Environmental Applications of Nano-Particles for Tackling Climate Change

Topics in Nanosciences
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Abstract
As we complete twenty years in the present century, we are amidst a very serious climate crisis and the significant increase in the earth's temperatures leading to melting glaciers and rising sea levels. This is coupled with a global deterioration in the air and water quality, the depletion of biodiversity in our oceans and rise in contaminant levels. In this study, we aim to study the crucial properties of nanotechnology that can help efficiently treat hazardous substances and manage wastewater and air pollutants. We study various nanoparticles such as carbon nanotubes and titanium dioxide and their fascinating characteristics that make them better than conventional bulk materials for reducing hazardous waste substances in air and water and help tackle climate changes. In particular, we look at
(1) the role of nanoparticles in **catalysis** that help in the **decomposition of methane** and other harmful gases and control air pollution.
(2) some remarkable properties of nanoparticles such as **adsorption** and **photoluminescence**.
(3) the structure of certain nanoparticles such as CNT's and TNT's which help eliminate pesticides and harmful contaminants like lead from wastewater.

1. Introduction

Nanotechnology shows promising applications for controlling air and water pollution. Nanotechnology is technology that works on the nanometer scale which can help prepare very useful materials and devices with interesting properties, which are distinct from the bulk form of the same element. Nanotechnology has many useful applications in various fields, such as biology, medicine and the food industry. In this term paper, we look at environmental applications of nanotechnology and how we can leverage the properties of nanoparticles to control air and water pollution to help control the ongoing climate crisis.

Due to rapidly advancing technology, industrialisation and population growth, there is an excessive amount of harmful substances and toxic materials being produced and polluting the air and water of our ecosystem. Harmful greenhouse gases emitted from factories, animal farms etc. are responsible for global warming and waste products from numerous industries such as heavy metals and pesticides are causing immense harm to the oceans and seas. There is an exigent need to monitor the release of such contaminants into our atmosphere and bring the air and water pollution levels under control.

In this paper, we look at the use of nanotechnology to help control (1) air pollution and (2) water pollution. In Section 2, we look at how we can use nanoparticles such as Metallic Nickel and Zirconium Hydroxide to control the emission of harmful gases like methane and sulphur oxide into the atmosphere. In Section 3, we explore the remarkable adsorption capabilities of nanoparticles and look at carbon nanotubes (CNT's) and titanate nanotubes (TNT's) for effective wastewater treatment.

2. Nanotechnology for GHG Elimination

The rise in industrialisation, anthropogenic and human activities, animal agriculture and the immense usage of fossil fuels has led to a colossal increase in the concentration of greenhouse gases in the atmosphere, causing the global temperatures to significantly rise. Introducing harmful substances and greenhouse gases such as Methane, Carbon Dioxide and Nitrous Oxide has led to air pollution and trapping heat in the earth's climate system. This has led to the increase in sea levels and the melting of glaciers which can have catastrophic implications on our planet.

Carbon Dioxide (CO2) is one of the most prominent greenhouse gases (GHG) in the atmosphere and many nanotechnology-based approaches exist which can help control its emission levels. Nanomaterials exhibit high adsorption capacity due to their large surface areas and can be use as adsorbents to capture carbon dioxide. For instance, calcium-based nano adsorbents are used for the capture of CO2 based on the carbonation reaction, as explained in [1]. The idea of nanoparticle adsorption is further heavily explored in Section 3 of this paper, and its role for controlling water pollution.

Since we will be talking about adsorption in the later sections, we focus this part of the term paper on another fascinating property of nanoparticles - they are excellent catalysts! Certain nanoparticles can be used as catalysts which can help in the decomposition of greenhouse gases like methane and nitrous oxide, before emitting them into the atmosphere. We now analyse the study conducted by Wang and Lua [2] on the decomposition of methane to produce hydrogen.

2.1 Metallic Nickel

For the thermal decomposition of methane, Wang and Lua [2] prepare metallic nickel nanoparticles as catalysts in order to carry out a thermal decomposition of methane (CH4) to produce hydrogen. They observed that the nickel particles worked as fantastic catalysts in the decomposition reaction due to their small particle size at the nanoscale.

These nickel particles were prepared by the decomposition of nickel oxalate in the methane atmosphere. The authors in [2] observed that the performance of the catalyst in the decomposition of methane is heavily reliant on the size of the catalyst particles. Here are the steps that were taken in this novel process of nickel nanoparticles, as elucidated in [2]:

1. Nickel particle aggregates were prepared by the precipitation of nickel nitrate and oxalic acid in ethanol solution.
2. This was followed by the thermal decomposition of nickel oxalate dihydrate under an oxygen-free atmosphere.
3. Methane was then added to the gas stream, creating aggregates of smaller particles with larger surface areas.

The resultant nickel nanoparticles had size at the nanoscale (30-40nm) and were then used as catalysts, resulting in the decomposition of methane to hydrogen. Next, we analyse another interesting property of nanoparticles - photoluminescence - for air pollutant remediation.

2.2 Zinc Oxide and and Zirconium Hydroxide

Zinc Oxide (ZnO) and Zirconium Hydroxide (Zr(OH)4) nanoparticle powders are both photo-luminescent, that is, they both show visible emission peaks in the UV and visible ranges. The exposure of these nanoparticles to Nitrogen Oxide (NO2) and Sulphur Oxide (SO2) can result in chemisorption and help remove these pollutants from the air, as put forth by Singh et al [7]. Using metal oxides and hydroxides are an effective way for the removal of toxic gases from our atmosphere. It has been discussed in [7] that photoluminescence is indeed sensitive to the nature of the adsorbate and ZnO has a photoluminescence spectrum and these molecules chemisorb by bonding to oxygen sites, thereby forming adsorbed NO3. Furthermore, it's also observed that the hydration of ZnO prior to exposure to SO2 improves its reactivity and a greater uptake of NO2 and SO2.

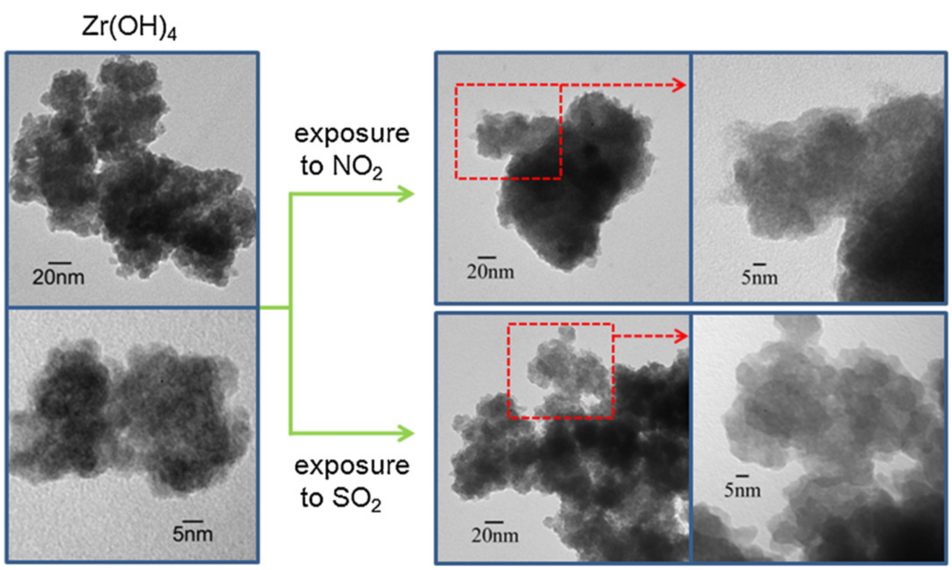

Fig 1: TEM images of hydrated Zr(OH)4 after exposure to nitrogen dioxide and sulfur dioxide, as experimented with in [7].

Thus, ZnO and Zr(OH)4 both exhibit photolu- minescence (PL) spectra, with peak intensities which change dramatically due to hydration. With hydration, there is a significant increase in their reactivity, and it reacts with more amounts of SO2 and NO2 gases, resulting in chemisorption of lesser harmful gases like SO3 and NO3. Thus, these nanoparticles help control the emission of such harmful gases into the atmosphere.

3. Nanotechnology for Effective Wastewater Treatment

The climate crisis today is fueled by the increasing contamination of water bodies with harmful and toxic substances, industrial and human waste and animal excreta. Such pollutants are negatively impacting our water bodies and the ecosystem, causing a loss in natural biodiversity of our oceans and causing worries in the global water supply systems. One significant way of tackling the increasing pollution of water bodies is by treating wastewater before dumping it into the rivers.

Wastewater treatment is a popular field of study in environmental science which deals with technologies such as sediment filters and ion exchangers. However, these water treatment methods are costly and can release secondary toxic substances into the atmosphere, as explained in [4]. However, we can leverage some interesting properties of nanoparticles, such as their great **adsorption capacity** to build cheap and efficient wastewater treatment systems, which would (1) **reduce the price** of treating waste (2) **reduce infrastructure** and increase adaptability so more industries can leverage it, and thereby, (3) significantly contribute to **reducing global warming.**

3.1 Strong Adsorption Capacity

Adsorption refers to the property of ions and molecules to *stick* or the adhesion of particles from a dissolved gas/solid or liquid to a surface. This popular process heavily studied in Chemistry creates a film of the adsorbate on the surface of the adsorbent. Some examples of adsorbents are silica gel, zeolites and activated carbon. We can see that this property is very crucial for wastewater treatment and can help remove contaminants and particulate pollutants from water. However, such conventional adsorbents have a **limited active site surface area** and are not the best choices. On the contrary, nanoparticles offer a phenomenal adsorption capacity due to:

(1) High specific area, and
(2) Highly active adsorption sites,

which help in effective and stronger adsorption.

Nanoparticles have high active adsorption sites which are created by high surface energy and a size-dependent surface structure at the nanoscale. Some examples of nano-adsorbents (adsorbents at the nanoscale level) are nanoscale metal oxides such as titanium dioxide and zinc oxide, which can be used for low-cost and efficient wastewater treatment due to their incredible adsorption capabilities.

Apart from metal oxides, carbon nanotubes (CNT's) are great alternatives to activated carbon and they exhibit a remarkable capability of adsorption for gases and liquids. We shall now look at two popular nanoadsorbents - (1) Titanium Dioxide (TiO_2), (2) TNT's and (3) CNT's, and their role in treating wastewater by analysing a few papers and studies. We shall also look at TiO_2 and its role in photocatalysis.

3.2 Titanium Dioxide

Titanium Dioxide is the naturally occurring dioxide of Titanium and at the nano-scale, it can act as a contaminant remover. Engates and Shipley [5] showed that TiO_2 nanoparticles are better sorbents than other metal oxide nanoparticles and activated carbon. In this study, it was observed that nanoparticles adsorbed much more than the bulk particles and the TiO_2 nanoparticles were able to simultaneously remove multiple metals (Zn, Pb, Cd, Cu, Ni) from tap water. Even at pH 8, even though the bulk particles were exhausted, there was no exhaustion occurring for the TiO_2 nanoparticles, as explained in [5].

3.3 TNT - Titanate Nanotubes

Lie et al [6] conducted a study on the adsorption of various metal ions onto titanate nanotubes. In particular, they study the adsorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} from aqueous solutions onto TNT's, which show a remarkable adsorption capacity for all of these heavy metals. This is due to the ion-exchange mechanism between metal ions Hydrogen/Sodium ions located in the inter-layers of the TNT's.

There are two major reasons why TNT's are excellent adsorbents:

(1) Ion Exchange due to low point of zero charge
(2) Abundant OH groups present on the surface.

The inter-layers of TNT's are referred to as titanate interlaminations. These contain -OH and -ONa ions which are key to the adsorption capacity of TNT's. An ion exchange takes place between these and the metal ions. The hydrated metal ions dissociate into free ions and they subsequently exchange with the Sodium/Hydrogen ions. This is pictorially depicted in Fig. 2, as first shown in [6].

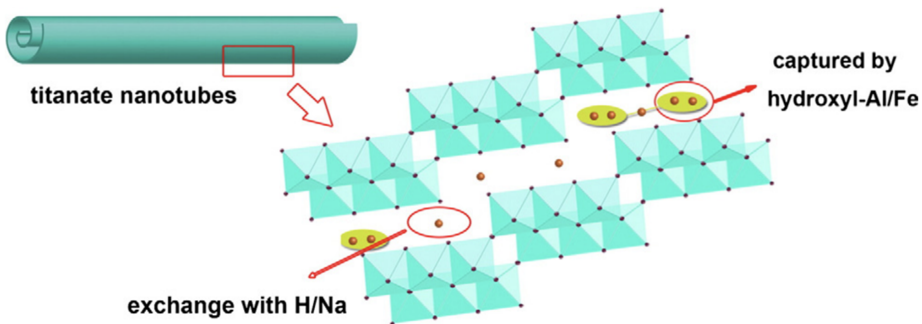

Fig 2: Titanate Nanotubes and their interlaminations containing Hydrogen and Sodium ions, which undergo ion exchange with metal ions easily.

There are two major reasons for the affinity of metal ions to TNT's, namely (1) ion radius and (2) hydration energy.

It is easier for ions that have a smaller ion radius to easily get into the interlaminations of TNT's and then subsequently undergo ion exchange, as explained in [6]. Hence, the ion with smaller radius would have larger adsorption capacity. For example, this study considers four metal ions, whose hydration energy levels are as follows:

$$Pb^{2+} < Cd^{2+} < Cu^{2+} < Cr^{3+}$$

Lead ion (Pb^{2+}) has the lowest hydration energy and separates very easily from water molecules and enters the TNT's layers as bare ions to exchange with H^+/Na^+ ions. Cr^{3+} ions on the other hand, have the highest hydration energy and therefore, the least adsorption capacity. The hydration energy is hence inversely related with the adsorption capacity of TNT's.

3.4 CNT - Carbon Nanotubes

Carbon nanotubes or CNT's, as the name suggests, are tubes made of carbon which have diameters at the nanoscale level. They are a relatively new class of nanomaterials composed of graphitic carbons. They exhibit remarkable electrical conductivity and tensile strength because of high bond strength and their nanostructure. In this paper, we are interested in its excellent adsorption capacity, that can aid in wastewater management and help significantly reduce the amount of contaminants in water bodies.

Diuron and Dichobenill are herbicides used for weed control on farms. Both are popularly used worldwide and detected frequently in water bodies due to their consistent use. Apart from these, Lead is a metal which is very commonly found in water bodies due to industrial wastes and discharges. The consistent use of herbicides and the contamination of oceans with harmful metal substances like lead has led to major biodiversity depletion of our aquatic ecosystem. The removal of these substances is a crucial step towards solving the climate crisis and nanoparticles such as Carbon Nanotubes have been found to be really useful for the same.

CNT's have strong adsorption affinity for heavy metals, pesticides and other organic chemicals, as explained in [3], due to large surface area and high reactivity. Chen et al [3] have studied the adsorption of pesticides such as Diuron and Dichlobenil using multi-walled carbon nanotubes (MWCNT). They also study the effect of lead and the increase in oxygen content of MWCNT's. They observe that CNT's show high removal efficiency for various pesticides and organic pollutants and can be used for the effective removal of herbicides from contaminated water. They also found that adsorption of the two pesticides increased with an increase in the surface area and total pore volume of the MWCNT. The presence of lead ions decreased their adsorption.

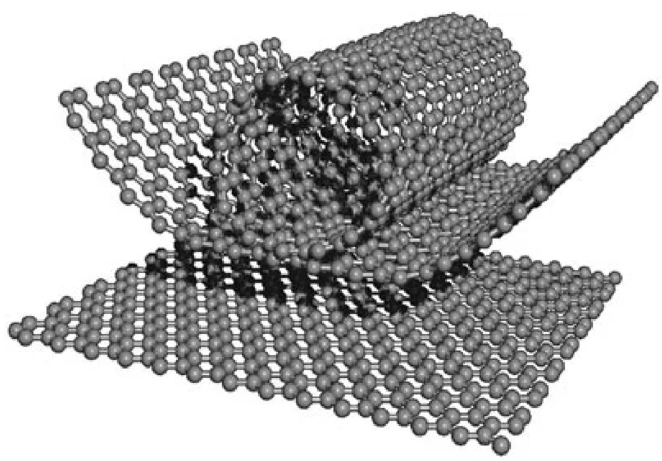

Fig 3: This figure depicts how graphene can roll up to form a Carbon Nanotube

Furthermore, it is also observed in [3] that with the introduction of oxygen-containing groups, the capability of the resulting nanoparticles (known as MWCNTs-O) to absorb lead also increases, but leads to a decrease in the adsorption of the pesticides. Hydrogen bonding is the mechanism responsible for the adsorption of these pesticides onto MWCNTs-O. Hence, we can use CNT's to remove toxic contaminants from wastewater before dumping them into the oceans, helping improve the quality of water in our oceans.

Conclusion

In this term paper, we have looked at some very interesting properties of nanoparticles such as adsorption, catalysis and photoluminescence and how to leverage them to effectively control air and water pollution. We study and analyse different papers to help understand the various environmental applications of nanotechnology. For air pollution control, we primarily look at metallic nickel particles that help in the decomposition of methane, and at metal oxides which undergo chemisorption to eliminate harmful gases. For water pollution control, we look at interesting nanoparticles such as CNT's and TNT's which help in the removal of toxic substances and contaminants from industrial water waste to help protect our oceans. Nanotechnology can be leveraged smartly and efficiently to control our emissions and help protect our ecosystem.

References

[1] Ibrahim, R.K., Hayyan, M., AlSaadi, M.A. *et al.* Environmental application of nanotechnology: air, soil, and water. *Environ Sci Pollut Res* 23, 13754–13788 (2016). https://link.springer.com/article/10.1007/s11356-016-6457-z

[2] Hong Yan Wang and Aik Chong Lua: Development of Metallic Nickel Nanoparticle Catalyst for the Decomposition of Methane into Hydrogen and Carbon Nanofibers. The Journal of Physical Chemistry C 2012 *116* (51), 26765-26775. DOI: 10.1021/jp306519t. https://pubs.acs.org/doi/10.1021/jp306519t

[3] Guang-Cai Chen, Xiao-Quan Shan, Zhi-Guo Pei, Huanhua Wang, Li-Rong Zheng, Jing Zhang, Ya-Ning Xie: Adsorption of diuron and dichlobenil on multiwalled carbon nanotubes as affected by lead, Journal of Hazardous Materials, Volume 188, Issues 1–3, 2011, Pages 156-163, ISSN 0304-3894, https://doi.org/10.1016/j.jhazmat.2011.01.095

[4] Gaya, Abdullah: Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. https://www.sciencedirect.com/science/article/abs/pii/S1389556708000300?via%3Dihub

[5] Engates, K.E., Shipley, H.J: Adsorption of Pb, Cd, Cu, Zn, and Ni to titanium dioxide nanoparticles: effect of particle size, solid concentration, and exhaustion. *Environ Sci Pollut Res* 18, 386–395 (2011). https://doi.org/10.1007/s11356-010-0382-3

[6] Wen Liu, Ting Wang, Alistair G.L. Borthwick, Yanqi Wang, Xiaochen Yin, Xuezhao Li, Jinren Ni: Adsorption of Pb2+, Cd2+, Cu2+ and Cr3+ onto titanate nanotubes: Competition and effect of inorganic ions, Science of The Total Environment, Volumes 456–457, 2013, Pages 171-180, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2013.03.082

[7] Jagdeep Singh, Anupama Mukherjee, Sandip K. Sengupta, Jisun Im, Gregory W. Peterson, James E. Whitten: Sulfur dioxide and nitrogen dioxide adsorption on zinc oxide and zirconium hydroxide nanoparticles and the effect on photoluminescence. Applied Surface Science, Volume 258, Issue 15, 2012, Pages 5778-5785, ISSN 0169-4332., https://doi.org/10.1016/j.apsusc.2012.02.093