Nanozymes Induced Air Purification - A State of the Art Review

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Abstract

Air decontamination is always a prime concern to society as the air to be inhaled should be free of contaminants so that living beings can get ample amount of energy to wheel their lives. Rapid urbanization causes drastic contamination in air that can create several life-threatening disorders. In this scenario, ultrahigh detection along with quick estimation of air pollutants has become an urgent need to the society. Nanotechnology enabled enzyme mimicking materials known as nanozymes, demonstrates elevated purification efficiency, sterilizability and low wind resistance. These materials when used in air-filter can work as a soldier to combat with air pollution. Incorporation of latest technology viz. Internet of Things (IoT), cloud computing, etc., brings a new flavor in air refinement. In this present work, several nanozymes are surveyed with high efficiency in air filtration. Single atom nanozymes have established themselves as proficient candidates in air decontamination. The implication in air refinement is attributed to the birth of pro-active superoxide ions and successive formaldehyde oxidation. Corona virus and microbes afflicted air may be purified by the redox commotion of nanozymes. Fiber centric air filter provides enhanced filtration efficiency in real time monitoring process with the aid of IoT conjugation. The present review aids in understanding the mechanisms and potentiality of nanozymes as air purifiers, and also optimizes the design of air purifier.

Keywords: Nanozyme, Formaldehyde recognition, Corona-virus, Indoor Air purification, Internet of Things (IoT), Nanofiber filter.
1. **Introduction**

Air, regularly inhaled for survival purpose, when is contaminated, possess serious threats to living beings, as the oxygen enriched air must be used in ATP synthesis at mitochondria where life energy is continuously generated. In this regard, maintaining purified air (air quality) is the prime responsibility of humans for securing the society. Maintanenance of air quality is achieved by technologically inspired air purification process. The Air Quality Index (AQI), a measure with a range of 0 to 301, is used to estimate the contagion level. A score of 0 to 50 indicates satisfactory air quality, while a score of more than 301 indicates hazardous air quality. Inorganic and organic chemicals that have evaporated and have an average size of less than 10 nm are known as molecular impurities. Mechanical impurities, such as liquid and solid aerosols, have an average size of between 100 nm and 0.1 nm.

Additionally there exists two basic types of air pollution such as indoor air and outdoor air pollution. It is often observed that indoor air is poorly contaminated by tobacco smoke, dust particles, spores, etc. that creates hazards to allergy sufferers and asthma patients [1]. According to established reports, the three main air pollutants that have an impact on the AQI are ground-level Ozone (O3), which is typically prevalent in densely populated cities, Nitrogen dioxide (NO₂), and particulate matter with a diameter of 2.5m (PM2.5). Due to their high vapour pressure at ambient temperature, Volatile Organic Compounds (VOCs) are a recent addition to the group of air contaminants with heightened volatility. Due to the greater consumption of fossil fuels and the frequent use of new chemicals, VOCs have increased in airborne concentrations. The lack of continual air circulation in interior spaces results in an interestingly larger concentration of VOCs than in open air. A recent study demonstrates that fast urbanisation increases the purchase of new materials like building supplies, fixtures, etc., which ultimately contributes to the exposure of VOCs in indoor air. Ozone, secondary aerosols, and smog are produced when VOCs and NO₂ react with each other[1].

Since corona virus can also spread through the air, protection from COVID-19 is essential. The government has put in place a number of regulations to protect healthy people from sick people, such as maintaining a social distance of two metres (about six feet), hand washing with soap, hand sanitizer, etc. at regular intervals, and maintaining personal cleanliness. To stop the rapid spread of the virus, COVID-19 patients and suspects are encouraged to self-isolate at home or in a quarantine facility. Masks and respirators are required in that circumstance when maintaining a physical distance is difficult in public.
settings. Lockdown was implemented in many nations to stop the rapid spread of COVID-19 and its lethal effects. Toxic aerosols have recently been eliminated from office buildings using ventilation and air filtration. Air filtration using nanomaterials is thought to be most efficient in terms of maximising aerosol-decomposition and preventing virus transmission. Nanozymes can be a promising choice in the abundance of nanomaterials for the prevention and treatment of COVID-19 [2].

Figure 1. Assessment of Nanozymes' potential for use in the detection, prevention, and treatment of the Corona virus [2]

These nanozymes when employed as filtration membrane in air purifier, the system will combat certainly with air pollutants in high potential. Technologically the air pollutants when comes in contact with the membrane due to high redox potential of nanozymes, spontaneous decomposition of pollutants occurs and by the effect of membrane functionality, quality air can be provided. This fundamental technique when is adorned with latest technology like Internet of Things (IoT), cloud computing, LoRa communication, etc., then real time monitoring and estimation of AQI are possible. Beginning with basic nanozyme ideas, more recent advancements in nanozymes and their use in air purifiers are studied, before emphasising the integration of IoT and cloud computing in the air purification process.

1.1 Nanozymes- Fundamental concepts
Nanozymes are a subset of the nanomaterial family that combine the properties of enzymes or catalysts with those of nanomaterials. The catalytic effectiveness of nanozymes is typically higher than that of macro level catalysts due to the significant amount of dangling bonds present in them [3]. In general, the terms "catalyst" and "enzyme" refer to substances
that can speed up or slow down chemical reactions, respectively. The natural enzymes that have been protein-enriched can be very productive on the substrate. Regrettably, several non-physiological events, like heat, alkali, acids, etc., cause the inhibition and denaturation of the enzymes. Superoxide dismutase and peroxidase, two natural enzymes catalyse the production of superoxide and hydrogen peroxide. The enzyme mimicking nanomaterials, or nanozymes, may be useful in a number of environmental applications, including air purification, heavy metal detection, organic pollutant removal, dye degradation, and removal. [3] Before diving into a full investigation of air pollutant removal mediated by nanozymes, it is important to first examine several enzymatic functional abilities.

1. Superoxide Dismutase (SOD) converts superoxide anion (O$_2^-$) primarily into atmospheric oxygen (O$_2$) and hydrogen peroxide (H$_2$O$_2$).
2. Peroxidase: This enzyme breaks down H$_2$O$_2$.
3. Catalase: A typical enzyme that encourages the breakdown of H$_2$O$_2$ into water and oxygen.

2. Air Decontamination by Catalytic Material- ROS Mediated Pathway

Catalytic materials have many uses in air filtration, especially NO$_2$ oxidation. Catalytic materials are inherently semiconducting materials that experience excess carrier production when exposed to UV, visible, and infrared light. When the light's energy exceeds or is equivalent to the catalytic material's band gap energy, the creation of surplus carriers is enhanced. The development of redox species, which enables the mineralization of the reactants and pollutants to CO$_2$ and water, results from the reaction of the light modulated excess carrier with aerial oxygen and water adsorbed in the catalytic material [1].

The following is a list of the redox reactions [4].

\[
\begin{align*}
O_2 + e^- & \rightarrow O_2^- \\
O_2^- + H_2O & \rightarrow HO_2 + OH^- \\
\cdot HO_2 + \cdot HO_2 & \rightarrow H_2O_2 \\
H_2O_2 + O_2^- & \rightarrow O_2 + \cdot OH + OH^- \\
h^+ + (H_2O)_{ads} & \rightarrow h^+ + (H^+ + OH^-)_{ads} \rightarrow OH + H^+ \\
h^+ + O_2^- & \rightarrow 1O_2
\end{align*}
\]
Reactive Oxygen Species (ROS) are the backbone of photocatalytic activity. Catalytic breakdown of air constituents, microbial population inhibition, scavenging ROS from smoke, etc. are all aspects of air purification [1]. Smoking cigarettes results in the significant creation of many ROS [5-7] that cannot be effectively eliminated by the built-in filter, and thus encourages air pollution [8]. The typical cigarette filter permits oxidative damage caused by ROS [9]. Oxidative stress stimulates immune system and lung tissue damage, which concurrently results in pulmonary illness and lung cancer [10]. There is a lot of research being done on creating new types of filters, such adding antioxidants to regular cigarettes. Many research studies emphasised the use of plant extract-mediated antioxidants in conventional filters to reduce the level of ROS [11-12]. Due to their negligible heat stability and declining antioxidant activity, natural antioxidants are constrained. Catalytic antioxidants have the potential to overcome the physical and chemical limitations of natural antioxidants. As an alternative to conventional cigarette filters, synthetic antioxidants such core-shell structured polymer catalase nanocapsules and manganese porphyrin derivatives were studied. Due to a synergistic reaction rate, catalytic antioxidant-inspired cigarette filters demonstrated increased ROS scavenging efficacy [13-15].

Nanomaterials or nanozymes that imitate enzymes have gained recognition as effective enzymes with the development of nanotechnology [16]. The increased stability of nanozymes in hard settings encourages the integration of antioxidants like nanozymes in cigarette filters to reduce the level of ROS released into the air, hence controlling the corresponding diseases. The nano-Copper Tannic Acid (CuTA) with sheet-like morphology showed hydroxyl radical (•OH) scavenging activity, SOD imitating behavior, and catalase mimicking behavior. Thus nano-CuTA acts as a powerful antioxidant. Hot smoke was produced as a result of the scavenging of ROS in the aerogel by CuTA nanozyme present in the cigarettes. The special coordination structure was said to be responsible for the stable scavenging property. This CuTA-loaded cigarette filter was tested in vivo to see if it might protect mice from TNF- and IL-1-induced inflammation. Nanostructured materials with inherent catalase and SOD-mimicking properties, such as Pt nanoparticles, Pd nanomaterials, CeO₂ and MnO₂ nanoparticles, may be useful for air purification [16].
3. **Air Purification by Single Atom Nanozymes**

Microorganisms, various sorts of volatile organic pollutants, and indoor formaldehyde are quickly degraded and eliminated thanks to the eco-friendly strategy of nanozymes. In this regard, Single Atom Nanaozymes (SANs) have demonstrated their superiority as air contaminant removers [17]. SANs are well known as emerging nanomaterials with distributed metal cores that increase the density of active sites and usage efficiency [16]. As a result, SANs are attracting far more attention than traditional nanozymes in the fight against environmental pollution. Due to low concentrations of active sites, conventional nanozymes are inefficient. Second, the typical nanozymes' unbalanced elements composition and facet structure disrupt the catalytic processes. A unique SAN made of Carbon Nanoframe-confined axially N-coordinated single-atom Fe (FeN$_5$SA/CNF) was described by Huang et al. This SAN exhibits a 70% higher catalytic rate constant than commercial Pt/C material, making it a superior oxidase mimicking material [17]. As previously mentioned, the formaldehyde molecule, one of the air contaminants, is likely to be bound to the organic pollutants' active sites and undergo oxidation through a series of redox reactions, producing various peroxide molecules as an intermediate, as well as carbon dioxide and water as a byproduct. In order to introduce themselves as effective formaldehyde decomposers, peroxidase-mimicking SANs are necessary. There are two steps in peroxidase mimicking action, including ROS generation and Electron transfer. The two steps are thought to be the main catalytic pathways [18].

4. **Fenton Reaction**

The Fenton or Fenton-like reactions in SANs are the foundation of mimicking activity. The respective processes are depicted below:

1. H$_2$O$_2$ adsorption takes place on SAN surfaces.
2. When a chemical bond, such as the O-O bond in H$_2$O$_2$, is broken into double OH, it may be maintained by an interaction involving partial electron exchange.

The generated OH either completely oxidises the substrate or further oxidises it to yield H$_2$O, CO$_2$, and some inorganic salts. Such a course of action might be subjected to the elimination of air pollutants like formaldehyde. The active centre of SAN is primarily dedicated to Fe, but several SANs could also display Mo, Cu, or Ti as the active centre [18].
According to Jiao et al., Fe-N-C single-atom nanozymes have peroxidase-like activity [20], and the reinforcement of Carbon Nanotubes (CNT) in the SAN structure greatly enhanced the peroxidase activity [21]. Due to their high structural cohesiveness and exposure of the greatest number of surface sites for single atom dispersion, Fe-N-C single-atom nanozymes that were combined with Polypyrrole coated CNT showed increased peroxidase activity [21].

\[
\text{Substrate}_{\text{reduced}} + \text{ROOH} \xrightarrow{\text{Peroxidase}} \text{Substrate} + \text{ROH} + \text{H}_2\text{O} \tag{7}
\]

Graphene embedded with a single Fe-N4 site (Fe-N-rGO) was also studied by Kim et al., as an enhanced form of peroxidase mimicking nanozymes (five million times more potent than Pt nanoparticles) that can specifically sense H₂O₂. The active Fe-N4 site must be exposed in order to determine the potential mechanism for such improved efficiency [22].

**Figure 2.** Applications of SAN in different fields including environmental applications [19]

**Figure 3.** Peroxidase mimicking operation of Fe-N-rGO [22]
In the case of air filtration, preventing the spread of viruses through the air should be a top priority, particularly in the event of a COVID-19 situation. Pramanik et al. investigated the rapid detection of SARS-CoV-2 by gold nanozymes in this context [23]. When compared to typical enzymes used in traditional colorimetric detection processes, such as horseradish peroxidases and basic phosphatase, nanozymes demonstrated greater sensitivity towards the detection of the CoV-19 virus [18].

5. Air Decontamination by Nanofiber Filter

Commerically, the use of a ventilator, respirator, facemask, and body protection can prevent the airborne spread of the Corona virus. Using a morphological measuring tool like scanning electron microscopy, researchers have discovered that coronaviruses have a crown-like structure and range in size from 60 to 140 nm [18]. They are frequently regarded as aerosols, which are considered to be the most dangerous air pollutants and induce respiratory system disorders and breathing difficulties [24]. Aerosols with a size of less than 300 nm can be captured by conventional microfiber air filters. Aerosols with a size of less than 300 nm can be captured by conventional microfiber air filters [25]. A charged nanofiber filter coated with graphene has intriguing filtration qualities that make it appropriate as an antiviral filter to stop aerial Coronavirus transmission. A typical microfiber filter is used sparingly to filter the 200 million aerosols per cubic meter that are released during periods of high traffic. Nanofiber filters may be a good option in this regard [26]. Aerosols with a size of less than 100 nm can be captured by the nanofiber filter, making it a promising contender for eradicating new Corona viruses. The single fiber filter's efficiency (E) is dependent on,

1. Air velocity
2. Fiber properties
3. Particle size.

The filtering efficiency of a single fiber filter is given as:

$$E = 1 - e^{-E_S S}$$  \hspace{1cm} (8)

Here, E, S, and Es, respectively, stand for overall efficiency, projected fiber area, and fractional fiber efficiency [27].

The filtration efficiency of multifiber filter is depicted as:

$$E_{S_{\text{Total}}} = \sum E_{S_i S_i}$$  \hspace{1cm} (9)
Where, $E_{si}$ stands for the single fiber efficiency [28].

![Figure 4. Air filter for corona virus detection [29]](image)

**Table 1. Comparative Study of Different Nanofiber Filters**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Fiber properties</th>
<th>Air pollutant particle size</th>
<th>Filtration Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25 mm and 37 mm diameter PVC filter with pore size of 5μm</td>
<td>100nm-250nm aerosols</td>
<td>Decrement in particle concentration (reduced by a factor of 10) [25]</td>
</tr>
<tr>
<td>2</td>
<td>PVDF nanofiber with mean diameter of 525 ± 191 nm.</td>
<td>50 nm, 100 nm and 300 nm aerosols</td>
<td>88%, 88% and 96% [30]</td>
</tr>
<tr>
<td>3</td>
<td>Multilayer PVDF nanofiber electret filter with fiber diameter of 525 nm and basis weight of 3.060 gsm</td>
<td>300 nm aerosols</td>
<td>98.3% [31]</td>
</tr>
<tr>
<td>4</td>
<td>Ribbon like structured Cellulose nanofibers /zein nanoparticles with diameter of 279 nm and basis weight of 525 gsm.</td>
<td>300 nm aerosols</td>
<td>93.71% [32]</td>
</tr>
<tr>
<td>5</td>
<td>Net like structured nylon-6-Polyacrylonitrile Nanofiber net (N6–PAN) electrospun nanofiber filter with diameter of 13 nm and 2.94 gsm</td>
<td>300 nm aerosols</td>
<td>99.99% [32]</td>
</tr>
<tr>
<td>6</td>
<td>Branched PVDF/TBAC filter with 5-10 nm diameter basis weight of 1 gsm</td>
<td>300 nm aerosols</td>
<td>99.99% [33]</td>
</tr>
</tbody>
</table>

As discussed earlier the nanozymes having SOD mimicking activities can be a suitable candidate for filtration of viruses including the Coronavirus due to dismutation reaction. From Table 1, it is evident that more hierarchical structure the nanofiber filter has, the more attachment of aerosols; thus, the filtration efficiency is enhanced. Also, the
higher specific area and porosity of the multistructured nanofiber air filter promote them as a new generation of air filter. Additionally, the nanozymes having SOD mimicking activities can be a suitable candidate for filtration of viruses including the Corona virus due to dismutation reaction.

6. **Smart Air Purification**

Continuous monitoring and controlling of air pollution is important nowadays, in order to provide air quality index 0 to 50. Smart approach is appreciable due to quick and precise control of air pollution. Plenty of research suggest IoT-based air purifier, where “Smart-Air” air quality sensor on a web server is established, and in the proposed system, the air purifier comprises of HEPA filter, activated carbon based membrane and UV light organization amalgamated with cloud computing and IoT, which is utilized for the evaluation of air quality. The traditional filter components are used to block the pollutants, whereas LTE device is employed to broadcast real-time data on air pollution to a web server. Besides this, ThingSpeak analytics is also employed to monitor air quality by Kalman Algorithm [34,35]. There are enormous works on the development of smart air purification in order to avoid unnecessary dependence on service personnel. Authors of [36] have designed wireless microcontroller STM32F407 MCU based semiautomatic air purifier, where the indication of superior, good, and bad quality of air is displayed and transmitted to air purifier, either by Bluetooth module through mobile phone or automatically. This typical system can achieve 97% air purification due to presence of activated carbon two-layer filter HEPA and Anion purification function. Another intelligent approach is the implementation of Bosch BME680 sensor with a microcontroller ESP32 microcontroller unit, Raspberry Pi server and Web server for air pollutant data transmission to a local server for storage on a MySQL database. In this case, no membrane was used but Bosch BME680 sensor detects the VOC, the prime pollutant for indoor air contamination [37]. Thus it can be realised that, incorporation of nanozymes in the smart air purifier yields better air purification and sterilization.

7. **Conclusion**

This study illustrates that nanozymes can be used to purify the air by oxidising formaldehyde or by trapping aerosols due to their unique features. Despite the fact that
nanozymes have a variety of uses, the peroxidase and superoxide dismutase activities of nanomaterials can be helpful for indoor and outdoor air purification. Due to the broad exposure to active sites, maximum atomic usage efficiency, and higher density of active sites, the advent of SAN has opened up a unique route in air purification. The focus of the current study is on nanozyme-based indoor air cleaning. Finally, using nanomaterials in air filters may be a successful strategy for battling the new corona virus generation. The nanofiber has been emphasised as a new generation of air filter material due to the hierarchical structure of the nanofiber-based membrane and the shape of nanoparticles embedded in the membrane. IoT based smart air purification system is a potential candidate to provide measure of real time data of air quality index and also the pollutant portfolio in a continuous time dependent fashion, and there is a good control of system functioning for proper measurement of air quality. The incorporation of nanozymes in the air filter adorned with IoT and Cloud server may produce most accurate and highly efficient air purification performance. Therefore, the present work may turn out to be a guideline for design and development of commercial outstanding air purifier to make a healthy living possible.

Conflict of Interest
The authors declare no conflict of interest.

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References


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