

A Review of the Use of Nano-Catalysts for Air Quality Improvement with Emphasis on Vehicle Exhaust Treatment

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Abstract

Air pollution remains a threat to human health and environment particularly in the places where traffic and industries are denser. Nano-catalysts have emerged as a promising prospect of enhancing the quality of air due to their high surface area and controllable reactivity alongside their capability to decompose pollutants at mild operating conditions. This review examines more recent advances in the field of nano-catalyst based air purification with specific focus on vehicle exhaust treatment. Photocatalytic nano materials have great potential for removing Nitrogen Oxides (NO_x), Volatile Organic Compounds (VOCs) and particulate matter with the help of adsorption and oxidation mechanisms. These materials include TiO₂, graphene, perovskites, metal oxides and metal-organic frameworks. They have also tested their performance in catalytic converters, diesel particulate filters and in photocatalytic coating that have been applied to transport infrastructures. This review will discuss the various categories of pollutants, limitations of traditional methods of air purification, nano-catalytic activity and as well as the updated advancements of nano-enabled filters. It also highlights the new technologies such as plasma-assisted photocatalysis, electrospun nanofibre filters and the graphene-enhanced filtration networks which are more durable and have higher degradation efficiency. Despite these materials showing good laboratory scale performance, there are still questions on their toxicity, environmental exposure, cost and long-term stability. This review also discusses these challenges along with future research interests that are focused on safer material designs and intelligent catalytic systems for vehicle emission control. In general, nano-catalysts offer cleaner air and more efficient purification of vehicle exhausts. These might support a shift towards healthier urban environments.

Keywords: Nanocatalysts, Air pollution, Volatile Organic Compounds (VOCs), photocatalysis, vehicle exhaust emissions.

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1. Introduction

Air pollution is an increasing global issue which is caused by the spread of industries, the fast urbanization process, and the rise in the number of vehicles use. Examples of pollutants include nitrogen oxides, carbon monoxide, volatile organic compounds, carbonaceous particles and living microorganisms. They have a drastic effect on human health and climate. The traditional filtration and catalytic systems implemented in vehicles and buildings have minimized pollutants to a certain extent, but the ability to handle pollution remains low when pollutant loads are higher or when harmful gases require deeper oxidation [1-2]. All these challenges have led to researchers seeking more advanced material with greater activity and selectivity. Nanocatalysts are particularly of interest over the recent years due to the presence of a large surface area and active sites as compared to bulk catalysts. These characteristics allow them to respond faster, improve the rate of electron transfer and increase pollutant degradation even when low energy is used [3-5]. TiO₂ doped metal oxides, graphene derivatives, metal organic frameworks (MOFs), and biochar-based catalysts have the capacity to transform harmful pollutants into less

dangerous products [6-9]. These photocatalytic materials are particularly significant because they utilize the light energy to produce the reactive species that oxidize the pollutants in the air streams (Figure 2). Vehicle exhaust purification is one of the most critical fields where nano-catalysts can make a meaningful contribution.

Photocatalytic TiO₂ coatings and catalytic converters supported by nano structured materials along with nano enabled diesel particulate filters have shown promising results in the reduction of Nitrogen oxides and hydrocarbons which are emitted from combustion engines [10-12]. In addition to this, previous nano-engineered concrete with TiO₂ has been studied for the reduction in roadside emissions. Therefore, it can be evaluated that nano-materials can also aid in passive purification systems within transport environment [11]. Despite their benefits, there are some concerns regarding the environmental effects, long-term stability, and safety of nanomaterials. Such problems as the release of nanoparticles, toxicity and possible accumulation in the ecosystems should be evaluated. Studies have emphasized on greener methods of synthesis, and controlled immobilization so that risks are minimized [13-14]. With the continuing

advancement of research, other efficient methods to purify air include plasma-assisted catalytic systems, multifunctional nanofiber filters and graphene-enhanced membranes. All these are promising and open the possibilities of efficient and sustainable air purification [15-18]. This review gives a general overview of the role of nanocatalysts in air quality enhancement with a reference to the use of nanocatalysts in vehicle exhaust treatment. It also tends to outline recent scientific advancements and compares various material systems discussing their limitations and outlining future opportunities of practical implementation (Figure 2).

2. Methodology

2.1. Types of Pollutants

Air pollution consists of a wide group of chemical and particulate pollutants emitted through indoor and industrial processes, and transport systems. Vehicle exhaust emission is still significant cause of various pollutants. High-temperature combustion results in formation of nitrogen oxides (NO and NO₂) that contribute to smog formation and respiratory irritation [1-12]. Such gases combine with hydrocarbons in air to form ozone and secondary organic aerosols which affect the chemistry of atmospheres. Another significant type of pollutants is volatile organic compounds (VOCs). They are formed as result of incomplete combustion and evaporation of fuel, industrial solvents and domestic goods. VOCs such as benzene, toluene and formaldehyde associated with development of neurological conditions and long-term carcinogenicity. They are hard to control and extremely persistent in cities due to their capacity to respond to sunlight [5-19]. Particulate matter (PM) is typically released from diesel engines and break friction. PM can be categorized into coarse (PM₁₀), fine (PM₂₋₅) and ultrafine particles. Ultrafine particles are especially concerning due to fact that they can travel deep into lungs, and can be transferred to blood-stream at least, which puts person at risk of developing cardiovascular and metabolic disorders [2].

These emissions have been captured using diesel particulate filters but the small size of nanosized particles makes total capture difficult at high engine loads. Another common by-product of combustion is carbon monoxide (CO) which limits the supply of oxygen in the blood. Even though most of the CO is changed to CO₂ using catalytic converters, inefficiency is common due to improper maintenance or where the engine is still cold when starting [1]. Indoor environments have their own challenges. Air pollutants can also be micro-organisms and bio aerosol with biological pollutants that may accumulate bacteria and bio aerosols in poorly ventilated environments, causing respiratory diseases. Current research points to the use of sophisticated catalytic compounds to eliminate both biological pollution and chemical pollution [6-13]. In general, the presence of different types of pollutants and different chemical behavior necessitates purification technology that is highly reactive, selective and stable in performance for which nanocatalysts have offered promising results.

2.2. Traditional Methods for Removal

The traditional air cleaning strategies have significantly contributed to the minimization of emission of vehicles, industries and interior spaces. Three-way catalytic converters are still the most common means to regulate NO_x, CO and unburnt hydrocarbons in automotive systems. High

temperatures of platinum, palladium and rhodium catalysts are used in these devices to reduce or oxidize the pollutants [1-10]. DFPs are commonly employed as traps against small particles and most contemporary engines include catalytic coatings to enhance the efficiency of oxidation [2]. Activated carbon filters play a role in domestic purifying and industrial exhaust systems. They have a large surface area which supports the adsorption of VOCs and odorous compounds. When used in a ventilation system, fibrous filters e.g. HEPA membranes used to collect P.M. by mechanical interception and diffusion. These are commonly applied in hospitals, governmental facilities and cleanroom areas in order to manage air particle level as small as nanometre diameter [18].

Photocatalytic substances, especially TiO₂, have been introduced to the surface of the interior and the exterior in building structures to eliminate VOCs and NO_x using UV light. They generate the reactive oxygen species, which break down pollutants into non-toxic final products [6-20-21]. Road surfaces have been built with pervious concrete that contains TiO₂ in order to reduce emissions caused by traffic passively [11]. The use of plasma treatment technologies has also been witnessed in the process of decomposition of complex organic pollutants. The systems produce reactive electrons and ions to initiate an oxidation reaction. Plasma-assisted purification when combined with catalysts, enhances the removal of resistant VOCs [15-16]. The majority of the existing air quality systems rely on such techniques. Nevertheless, the growing size of the ultrafine particles, mixtures of complex VOCs, and tightened air quality standards has revealed a number of deficiencies that limit the success of traditional technologies in long-term perspective.

2.3. Limitations of Traditional Methods

Even though over the last decades the air quality has been improved by the use of conventional filtration systems or catalytic systems, there are a number of limitations that prevent them to effectively handle the present level of pollution. At low temperatures one of the key problems is low efficiency. The catalytic converters need high operating temperatures to get full oxidation or reduction reactions. Under cold-start conditions, the catalyst is in an inactive state and it lets large amounts of NO_x and hydrocarbons escape [1-10]. The second significant limitation is catalyst deactivation. Sulfur and phosphorus as well as other additives added to fuel are likely to poison metal catalysts. However, thermal degradation and sintering decrease the number of active sites with time, which results in the reduction of performance. Maintenance or replacement may be necessary periodically, and this raises the operation cost [2]. Physically based filters, including HEPA filters, DPF filters, etc. have problems with regard to clogging and pressure drop. Sedimented particles restrict airflow, escalate fuel consumption and require regeneration operations.

Regeneration may either give off secondary pollutants or absorb ultrafine particles that may not be completely removed [2-18]. Activated carbon filters have low adsorption capacity and low regeneration ability. After becoming saturated, they are no longer able to hold VOCs and therefore need to be changed. Adsorption is also not selective and it is thus hard to target certain pollutants in complex mixtures [14-19]. Pure TiO₂ has been shown to be a traditional photocatalyst that is not very active when used in the visible light range, thereby reducing its usefulness in

practical sense when the UV light intensity is low. Even humidity and competing species and surface contamination make photocatalytic performance even less [6-20]. Plasma technologies are energy-intensive and capable of producing undesirable by-products without appropriate optimization despite their effectiveness [15-16]. These drawbacks present the need of having sophisticated materials with greater efficiency, stability and selectivity with reduced energy requirements. The nanocatalysts are expected to cover these gaps by offering increased surface area, improved light activation and catalytic behavior in a wide variety of environmental conditions.

2.4. Introduction to Nanocatalysts and their Types

Nanocatalysts refer to a category of materials that are characterized in the nano scale in order to improve catalytic processes to eliminate unpleasant pollutants in the atmosphere. Their characteristic strength is that they possess a very high surface-area-to-volume ratio and this enables more reactive sites to react with pollutants. The characteristic greatly increases the rate, efficiency and selectivity of catalytic reactions, in comparison to bulk materials. Nanocatalysts are able to work under non-vigorous conditions, and react on a broader variety of pollutants, it is also more durable to respond on pollutants in harsh environment like the vehicle exhaust streams. With these strengths they are at the center of the new generation of air purification systems [3-4]. Majority of the nanocatalysts to be designed to purify the air depend either on photocatalytic, oxidative or reductive, or on adsorptive reaction. The photocatalytic nanomaterials, including TiO₂, have been the most extensively studied and used because they are chemically stable, inexpensive and have a great oxidizing power when exposed to UV or visible light [6-8]. Upon activation of TiO₂, electrons and holes are formed on the surface, resulting in formation of reactive oxygen species that degrade VOCs, NO_x and microbial contaminants to make end products that are not harmful.

Nonetheless, pure TiO₂ is restricted by the fact that it lacks response to the visible-light which has prompted scientists to modify their structure, add dopants, or create composites with graphene and metals to enhance its performance (Figure 3) [6-21]. Nanocatalysts that are based on graphene are a topic of increased interest because they have all the conductivity, high surface area, and ability to stabilize metal nanocrystals. The reduced graphene oxide and doped graphene materials increase the rate of charge transfer and the rate at which electrons and holes are concentrated on recombination by reducing recombination of electrons and holes in the photocatalytic reaction. These characteristics contribute immensely to the degradation of VOCs and NO_x in both in-door and outdoors [8-17]. As coatings in filtration and catalytic membranes, the graphene composites achieve higher removal speed as well as accelerated self-cleaning activities [17]. Another advanced type of nanocatalysts is metal-organic frameworks (MOFs). These crystalline porous frameworks have metals and organic connectors that are organized into frameworks which can be tuned and with very high internal surface areas. Their chemical versatility makes them an excellent candidate for adsorption of VOCs, catalytic oxidation, and even the detection of pollutants.

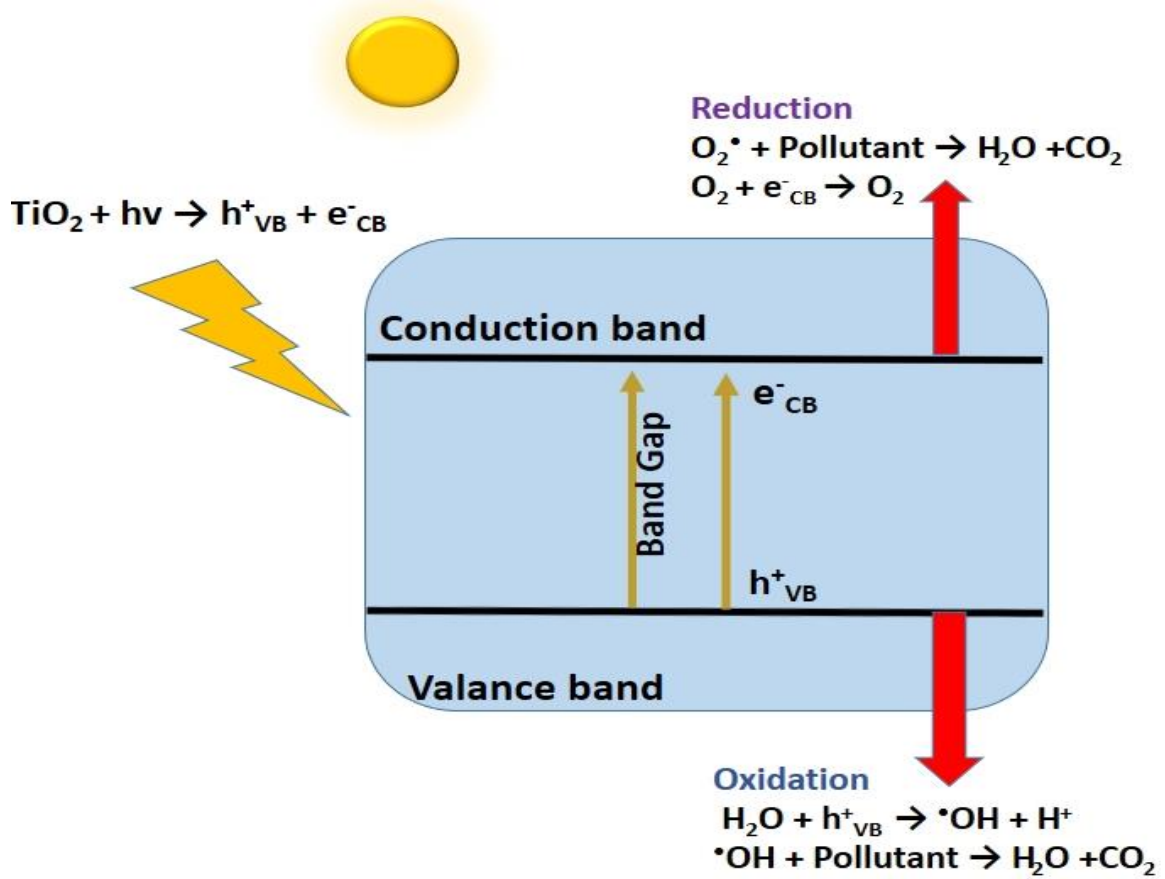
Modern MOFs have a high affinity towards formaldehyde, benzene and aromatic compounds and have

been applied in the purification of indoor or treatment of car exhausts [7-22]. Perovskite nanocatalysts are also being considered in the VOC oxidation in the industrial and transport contexts. They can change their oxidation state, which is coupled with high oxygen mobility to catalyze complex organic pollutants low-temperature degradation [23]. They are exploring these materials as alternatives to costly noble metals to potentially provide the same type of catalytic advantage at a reduced cost and greater sustainability. An alternative method is the use of biochar based nanocatalysts where the carbon-rich materials are made by a biomass. The porous nature of their construction, extensive surface area and the capacity categorize between adsorption, and catalytic oxidation make them suitable for both adsorption and catalytic oxidation of VOCs and nitrogen containing pollutants. Nanocatalysts with biochar have shown promising results and upscale potential in industry [9]. Spinel ferrites are appreciated as a result of their magnetic characteristics, steadiness & straight catalytic characteristics.

They can be included in antibacterial air filters to eliminate microbial contaminants and at the same time, they break down organic contaminants when in contact with light [13]. Their dual functionality makes them suitable for ventilation systems in public environments. Nanocatalysts via plasma activation and hybrid plasma photocatalysts are emerging for rapid destruction of VOCs and bioaerosols. Reactive electrons are generated by the use of plasma and nanocatalysts improve selectivity and reduce energy consumption amounts. It is this synergy that allows strong purification of centralized ventilation systems [15-16]. Another type of nanocatalytic nanostructures electrospun nanofibers. They offer a porous network that is large, and they can accommodate catalytic nanoparticles that can be used to capture particles and degrade pollutants at same time [18]. The lightweight design of them is suitable for their use as vehicle cabin filters & industrial membranes. Collectively these classes of nanocatalysts constitute a platform of future generation of air purifying agents. They are important ingredients in new environmental cleanup methods, due to tunable characteristics they have, high catalytic efficiency and capability to operate in realistic conditions.

2.5. Applications in Vehicle Air Filters

Among the most significant areas in the usage of nanocatalysts, vehicle exhaust treatment is considered. Transport emissions include NO, CO, VOCs and PM that cause a substantial amount of air pollution in the cities. These have been used in traditional catalytic converters and diesel particulate filters, which have enhanced the control of emissions, however, the present systems are experiencing losses in their efficiency of control at low temperature as well as poisoning and failure to totally oxidize their catalysts. Nanocatalysts can address these drawbacks because they enhance reactivity, expand light response, and expand resistance to individual variable engine conditions [1-12]. Nanocatalysts are also notable in improving three-way converts (TWC) in petrol engines. As compared to bulk metals, Pt, Pd and Rh nanoparticles driven by ceramic monolith surfaces are more dispersible and offer an increased number of active sites. This enhances the efficiency of conversion to the NO_x, CO and hydrocarbons even with smaller catalytic loads. Nanostructured supports have also the ability to increase the thermal stability and lower the amount



of sintering as the high temperature functionality progresses [1-10].

Figure 1: Photocatalytic Mechanism of TiO₂ in Air Purification [6]

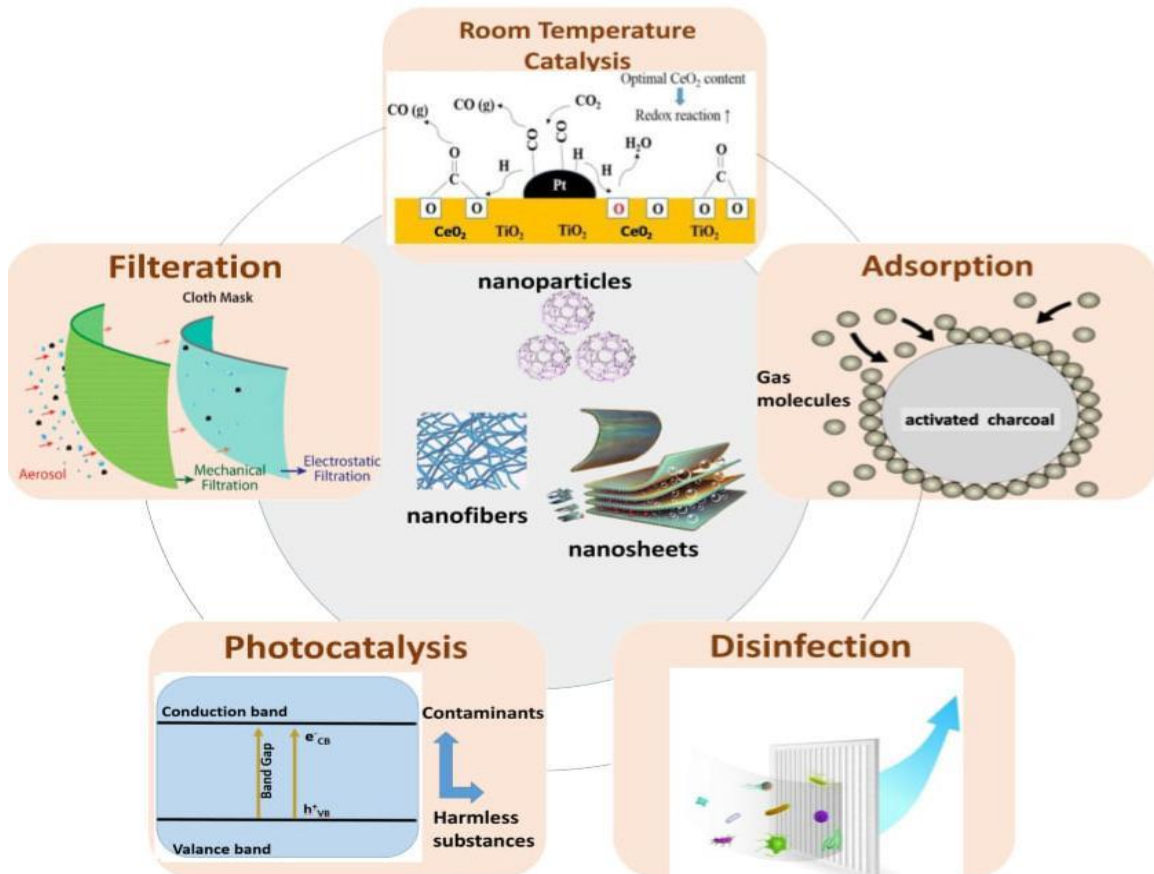


Figure 2: Technologies used for Ambient Air Purification in Nanomaterials [3]

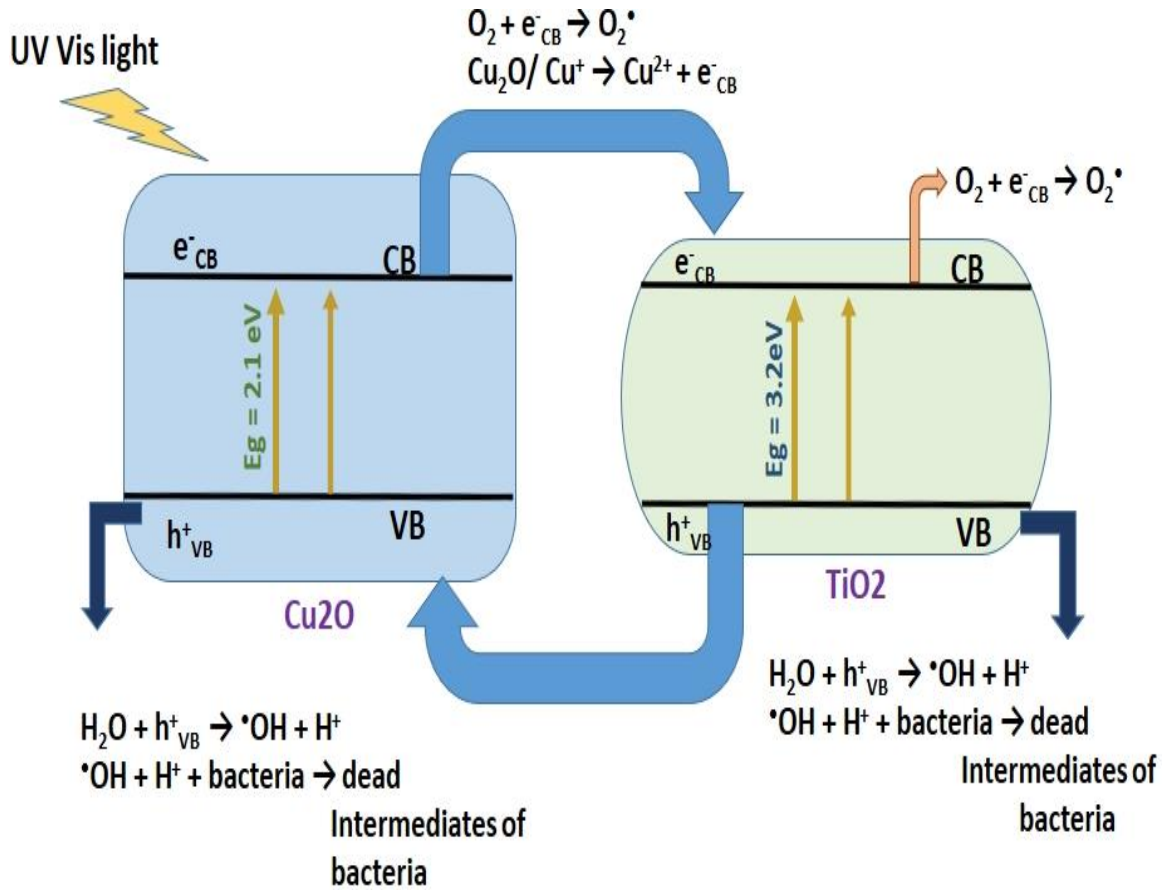


Figure 3: Photocatalytic anti-bacterial mechanism of TiO₂ with Cu₂O under UV/Vis light [6]

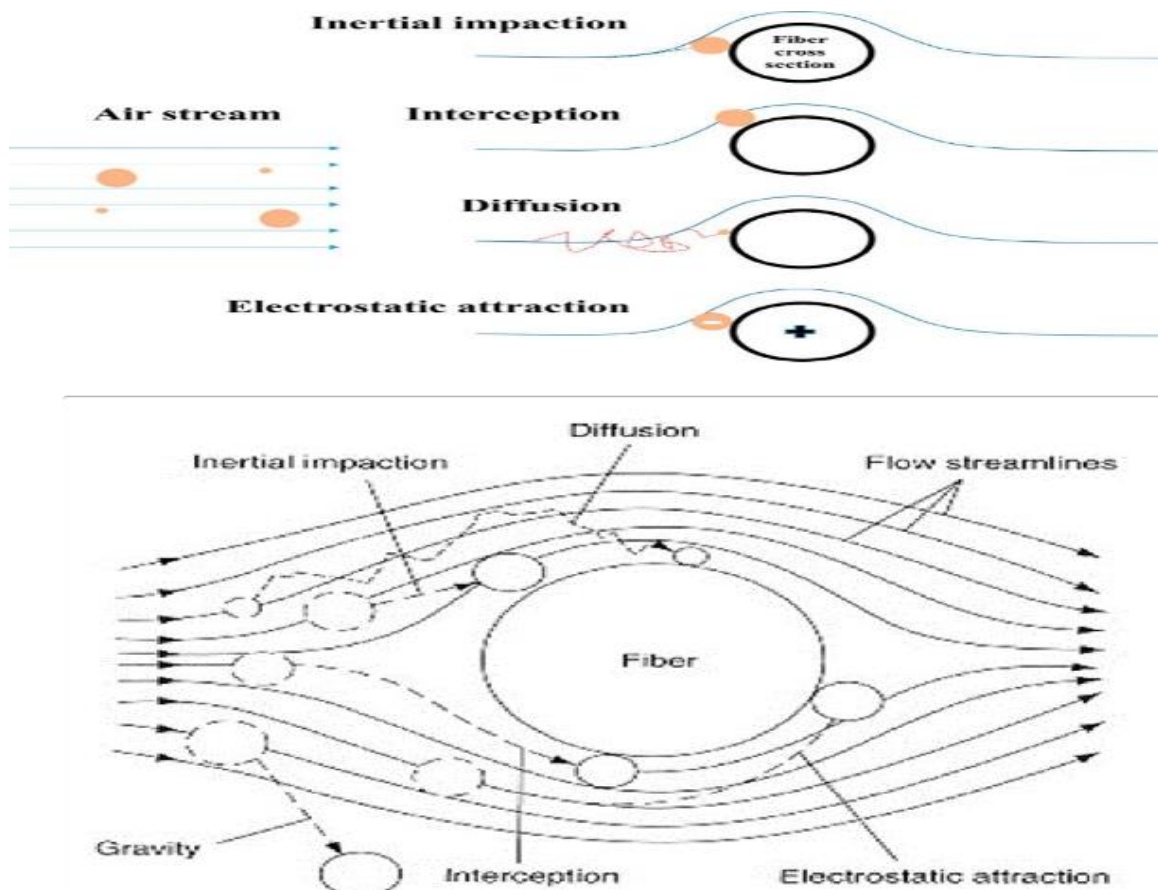
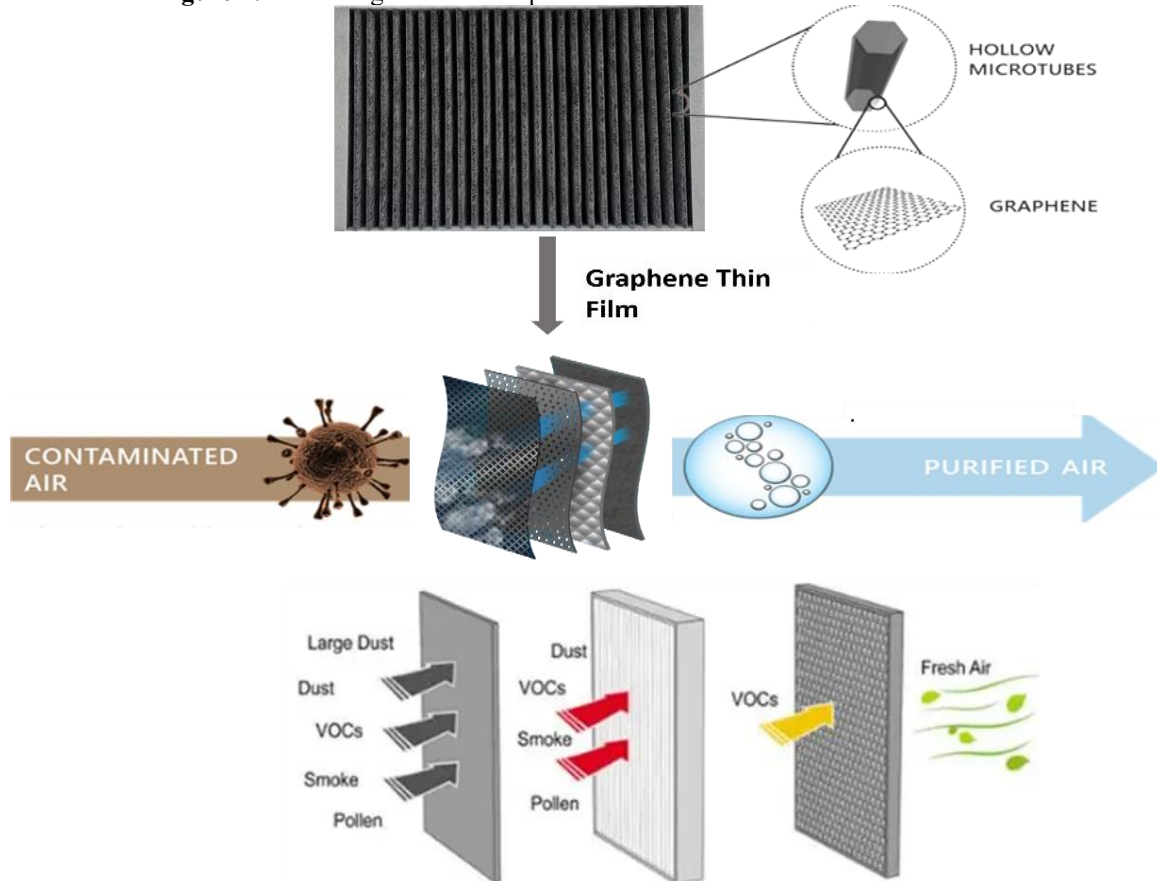


Figure 4: SEM images of Electrospun Nanofiber Membranes used in Air Filters**Figure 5:** The graphene-enhanced filter medium (GeFM) [17]

Photocatalytic nanomaterials are also incorporated in the exhausts to purify NO_x and VOCs. Catalysts based on TiO₂ such as doped or composite catalysts exhibit potent photocatalytic degradation under the UV or visible light, at the temperature of engine heat sources, or on board LEDs [6-12]. Studies have explored the applications of the pervious concrete roads surface covered with the nano-TiO₂ to reduce the road level NO_x by the passing vehicles and a passive yet effective purification process has been recorded (Figure 4) [11]. Electrospun nanofiber membranes are the other rapidly developing use is vehicle cabin air filters. Electrospun nanofiber membranes enhance the collection of PM 2.5 and ultrafine particles because the membranes have an interconnected porous structure and a huge surface area. Once designed with photocatalytic nanoparticles installed, these membranes are capable of capturing not only the pollutants, but also destroying the VOCs, odours and microorganisms which are introduced to the air conditioning systems [13-18].

The enhancement of filters with graphene increases antimicrobial and self-cleaning capabilities and preserves airflow resistance at acceptable levels (Figure 5) [17]. Metal-organic structures (MOFs) are becoming the potential next candidates in vehicle filtration. Their choice of adsorption offers them the capacity to capture aromatic hydrocarbons, aldehydes and other VOCs produced by the exhaust before making contact with the cabin. Catalytically active MOFs might further break down these molecules, reducing the need for filter replacement [7-22]. Overall, nano catalysts are reshaping vehicle emission control. Their versatility allows

solutions to the persistent problems of cold start inefficiency, catalyst deactivation and particulate emissions. As global regulations become strict, Nanocatalyst based filtration systems are anticipated to become the standard for next generation automotive emission technologies.

2.6. Environmental and Health Concerns

Although nanocatalysts have high potential in cleaning air, their health and environmental effects need to be evaluated. Certain nanoparticles, namely TiO₂, metal oxides and engineered carbon materials are capable of being released off the filters over time and travel into the air. The respiratory risks of nanosized particles inhalation are associated with the capability of particles to enter deep lung tissues and create oxidative stress [9-14]. Intermediate products can also be produced by photocatalytic materials during degeneration of VOCs, these intermediate products are potentially more reactive or toxic if not completely mineralized [5]. Still another issue is the release of environment. The nanocatalysts employed in exhaust systems, catalytic converters or road coatings can be built up in soil and water bodies, where they could change microbial communities or produce reactive oxygen species (ROS) under sunlight [3-6]. Certain MOFs and metal catalysts can leak out ions which have impacts on aquatic life [7-22]. Catalyst deactivation and thermal stress can also result in fragments of metal nanoparticles in vehicle exhaust streams. Continuous exposure to such particles can affect cardiovascular and inflammatory processes in humans [2]. Despite the high stability and low toxicity of most

nanomaterials, there remains a need to do a complete life-cycle assessment to be sure that when integrated into supports it is safe so that it may be used safely in the long term in both automotive and indoor settings [9-14].

3. Future Directions

In the research, the area of interest in the future is to design better nanocatalysts in terms of usability, stability and environmental friendliness. Graphene hybrids and redesigned TiO₂ structures are visible-light-active photocatalysts that have high potentials of application in the real world [6-8]. It is possible that MOFs and perovskites can be tailored to specific activity, yet enhanced moisture stability and longevity are obligatory [7-23]. The Introduction of smart filters with combined photocatalysis, adsorption and self-cleaning capabilities can improve the long-term effectiveness of vehicles [17-19]. Plasma-assisted catalytic systems and electrospinning nanofiber membranes are also likely to contribute significantly because of their high reaction rates and lightweight structure [15-16]. Human safety, life-cycle testing and largescale production are areas where more efforts are required in order to ensure advanced nanocatalysts are shifted into commercial level systems without any environmental harm.

4. Conclusions

Nanocatalysts can be used as an effective route to enhancing air quality by facilitating quicker and effective elimination of dangerous pollutants used by vehicles and indoor settings. Their large surface area, easily tunable properties and strong catalytic action enables them to outperform traditional purification treatment methods of VOCs, NO_x, and particulate matter (PM). Its use in catalytic converters, diesel particulate filters, cabin filters and hybrid purification systems has proven to be a great step in the right direction towards a cleaner transportation system and safer urban environment. However, long-term environmental safety and stability should also be a priority. A more sensible strategy that integrates creativity and sustainable material design will encourage the broader use of such technologies. With the development of the research, nanocatalyst-based filters should become the main elements of sustainable air purification and future systems of vehicle emissions.

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