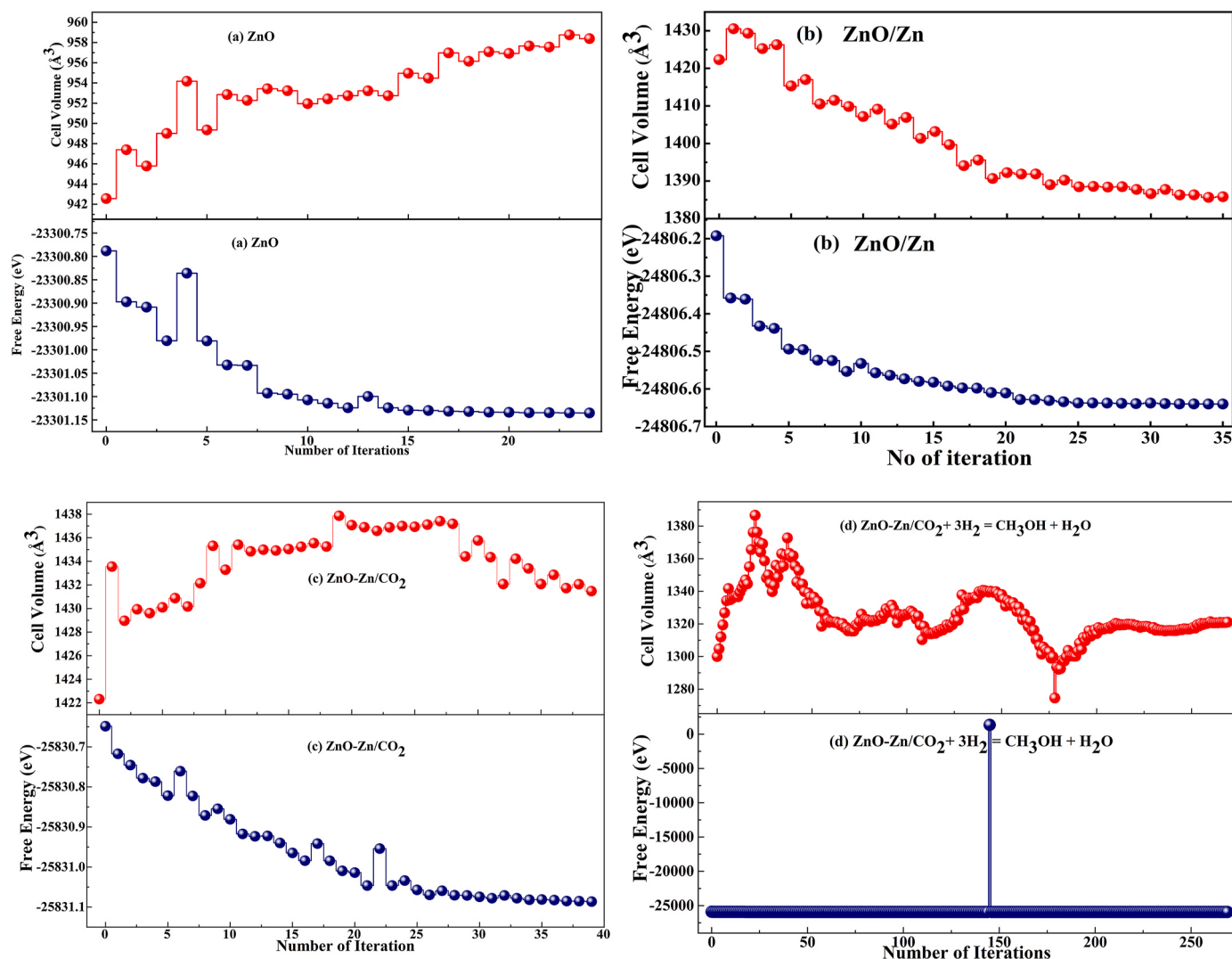


Fig. 4. Cell volume vs free energy (a–d) of the complete reaction pathway versus the number of iterations of pristine and Zn-decorated ZnO nanocage.

and seasonal aerosol concentrations [51]. Fig. 2 (i–vi) shows the daily mean scatter plots drawn between AOD at a wavelength of 550 nm and AE at wavelengths of 440–870 nm over the selected cities in South Asia from 2006 to 2014. The AOD and AE threshold values are in the range of 0.8–2.9 and 0.01–0.6, respectively, representing higher concentrations of coarse aerosol particles, including major dust (MD) with higher AODs and lower AE values. Industrial urban (IU)/vehicle emission (VE) and biomass burning (BB) were marked for each site in the range of 0.3–0.9 and 1.0–2.9, respectively. Compared to other sites, Dhaka and Kathmandu had lower MD concentrations throughout the study period, whereas Karachi had an extremely low BB concentration. Lahore had higher AOD values and lower AE values, corresponding to the existence of MD (coarse-mode) aerosols that mostly originate from the desert areas of the IGP in the summer and before the monsoon. In addition, higher concentrations of IU/VE and BB were detected throughout the selected cities in South Asia during the winter and post-monsoon seasons. The remaining scattered and encircled points associated with a wide range of aerosols (AOD vs. AE) throughout all the seasons were classified as a mixture of these aerosols, resulting from natural and unnatural sources [52] (see Table 1).

3.2. Geometrical study of pristine and Zn-decorated ZnO nanocages

A ZnO (ZnO)₁₂ nanocage composed of 24 atoms was arranged in a

tight octahedron composed of six tetragons and eight hexagons. In accordance with the experimental values for ZnO nanocage bonds, the nanocage has two different bond lengths: 1.901 Å between two hexagon rings and 1.972 Å shared between a tetragon and hexagon ring [53]. The ZnO nanocage four and six-membered rings exhibit angle variations from 90.907° to 87.043° and from 126.043° to 107.847°, respectively. The Zn atom was placed 2.8 Å above the center of the tetragonal ring. After optimization, the distance was decreased to 2.553 and 2.490 Å, as shown in Fig. 3(b). The ZnO–Zn nanocage exhibited a physisorbed nature, indicating the most stable configuration. Previous study [54] reveals an adsorption energy (E_{Ad}) of ~ -0.85 eV for Zn–ZnO nanocage, suggesting an exothermic process [28]. The high instability in the highest occupied molecular orbital (HOMO) of the ZnO nanocage significantly lowers the bandgap E_{gap} of the pristine ZnO nanocage to 2.18 eV from 4.05 eV with Zn adsorption, as depicted in Table 2.

CO₂, a stable molecule with strong C=O bonds and an energy of 7.8 eV, renders its reduction more difficult than C–C and CO bonds, with energies of 3.48 and 3.38 eV, respectively. During photocatalytic reduction, high energy is required to break the C=O bond. In this study, CO₂ was efficiently activated using Zn as the nanocatalyst, resulting in the conversion of CO₂ to methanol. Initially, CO₂ was placed 2.915 Å above the ZnO–Zn surface, which decreased to 2.616 Å after optimization, indicating the physisorption of CO₂, as shown in Fig. 3(c). The angle varied in the range of 180°–175.52°. The binding energy of CO₂

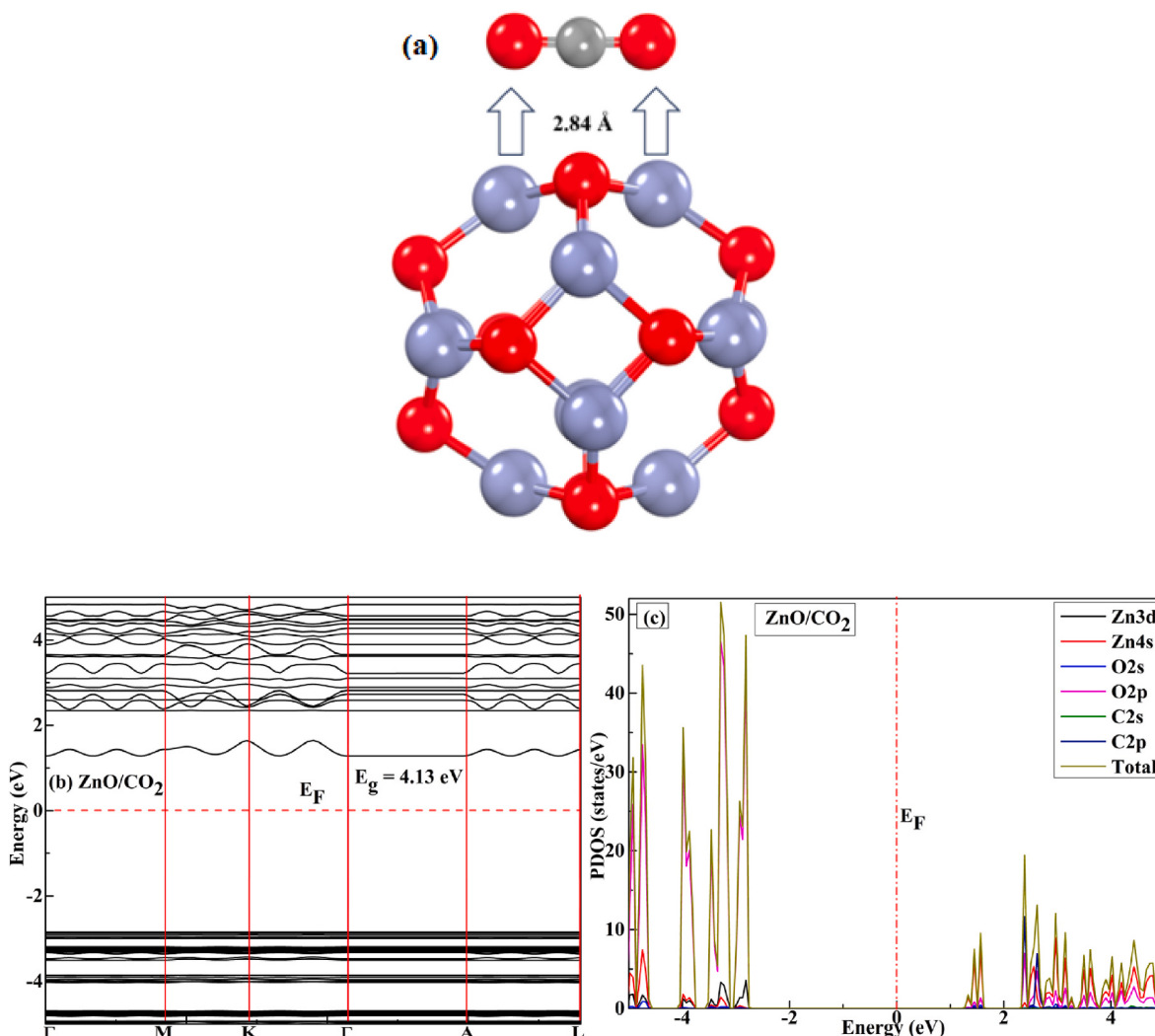


Fig. 5. Bandgap and projected density of states (PDOS) for the interaction of CO₂ with the pristine ZnO nanocage (a–c).

with the Zn-decorated ZnO nanocage confirms CO₂ activation. Subsequently, activated CO₂ was surrounded by 3H₂ molecules to observe their interactions. The 3H₂ molecules interact with activated CO₂ and produce CH₃OH and H₂O from the catalyst (ZnO–Zn) through the chemical reaction $[\text{CO}_2 + 6\text{e}^- + 6\text{H}^+ \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}]$, as illustrated in Fig. 3(d). The negative E_{ads} of -0.85 eV confirms the thermodynamic favorability of the process [56]. The computed E_{Ads} of -2.22 eV suggested that the desorption energy of the resulting CH₃OH + H₂O from the ZnO–Zn surface was more negative than that in previously published results [56]. Thus, an exothermic reaction process occurred due to ZnO nanocage catalytic activity which produce methanol and water molecules.

Fig. 4(a) and (b) show the iterations versus the energy and cell volume of the optimized pristine and Zn-decorated ZnO nanocages. During the optimization of the entire reaction, the cell volume and free energy varied until a stable state configuration was achieved. As such, the system aims to reduce its free energy and attain a stable position [57]. The introduction of additional reactants enhanced the highly negative [56,58] value of the free energy, implying that activated CO₂ gas reacted with 3H₂ gas molecules and ultimately separated from the surface of the ZnO–Zn nanocage after the formation of CH₃OH and H₂O molecules with a desorption energy of -2.22 eV, as indicated by the decrease in the cell volume (Fig. 4(c) and (d)).

3.3. Adsorption energies for CO₂ gas and complex on the ZnO–Zn nanocage

The adsorption energies for the entire chemical pathway of the Zn-decorated ZnO nanocage, CO₂ adsorption, and 3H₂ gas interaction with activated CO₂ were calculated using the following equation [59]:

$$E_{\text{ads}} = E_{\text{ZnO-Zn/CO}_2 + 3\text{H}_2} - E_{\text{ZnO-Zn/CO}_2} - E_{3\text{H}_2} \quad (1)$$

where $E_{\text{ZnO-Zn/CO}_2 + 3\text{H}_2}$ indicates the total energy of the whole complex. CO₂ adsorption is catalyzed by ZnO–Zn, and a negative E_{Ad} indicates an exothermic process [60]. The adsorption energies for all the configurations were calculated; the results are tabulated in Table 2. A more negative adsorption energy indicates greater structural stability [61].

3.4. Molecular-level analysis of orbitals

The energy difference is determined by E_{gap} , as expressed in Equation (2) [62], which indicates the kinetic stability and chemical reactivity of the system.

$$E_{\text{gap}} = E_{\text{L}} - E_{\text{H}} \quad (2)$$

where E_{L} and E_{H} represent the lowest unoccupied molecular orbital (LUMO) and (HOMO), respectively. Molecules with a lower E_{gap} have higher polarizability, degree of chemical reactivity and lower kinetic

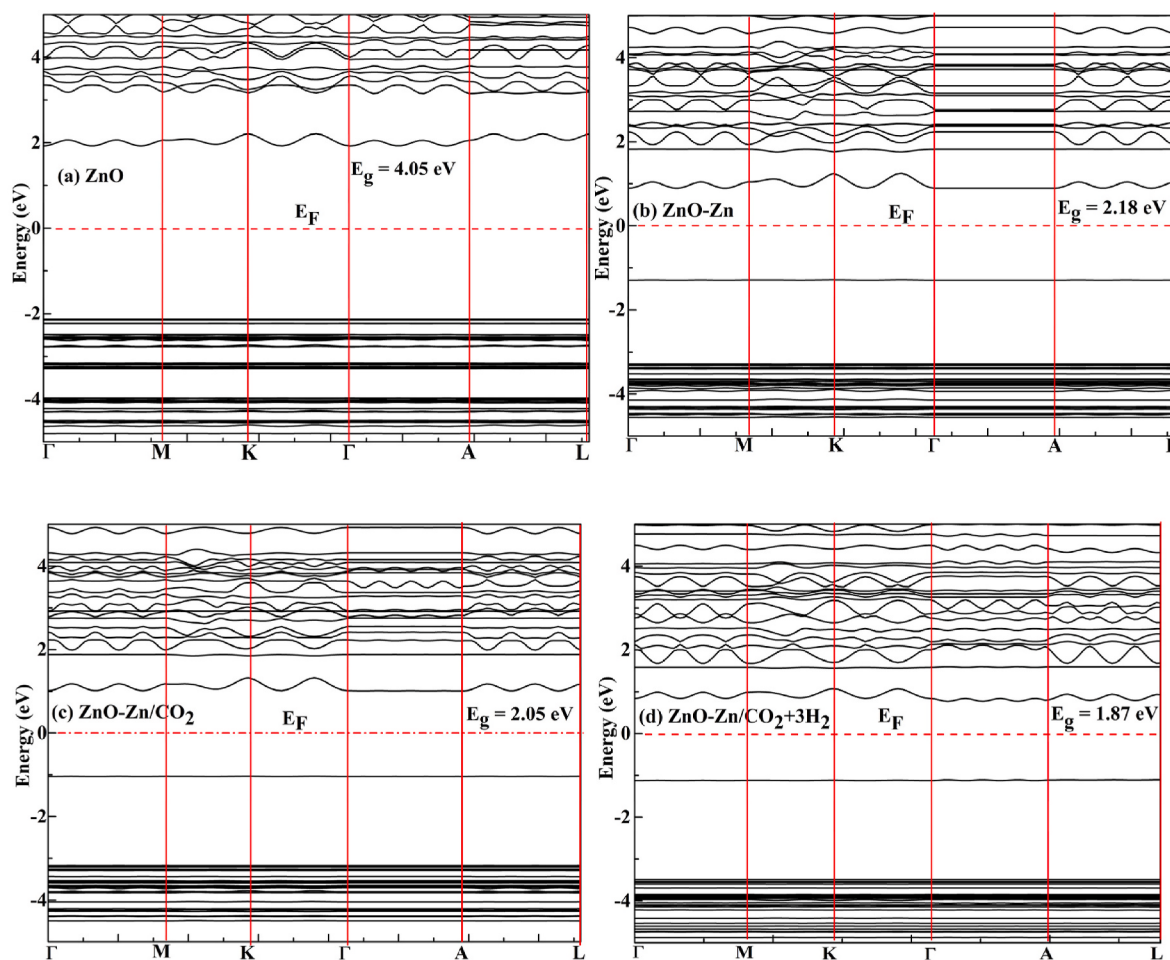


Fig. 6. Band structures of (a) pristine and (b) Zn-decorated ZnO nanocages and (c, d) CO₂ gas complex adsorbed on the ZnO–Zn nanocage.

stability [63].

The E_{gap} values for all the reactive species are depicted in Fig. 6(a–d). A E_{gap} of 4.05 eV for pristine ZnO is shown in Fig. 6(a) which is consistent with the literature [64]. The bandgap of the pristine ZnO nanocage was not significantly affected by CO₂ adsorption, resulting in its low response to CO₂ sensing. Initially, CO₂ was placed 2.65 Å above the pristine ZnO nanocage. The distance and bandgap increased, indicating the inertness of the ZnO nanocage toward CO₂ detection, as portrayed in Fig. 5(a)–(c), and Table 2.

Zn adsorption on the pristine (ZnO)₁₂ nanocage decreased the E_{gap} to 2.18 eV, suggesting an improved conductivity. Moreover, shifts in the E (HOMO) and E(LUMO) levels were observed with Zn adsorption. The effect of 3H₂ molecules on the electronic properties was examined. Resultantly, the E_{gap} decreased to 1.87 eV owing to the formation of intermediate states near the Fermi level, as depicted in Fig. 6(d).

Fig. 7 presents the PDOS for all the different structures. The conduction band of pristine ZnO is mainly composed of O-2p and Zn-3d states, whereas the valence band is concentrated within Zn-4 s and O-2p orbitals. Zn incorporation in pristine ZnO strengthened the contribution of the Zn-4 s and O-2p states to the valence and conduction bands near the Fermi level, as depicted in Fig. 7(b). The HOMO energy ultimately improved the optical characteristics of the nanomaterial and accelerated the transfer of electrons between the valence and conduction bands [65].

Fig. 7(c) shows the PDOS for the ZnO–Zn/CO₂ complex, where new intermediate energy levels are formed between the LUMO and HOMO of ZnO–Zn owing to the addition of O-2p and O-2 s energy levels. Moreover, the addition of 3H₂ molecules to the pre-adsorbed CO₂ gas

complex eliminated the O–O bond and promoted the formation of CH₃OH and H₂O by overlapping the O-2 s, H-1 s, and C-2 s energy levels. The binding energies of the resulting products demonstrated that the reaction was promoted at room temperature. Consequently, the ZnO–Zn nanocage has the potential to directly transform CO₂ gas into electrical signals, highlighting its potential application in CO₂ sensors [66].

3.5. ZnO–Zn nanocage sensitivity

The sensitivity, as expressed in Equation (3), is the difference between the initial E_{gap} measured in the clean cluster ($E_g A$) and after the adsorption of CO₂ on the ZnO–Zn surface ($E_g B$) [67].

$$\text{Sensitivity} = \frac{(E_g B - E_g A)}{E_g A} \quad (3)$$

An extremely low sensitivity of 1.98 % toward CO₂ was observed for pristine ZnO, which considerably increased to 49.38 % after Zn decoration, as tabulated in Table 2.

3.6. Conductivity of the ZnO–Zn nanocage

The conductivity changes with the variations in E_{gap} [68]. The pristine ZnO nanocage has low conductivity, which increases with the surface decoration of the ZnO nanocage with Zn. Equation (4) expresses the electrical conductivity in terms of E_{gap} [69].

$$\sigma = A T^{3/2} \text{Exp} \left(- E_{gap} / 2KT \right) \quad (4)$$

where A is a constant (electrons/ $m^3 k^{3/2}$), K is the Boltzmann constant,

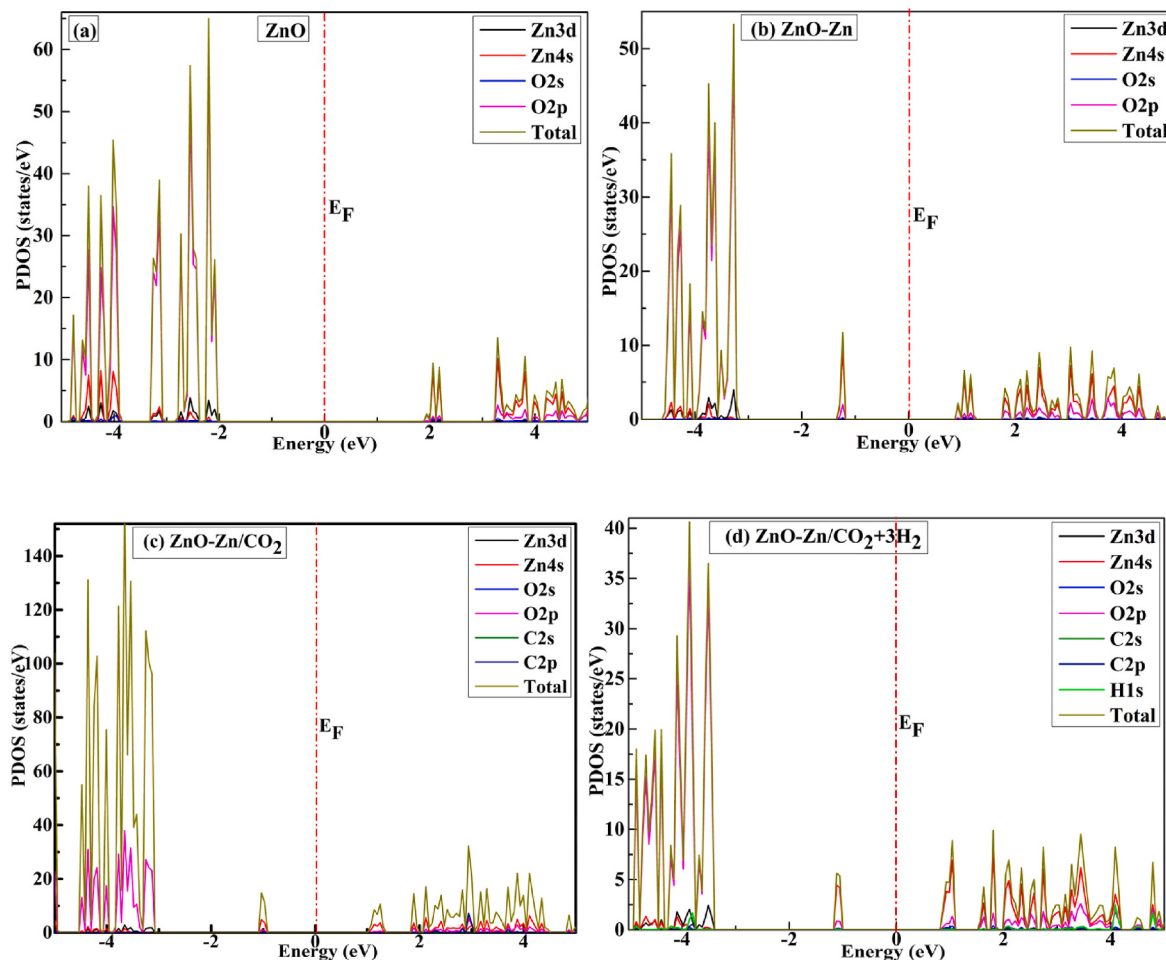


Fig. 7. PDOS of the (a) pristine and (b) Zn-decorated ZnO nanocage and (c, d) CO₂ and complexes adsorbed by the ZnO–Zn nanocage.

Table 3

Temperature (K), sensing response (Sr %), and recovery time (t_r, s) after CO₂ adsorption on the Zn-decorated (ZnO)₁₂ nanocage.

System	Temperature	Sensing Response	Recovery time
ZnO–Zn/CO ₂	300	– 91.9	2.249×10^{-11}
	320	– 90.5	1.603×10^{-11}
	340	– 89.1	1.189×10^{-11}
	360	– 87.7	9.118×10^{-12}
	380	– 86.3	7.191×10^{-12}
	400	– 84.8	5.807×10^{-12}

and σ is the conductivity. Han et al. experimentally explored the trend in the sensing response, conductivity, and recovery time of a nanocage toward CO₂, which was very low in the absence of a transition metal [70].

The sensing response was calculated using Equation (5):

$$Sr (\%) = \frac{\left| \frac{1}{\sigma_{Gas}} - \frac{1}{\sigma_{pristine}} \right|}{\frac{1}{\sigma_{pristine}}} = \left| \frac{\sigma_{pristine} - \sigma_{Gas}}{\sigma_{Gas}} \right| = \left| \frac{\sigma_{pristine}}{\sigma_{Gas}} - 1 \right| \quad (5)$$

where Sr , σ_{pure} , and σ_{gas} represent the sensing response as a percentage, the conductivity of the pristine ZnO nanocage, and the conductivity of the CO₂ gas adsorbed on the ZnO nanocage, respectively. The surface decoration of ZnO with Zn significantly enhances the sensing response at various temperatures, as shown in Table 3.

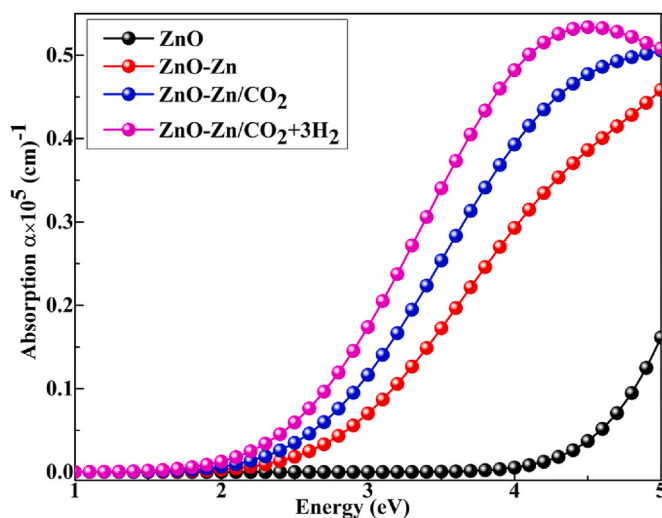


Fig. 8. Improved optical absorption of the Zn-decorated ZnO nanocage after CO₂ and complex adsorption, as obtained using the HYBRID DFT + U method.

3.7. Recovery time

The recovery time refers to the time taken to return to the baseline value and can be calculated using the following equation [54]:

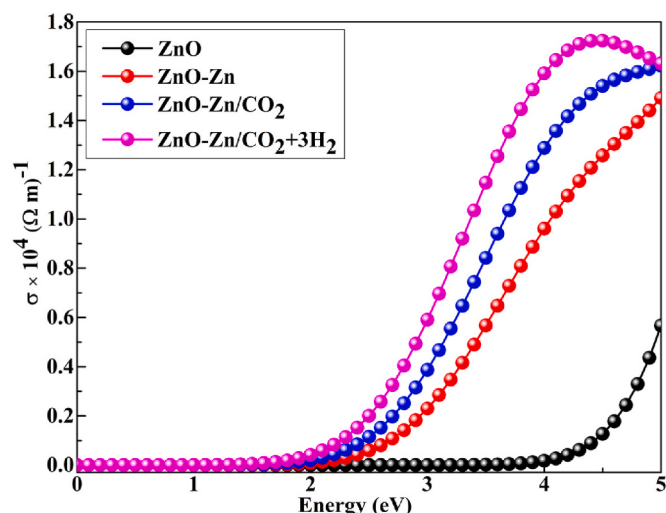


Fig. 9. Improvement in the optical conductivity of the Zn-decorated ZnO nanocage after CO₂ complex adsorption, as obtained using the HYBRID DFT + U method.

Table 4

The ionization potential, electron affinity, Mulliken electronegativity, softness, hardness, chemical potential, and electrophilic index (all in eV) were calculated, as was the charge transfer of the different complexes.

Chemical characteristics	ZnO	ZnO/ CO ₂	ZnO-Zn	ZnO-Zn/ CO ₂	ZnO-Zn/ CO ₂ +3H ₂
Ionization Energy I (eV)	2.13	2.85	1.30	1.0351	1.1053
Electron affinity A (eV)	-1.92	-1.28	-0.90	-1.0112	-0.773
Chemical hardness η	2.03	2.07	1.095	1.0232	0.948
Chemical softness s (eV) ⁻¹	0.25	0.242	0.50	0.489	0.5343
Electronegativity χ (eV)	0.105	0.785	0.198	0.01195	0.169
Chemical-potential μ (eV)	-0.105	-0.785	-0.198	-0.01195	-0.169
Electrophilic-index w (eV)	0.011	0.64	0.0214	7.3054 × 10 ⁻⁰⁵	0.0134
Charge transfer (ΔN)	–	–	–	-0.046	0.0296

$$t_R = V_0^{-1} \text{Exp}(-E_{Ad}/KT) \quad (6)$$

where V_0 , T , and K represent the attempt frequency, temperature, and Boltzmann constant, respectively ($\approx 8.61 \times 10^{-5}$ eV). Table 3 presents the calculated recovery times for CO₂ sensing on the ZnO-Zn nanocage at the selected temperatures. At the optimal room temperature, ZnO-Zn has a high sensing response of -91.9 % with a swift recovery time of 2.249×10^{-11} s. The Zn-decorated nanocage exhibited an improved sensing response and recovery time compared with those of the Ag-decorated ZnO nanocage, this exhibiting efficient catalytic performance as compared to the previous report [71]. Kumar et al. reported the maximum response for a metal-decorated ZnO nanocage at 323 K [54,72]. The recovery time decreases at temperatures above the normal temperature.

3.8. Optical property calculations of the Zn-decorated ZnO nanocage

Fig. 8 shows the optical absorption spectra of all the complexes. The ZnO nanocage exhibited absorption onset at 4.05 eV in the UV range, which agrees with the experimental findings [73]. After Zn decoration, the optical spectrum absorption improved owing to bandgap engineering. When CO₂ and H₂ gas molecules interacted with the decorated ZnO

nanocage, the absorption in the electromagnetic spectrum is further enhanced, as shown in Fig. 8. Moreover, CO₂ complex absorb Infrared radiations (IRs) reflected back from the earth surface and resulting into global warming [74,75].

The optical conductivity, as shown in Fig. 9, is in accordance with previously reported absorption spectra and experimental data [76], in which CO₂ complexes have excellent optical conductivity from the visible to the ultraviolet region (4.50–1.63 eV) of the solar spectrum. Visible light induced photocatalysis is more potent in the presence of carbon and decrease the rate of electron-hole pair recombination, thereby enhancing the overall conductivity [77]. Under visible-light irradiation, the ZnO-Zn nanocage exhibited greater photocatalytic absorption and optical conductivity than the pristine ZnO nanocage.

3.9. Quantum-molecular explanation

The quantum chemical characteristics of the pristine and other complexes shown in Table 4 provide insights into the chemical reactivity of the gas molecules [78]. The formulae used in calculating the electronegativity, chemical potential, ionization energy, electron affinity, chemical hardness and softness, electrophilicity index, and charge transfer between the substrate and adsorbate were adopted from previous work [79].

The Zn-decorated ZnO nanocage functions as an electron donor to CO₂, as confirmed by the negative values of ΔN in Table 4 [80]. The lower ionization energy of the Zn decorated ZnO/CO₂ confirms that more energy is needed for the complex to become a cation than for pristine ZnO/CO₂. The CO₂ complex has a high negative electron affinity [81], indicating its highly reactive and energy-releasing nature. Furthermore, the high electron affinity of these materials suggested that they had an electrophilic structure that produced stable negative ions. The polar characteristics of the obtained product, as shown by the negative electronegativity values, suggest higher softness and lower hardness and electrophilicity indices [78], as tabulated in Table 4. A decrease in the hardness lowers the resistance of the species to the loss of electrons owing to a narrow bandgap. Moreover, the reduced electrophilic index after CO₂ adsorption diminishes the charge transfer from the decorated surface, thereby forming methanol and H₂O upon interaction with 3H₂ molecules.

4. Conclusion

AERONET datasets were utilized to characterize aerosols in major South Asian cities by identifying MD particles in the summer and pre-monsoon seasons, IU/VE and BB particles in the winter and post-monsoon seasons, and a mixture of these particles throughout the year via AOD and AE clustering. Moreover, the structural, adsorption, and optoelectronic properties of the Zn-decorated ZnO nanocage used for sensing carbonaceous aerosols, particularly CO₂ in the presence of 3H₂ molecules, were investigated using DFT. CO₂ activation tuned the optoelectronic properties of the Zn-decorated ZnO and produced methanol and water. Besides, the more negative values of the adsorption energies (-0.85 and -0.14 eV) and desorption energy of -2.22 eV quickly increased the nanocluster sensitivity from 1.98 % to 49.38 %. At ambient temperature (300 K), the nanocage displayed a robust sensing response of 91.9 % with a short recovery time of 2.249×10^{-11} s for CO₂ detection, significantly surpassing that of Ag-decorated ZnO nanocages. Moreover, high temperatures had a minimal effect on the sensing response but considerably increased the recovery time before detection. The negative electronegativity values suggested the polar nature of the nanocage with increased softness and decreased hardness, whereas a higher negative electron affinity increased the reactivity and energy in the CO₂ complex. Therefore, this study offers a groundbreaking approach for CO₂ activation and conversion into crucial products using ZnO-based nanocatalyst.

CRediT authorship contribution statement

Sheraz Ahmad: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis. **Shabeer Ahmad Mian:** Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Data curation, Conceptualization. **Akbar Hussain:** Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis. **Ejaz Ahmed:** Writing – review & editing, Validation, Conceptualization. **Muhammad Saleem Khan:** Writing – review & editing, Validation, Resources, Methodology, Conceptualization. **Gul Rahman:** Writing – review & editing, Validation, Methodology, Conceptualization. **Joon-kyung Jang:** Writing – review & editing, Validation, Software, Resources, Conceptualization.

Declaration of competing interest

The authors declare no competing financial interests but acknowledge competing non-financial interests.

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Data availability

All the available data in which most of it is presented in the tables, simulation and environmental data for this work will be provided upon request.

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