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COMPARATIVE ANALYSIS OF METALLIC OXIDES AND NANOSTRUCTURED MATERIALS FOR AIR PURIFICATION APPLICATIONS

Omar AHMED[1], Adriana-Gabriela SCHIOPU[1,2], Mihai OPROESCU[3]
[1] Science and Materials Engineering Doctoral School, National University of Science and Technology POLITEHNICA Bucharest, Romania
[2] Faculty of Mechanics and Technology, National University of Science and Technology POLITEHNICA Bucharest - Pitești University Centre, Romania
[3] Faculty of Electronics, Communication and Computers, National University of Science and Technology POLITEHNICA Bucharest- Pitești University Centre, Romania
e-mail: omaralsaadi@yahoo.com; gabriela.schiopu@upb.ro; mihai.oproescu@upb.ro

ABSTRACT

Air pollution represents one of the major environmental and public health challenges worldwide, generating an increasing demand for efficient air purification technologies. Nanostructured materials have attracted significant attention due to their high surface area, enhanced reactivity, and multifunctional pollutant removal mechanisms. This paper presents a comparative analysis of metallic oxides employed in air purification applications, focusing on titanium dioxide (TiO_2), zinc oxide (ZnO), copper oxide (CuO), nickel oxide (NiO), and magnesium oxide (MgO). The fundamental purification mechanisms, including heterogeneous photocatalysis, reactive oxygen species generation, gas adsorption, and chemisorption processes, are discussed in relation to the structural and electronic properties of each material. The study evaluates the advantages and limitations of these oxides in removing volatile organic compounds, nitrogen oxides, sulphur oxides, and biological contaminants. Furthermore, the performance of metallic oxides is compared with that of carbon-based nanomaterials and metal-organic frameworks, highlighting the benefits of hybrid nanocomposite systems. Attention is given to practical implementation challenges, such as charge carrier recombination, photocorrosion, catalyst deactivation, mass transfer limitations, formation of toxic by-products, and nanoparticle immobilization requirements. The analysis indicates that no single material can provide a universal solution for air purification; instead, future developments should focus on engineered heterojunctions and multifunctional hybrid systems capable of combining adsorption, photocatalytic degradation, and long-term operational stability. These approaches offer promising perspectives for the development of next-generation sustainable air purification technologies.

KEYWORDS: air purification, mechanism, comparative analysis, environmental applications, metallic oxides application, air quality

1. Introduction

In Romania, the monitoring and evaluation of ambient air quality are strictly regulated, being fully aligned with European Union legislation. The main legal framework in Romania is represented by Law no. 104/2011 on ambient air quality, which directly transposes the European Directive 2008/50/EC (Framework Directive on ambient air quality for cleaner air in Europe) and Directive 2004/107/EC [1].

From a technical and legal point of view, there are no differences between the limit values imposed in Romania and those in the rest of Europe, as all EU member states must comply with the same thresholds. However, major differences arise at the level of implementation, effective monitoring and penalties (infringement procedures) [2].

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The efficiency of nanomaterials such as ZnO, TiO_2, graphene, metal-organic frameworks (MOFs) or carbon nanotubes in the gas phase is due to clear physical laws. As the particle size decreases below 100 nm, the percentage of atoms exposed to the surface increases exponentially. For air purification, this means high density of active adsorption sites and reaction sites per unit mass. The modification of the structure of the energy bands (widening of the forbidden band to very small sizes or the generation of surface defect states, such as oxygen vacancies in ZnO) allows for a more efficient generation of reactive oxygen species (ROS:•OH,•O2−). Nanomaterials can operate simultaneously through three mechanisms: physical/chemical adsorption (storage of the pollutant), heterogeneous photocatalysis (destruction of the pollutant under the action of light) and antimicrobial activity (destruction of bioaerosols and bacteria) [3].

The performance of nanomaterials employed in air purification technologies is strongly governed by their structural and physicochemical characteristics. At the nanoscale, the reduction of particle dimensions results in a substantial increase in the surface-to-volume ratio, leading to a higher density of active sites available for adsorption and catalytic reactions. Consequently, nanostructured materials exhibit significantly enhanced interaction with gaseous pollutants compared to their bulk counterparts [4].

Surface morphology represents a critical parameter influencing pollutant capture efficiency. Nanorods, nanowires, nanosheets, hollow spheres, and hierarchical porous structures provide different diffusion pathways and adsorption capacities. Materials exhibiting interconnected mesoporous networks facilitate rapid mass transfer and improved accessibility of active sites, thereby increasing the degradation rate of volatile organic compounds (VOCs), nitrogen oxides (NOx), sulphur oxides (SOx), and biological contaminants [5-8].

Defect engineering has emerged as a powerful strategy for improving the environmental performance of metal oxide nanomaterials. Structural defects such as oxygen vacancies, cation vacancies, grain boundaries, and surface disorder introduce localized electronic states that enhance charge separation and promote the formation of reactive oxygen species (ROS). These species, including hydroxyl radicals (•OH), superoxide radicals (•O2−), and singlet oxygen, play a fundamental role in the oxidation and mineralization of airborne contaminants [8].

Furthermore, crystal phase composition directly influences photocatalytic efficiency. Highly crystalline structures generally facilitate charge carrier transport and reduce recombination losses, whereas controlled defect concentrations can create additional active centres without excessively increasing electron-hole recombination rates. Therefore, optimization of morphology, porosity, crystallinity, and defect density remains essential for the rational design of advanced air purification nanomaterials.

2. Comparative analysis of metallic oxides used for air purification

Nanomaterials used in air purification can be broadly classified into semiconductor metal oxides, carbon-based nanomaterials, metal-organic frameworks (MOFs), and hybrid nanocomposites. Each class exhibits distinct advantages and limitations that determine its suitability for specific environmental applications.

Semiconductor metal oxides such as TiO_2, ZnO, CuO, NiO, and WO_3 remain the most extensively investigated materials due to their photocatalytic properties, chemical stability, and relatively low production costs. TiO_2 is considered the benchmark photocatalyst because of its excellent photostability and oxidation capability; however, its wide band gap restricts activation primarily to ultraviolet radiation. ZnO exhibits comparable photocatalytic activity while additionally possessing intrinsic antibacterial properties [9-12]. Nevertheless, ZnO may suffer from photocorrosion under prolonged operating conditions [13].

Carbon-based nanomaterials, including graphene, graphene oxide, reduced graphene oxide, carbon nanotubes, and activated carbon nanostructures, primarily contribute through adsorption mechanisms. Their exceptionally high specific surface area facilitates efficient capture of volatile organic compounds and particulate matter. Moreover, their high electrical conductivity enhances charge transport when integrated into photocatalytic heterostructures [14, 15].

Metal-organic frameworks represent a rapidly growing class of porous crystalline materials characterized by unprecedented surface areas and tuneable chemical functionality. MOFs exhibit remarkable selectivity toward specific pollutants, particularly carbon dioxide, ammonia, and volatile organic compounds. However, long-term stability under humid atmospheric conditions remains a significant challenge for practical implementation [16, 17].

Hybrid nanocomposites combine the advantages of multiple material classes. Systems such as TiO_2/graphene, ZnO/CuO, TiO_2/MOF, and ZnO/carbon nanotube composites exhibit improved charge separation, broader light absorption ranges, enhanced adsorption capacity, and superior

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photocatalytic efficiency. Consequently, hybrid nanostructures currently represent one of the most promising directions for next-generation air purification technologies.

Despite laboratory performance (where pollutant degradation rates of over 95% are often reported), transfer to real-world applications faces several critical barriers [18].

Table 1. *Comparative analysis of metallic oxides for air purification*

Metal oxide	Semiconductor Type	Band Gap (Eg)	Activation spectrum	Main mechanism in purification	Major advantage	Major limitation
TiO_2	n	≈3.2 eV (Anatase)	UV (λ< 387nm)	Heterogeneous photocatalysis (generate ·OH and·O_2)	Chemical stability, standard in photocatalysis	Inactive under visible light; relatively fast recombination
ZnO	n	≈3.37 eV	UV (λ< 368nm)	Heterogeneous photocatalysis; intrinsic antibacterial activity	Morphological versatility, low cost, biocompatible	Susceptible to photocorrosion in aqueous/acidic media.
CuO	p	1.2 - 1.7 eV	Visible/Near IR	Co-catalyst (heterojunctions); Catalytic decomposition	It absorbs strongly in the visible spectrum.	Extremely fast recombination of carriers when used alone.
NiO	p	≈3.6 - 4.0 eV	UV	Gas adsorption; co-catalyst in NOx decomposition	Excellent hole mobility (h^+).	Higher toxicity; Very wide Eg
MgO	Insulator / Wide semiconductor	≈6.0 eV	Primarily non-photocatalytic; active mainly under UV-C irradiation	Acid-base chemical adsorption (chemisorption) of toxic gases	Strong basic surface, excellent for retaining CO, SO_x, NO_x	Lack of photocatalytic activity under sunlight/indoors.

For the removal and neutralization of inorganic pollutants from the air, a category dominated by nitrogen oxides (NOx, especially NO and NO_2, sulphur dioxide (SO_2), carbon monoxide (CO) and tropospheric ozone (O_3) – metal oxides act through completely different mechanisms than those used for volatile organic compounds (VOC) [19].

Unlike VOCs, which are degraded to CO_2 and H_2O by complete mineralization, inorganic pollutants are cleaned up by two major pathways:

A. Selective photocatalytic oxidation: On the surface of n-type semiconductors (ZnO, TiO_2), nitric oxide (NO) is successively oxidized by hydroxyl radicals (•OH) and superoxide (•O_2) generated under the action of light. The goal is to transform a highly toxic gas into a stable and much safer species (nitrogen ion, NO_3^-):

$$NO \rightarrow NO_2 \rightarrow HNO_3 \rightarrow NO_3^-$$

If the photocatalyst is not active enough, the reaction can stop halfway, releasing NO_2, which is about 10 times more toxic than NO. ZnO often exhibits higher selectivity than TiO_2, favouring direct conversion to NO_3^-, blocking intermediate NO_2 desorption.

B. Acid-base chemisorption and reactive adsorption: Nitrogen and sulphur oxides are gases with an acidic character. Metal oxides with a pronounced basic character (especially MgO) interact with them extremely strongly electrostatically and chemically, fixing them on the surface in the form of sulphites/sulphates or nitrites/nitrates, without necessarily requiring light activation:

$$MgO + SO_2 \rightarrow MgSO_3$$
$$MgO + 2NO_2 \rightarrow Mg(NO_3)_2 + NO\uparrow$$

Semiconductor metal oxides (ZnO, TiO_2) are stable and inexpensive, but they suffer from rapid recombination of charge carriers and often require UV energy. For indoor air, where the light is LED (visible), their photocatalytic efficiency becomes significantly reduced if they are not doped with noble metals (Ag, Pt) or associated in heterojunctions (e.g. ZnO/CuO) [20-23]. A comparative analysis of the behavior of metal oxides is presented in Table 1.

Carbon-based nanomaterials (Graphene, Graphene Oxide - GO) have an exceptional physical adsorption capacity for VOCs due to π-π interactions. However, they do not have their own high catalytic activity of destroying gaseous inorganic pollutants, functioning optimally only as conductive carriers for metal oxides.

Metal-Organic Frameworks (MOFs) represent one of the most promising classes of materials

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currently investigated for air purification. Their major limitations, however, remain their low thermal and hydrothermal stability (many MOF structures structurally collapse under conditions of high atmospheric humidity) and the prohibitive cost of production.

3. Carbon-Based Nanomaterials for Air Purification Applications

Carbon-based nanomaterials have emerged as one of the most promising classes of advanced materials for air purification applications due to their exceptional physicochemical properties, including high specific surface area, tuneable pore structure, superior electrical conductivity, chemical stability, and versatile surface functionalization capability [15, 24]. Unlike semiconductor metal oxides, whose primary mechanism relies on photocatalytic degradation, carbon nanomaterials predominantly operate through adsorption processes, although recent studies have demonstrated their ability to participate actively in catalytic and photocatalytic reactions when integrated into hybrid nanostructures.

The remarkable adsorption capacity of carbon nanomaterials originates from their highly developed surface area and the presence of extensive π-electron systems. These characteristics promote strong interactions with gaseous pollutants through van der Waals forces, π–π stacking interactions, electrostatic attraction, and surface complexation mechanisms. Consequently, carbon-based materials have demonstrated high efficiency in the removal of volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), nitrogen-containing pollutants, sulphur compounds, and ultrafine particulate matter.

Among the various carbon nanomaterials investigated for environmental remediation, graphene and graphene oxide have attracted considerable attention [25]. Graphene consists of a single atomic layer of sp^2-hybridized carbon atoms arranged in a two-dimensional honeycomb lattice. This unique structure provides an exceptionally large theoretical specific surface area exceeding 2600 $m^2\ g^{-1}$, facilitating efficient adsorption of gaseous contaminants. Furthermore, graphene exhibits excellent electrical conductivity, which promotes rapid electron transport and suppresses charge carrier recombination when incorporated into photocatalytic systems.

Graphene oxide (GO) represents an oxidized derivative of graphene containing abundant oxygen-containing functional groups, including hydroxyl, epoxy, carbonyl, and carboxyl moieties. These functional groups significantly increase the hydrophilicity and chemical reactivity of the material, enabling enhanced interactions with polar gaseous pollutants such as ammonia, formaldehyde, nitrogen oxides, and sulphur dioxide. Moreover, the oxygenated surface provides anchoring sites for metallic nanoparticles and semiconductor oxides, facilitating the fabrication of multifunctional composite materials with improved environmental performance [14].

Reduced graphene oxide (rGO) combines the advantages of graphene and graphene oxide by partially restoring the conjugated carbon network while retaining a fraction of the oxygen-containing functional groups. As a result, rGO exhibits improved electrical conductivity compared to GO while maintaining sufficient chemical activity for pollutant adsorption and catalyst immobilization. Numerous studies have reported that TiO_2/rGO and ZnO/rGO heterostructures display substantially enhanced photocatalytic activity under both ultraviolet and visible light irradiation due to improved charge separation and electron transport efficiency [20, 23, 26, 27].

A comparative analysis of carbon nanomaterials used for air purification is presented in Table 2.

Table 2. *Comparative analysis of carbon-based nanomaterials for air purification application*

Carbon nanomaterial	Specific surface area (m^2/g)	Main mechanism	Target pollutants	Major limitation
Graphene	2000–2600	Adsorption, electron transport	VOCs, NOx	Agglomeration
Graphene Oxide (GO)	500–1500	Adsorption, surface functionalization	NH_3, HCHO, NOx	Lower conductivity
Reduced Graphene Oxide	800–1800	Adsorption + photocatalytic support	VOCs, NOx	Cost of reduction
SWCNTs (single wall carbon nanotube)/ MWCNTs (multiwall carbon nanotubes)	200–1200	Adsorption, conductive support	VOCs, aromatic compounds	Difficult large-scale production
Activated Carbon	500–2500	Physical adsorption	VOCs, odors	Saturation of active sites

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Carbon nanotubes (CNTs) constitute another important category of carbon-based nanomaterials employed in air purification technologies. Depending on their structure, carbon nanotubes may be classified as single-walled (SWCNTs) or multi-walled (MWCNTs). Their cylindrical geometry, high aspect ratio, and hollow internal structure provide multiple adsorption pathways for gaseous contaminants. In addition, carbon nanotubes exhibit excellent mechanical strength and thermal stability, making them suitable candidates for incorporation into filtration membranes and multifunctional air-cleaning systems.

The adsorption performance of carbon nanotubes is strongly influenced by their diameter, surface functionalization, defect concentration, and degree of graphitization. Functionalized CNTs containing oxygen- or nitrogen-containing groups have demonstrated enhanced affinity toward acidic and polar pollutants, while pristine nanotubes exhibit superior adsorption of aromatic volatile organic compounds through π–π interactions. Furthermore, CNTs can serve as conductive support for metal oxide nanoparticles, improving photocatalytic efficiency by facilitating interfacial electron transfer [28-30].

Activated carbon nanostructures remain among the most widely implemented commercial materials for air purification. Their hierarchical pore network, consisting of micro-, meso-, and macropores, enables simultaneous adsorption of molecules of different sizes. Although activated carbon generally lacks intrinsic photocatalytic activity, its low cost, high adsorption capacity, and industrial scalability continue to make it a key component of commercial filtration systems. Recent developments focus on combining activated carbon with photocatalytic nanoparticles to create self-regenerating filters capable of degrading adsorbed pollutants.

Despite their numerous advantages, carbon-based nanomaterials also present several limitations. Adsorption sites may become saturated during prolonged operation, leading to reduced pollutant removal efficiency. Additionally, regeneration processes often require thermal treatment, chemical oxidation, or ultraviolet irradiation, which may increase operational costs. Concerns related to nanomaterial release, environmental persistence, and potential respiratory toxicity have also stimulated research toward safer immobilization strategies and sustainable composite structures.

Current research trends increasingly focus on the development of hybrid carbon-based nanocomposites integrating graphene, carbon nanotubes, activated carbon, metal oxides, and metal-organic frameworks. Such multifunctional systems combine high adsorption capacity with photocatalytic degradation, antimicrobial activity, and improved structural stability. These synergistic effects offer significant potential for the design of next-generation air purification technologies capable of simultaneously removing gaseous pollutants, particulate matter, and airborne microorganisms under realistic environmental conditions.

4. The limitations and technical challenges

A. Mass transfer and gas-phase kinetics: Unlike water decontamination, where pollutants are in intimate and prolonged contact with the catalyst, in air purification we are dealing with high dynamic flow (the air passes quickly through the filter) and typically below 1 ppm.

Many nanostructured photocatalysts have too slow reaction kinetics. The residence time of the gas molecule (e.g. NO or formaldehyde) on the surface of the nanomaterial is often in the order of milliseconds, insufficient for the redox reaction to take place completely.

B. Risk of by-products more toxic than the original pollutant: This is one of the biggest safety issues in air photocatalysis. If the mineralization of a volatile organic compound (VOC) is not complete due to low light intensity or deactivation of active sites, partial degradation of a benign pollutant can generate much more dangerous intermediates. For example, the partial photodegradation of some alcohols or hydrocarbons on TiO_2 or ZnO nanostructures can release formaldehyde or acetaldehyde into the airstream. In the case of NOx, incomplete oxidation releases NO_2, a gas considerably more toxic than NO initially.

C. Deactivation of the catalyst ("poisoning" of active sites): Real air contains a multitude of compounds, including variable humidity, sulphur compounds (SO_2, H_2S), or organic compounds with a high molecular weight. Nanostructured metal oxides tend to irreversibly adsorb sulphate species or heavy carbonic compounds. They block ("poison") the active sites of the nanomaterial, dramatically decreasing its efficiency after just a few tens of hours of operation, making filter regeneration difficult and expensive.

D. The problem of immobilization and ecotoxicity (Nanodusting): The use of free nano powders is excluded in air purification due to the risk that the nanomaterials will be entrained by airflow and inhaled by humans, causing cellular oxidative stress and severe lung toxicity. Therefore, their immobilization on supports (textiles, geopolymers, glass) is mandatory. However, immobilization techniques (using polymer binders or silanes) bring a massive compromise: they partially encapsulate the

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nanomaterial, reducing the active surface area accessible to gases by up to 40-60%.

5. Conclusions and future perspectives

Nanomaterials should not be regarded as a standalone solution but as a high-performance component that must be integrated into hybrid systems. For nanomaterial-based air purification technologies to become viable on a large scale, the scientific community needs to shift its attention from simply reporting "degradation rates under ideal conditions" to:

• the design of dynamic reactors capable of ensuring an optimal contact time without generating high pressure losses (pressure drop) in ventilation systems;

• in-situ green synthesis of heterojunctions (such as ZnO/CuO or ZnO/C), ensuring a strong covalent bond with the filter material to completely eliminate the risk of nanoparticle detachment;

• systematic study of the selectivity of the mechanisms, guaranteeing that the reaction by-products are strictly benign (CO_2, H_2O and immobilized NO_3^- ions).

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