

# A review of the development of synthesis and catalytic applications of inorganic-organic hybrid nanomaterials: silica and graphene oxide Charlene Chang Kurniawan<sup>1</sup>, Yannick Eatmon<sup>2</sup> <sup>1</sup> NationalHigh Jakarta School, Jakarta, Indonesia

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ABSTRACT

With the growing need to address global threats such as global warming and climate change, the demand for green chemistry has never been greater before. As a result of detrimental human activities including fossil fuel combustion and deforestation, climate change has irreversibly caused an anomalous rise in the average global temperature, extreme weather, and other climate phenomena. In fact, according to the IPCC Fifth Assessment Report, "It is extremely likely (95% confidence) that human influence on climate caused more than half of the observed increase in global average surface temperature from 1951 to 2010". Additionally, the third chapter of IPCC's Special Report of the Intergovernmental Panel on Climate Change has also confirmed that other obvious signs of climate change have wrought havoc across the continent as ocean acidification, melting glaciers, and ice sheets continue to emerge while extreme weather phenomenons such as tropical storms, floods, heavy precipitation, heat waves, droughts, cold waves, and snowstorms increase tenfold. To combat this issue, scientists throughout history have developed chemical products and synthesis pathways that aim to minimise the harmful impacts of hazardous substances in industry and healthcare. Specifically, inorganic-organic hybrid nanomaterials with their highly desirable features, such as high activity and selectivity, excellent stability, efficient recovery and recyclability, enable benign catalytic processes and are environmentally friendly. In this paper, a historical perception of the evolution of inorganic-organic hybrid nanomaterials will be discussed as well as the different effective synthesis pathways scientists with diverse expertise have come to discover, focusing on their catalytic applications on a global scale. For instance, using the sol-gel method or hydrothermal synthesis to form silica nanoparticles which can act as catalysts in reactions such as oxidation, reduction, and decomposition.

#### INTRODUCTION

With the threat of global warming and climate change in mind, scientists for the past century have been working on a solution toward a greener world in which they will be able to produce a cost-efficient, durable, easily accessible, and effective product that attempts to minimize the detrimental impacts man-made creations have caused upon this dying world. Hence, the production of organic-inorganic hybrid nanomaterials via nanocatalysis is an increasingly popular field incorporating the use of nanoparticles as catalysts instead of maintaining the usage of inefficient chemical transformations which will require more time and resources. In fact, it has brought about a revolution in the scientific community as it excels in controlling the size, shape, composition, and structure of nanoparticles for catalytic applications. [4] However, we must still consider the risk of nanotoxicity which might be harmful to human health and the eco-environment. [5]



Traditionally, scientists are inclined to utilise the homogeneous catalytic system wherein the reactants and the catalysts are in the same phase, increasing interaction between the two species which results in a higher productivity rate. Specifically, higher activity to avoid drastic reaction conditions with efficient energy use, higher selectivity to specify the mechanics of a reaction and minimize waste products, higher turnover yield, and the possibility of modifying the active catalyst molecules by adjusting the chemo-, regio- and enantioselectivity of the catalyst. While they are easily employable in industries for a wide breadth of organic transformations, most have not been commercialised due to the level of complexity it requires to separate the catalysts and the final reaction mixture. For pharmaceutical industries, this quality is unfavourable as metal contamination is a large possibility and is highly detrimental to the functionality of their products. On the contrary, an opposing traditionally used catalytic system particularly known for easy separation and low activity or selectivity is heterogeneous catalysis. It occurs when the phases of the catalysts differ from that of the products or reactants. To attain the desirable features of both forms of catalysis, nanocatalysis is applied to bridge the gap between these two systems. [3]

While a wide variety of organic-inorganic materials have been developed throughout history, they are generally based on the "polymerization" or "insertion" of molecular, polymeric precursors or nano-objects, combining the desirable properties of organic molecules and inorganic compounds. Hence, piqued the interest of industries and academia with their astounding physical and chemical properties as well as their role in engineering methodologies that ease the production of easy processing of many hybrid materials as a consequence of their distinctive and versatile physiochemical properties such as high surface area, nanometre size and rigid framework, impressive chemical, thermal and mechanical stability. [3] Their ability to act as a multifunctional support material owing to the availabilities of a couple of their organic molecules in addition to their exterior and interior pore surfaces further proved their functionality in different industries.

### HISTORY



**Figure 1:** Timeline of the development and multidisciplinary evolution of the organic-inorganic hybrid materials. [6]



## A. Prebiotic Chemistry & Hybrid Materials: Arts

Starting around 20,00 years ago to the tenth century AD, the first known organic-inorganic materials were *clay-based hybrids*. Clay, a hybrid compound commonly found in nature, is thought to have particles with variable stability owing to the organic-inorganic interactions which involve Van der Waals forces, hydrogen bonding, proton and electron transfer, etc. It's proven to be a "molecular replicator" as its surface exhibits characteristics of cyclic processes of adsorption-transformation-desorption which results from spontaneous intercalation and catalyzing the transformation of diverse molecular species repetitively similar to those of living organisms. In addition, its high adsorption selectivity and capability to concentrate prebiotic organic components from the hypothetic primordial soup form ideal complex systems along with supporting theories and examples, such as the "clay hypothesis" and its striking affinity to protect nucleic acids like pyrimidines and purines against extreme conditions and enzymatic actions, proves that clay is crucial in the development of life on Earth. With these properties, they are able to act as catalysts by encouraging the interaction and modification of dispersed organic matter, aiding the formation of hydrocarbons like petroleum at moderate temperatures. In fact, clays found in the prehistoric caves of Altamira, Chauvet, and Lascaux tend to be employed for multiple artistic purposes. For instance, a bleaching agent in the era of Cyprus-Ancient Rome, forming Chinese rice-lime mortars or porcelain better known as "Egg Shell", and pigments of different types such as Maya Blue or Prussian Blue (see Figure 1). [6]

### B. Silicon Era

Between 1600 and 1940, came the silicon era. With the new and improved silicon chemistry, reactions can now be carried out at much milder conditions, just enough for it to react with its organic counterpart. Silicon chemistry established two main branches, silicate chemistry which is more abundant than organosilicon chemistry. In the beginning, experiments to synthesise sand-derived silicate were carried out by many, notably, the Flemish chemist, physiologist and physician J.B. van Helmont in 1640 as well as the Swedish chemist T. Berman in 1779. [6] In this experiment, sand is dissolved in a basic solvent forming an alkali-silicate solution or "water-glass" that would revert to sand (silica) after its PH is lowered by an acidic solvent. Hence, proving that even at milder conditions or specifically, room temperature, silica chemistry is attainable by simply adjusting PH. Nevertheless, even after the experimental variables were improved in a more controlled manner by T.Berman, there were not many improvements in the results as this method is still unfavourable due to its lacking accessibility.

After some time, a game-changer appeared. Swedish chemist J. J. Berzelius founded the synthesis of silicon halides such as SiCl<sub>4</sub>, a vital precursor needed for the on-the-rise inorganic polymerization. [6] Berzlius' discoveries ultimately aided the development of silicon alkoxides in the coming years. As a result, the "grandfather" of sol-gel chemistry J.J. J. Ebelman discovered the first ever inorganic hydrolysis and polycondensation mechanisms in 1846, albeit unknowingly at that time. [6] Determined by multiple distillation experiments and as proven by the "penetrating ethereal odour and strong peppery taste" formed, silicic ethers can be formed by adding absolute alcohol to silicon tetrachloride. Additionally, it was reported that in moist conditions, silicic ethers can readily react to form silica gel, a transparent product with a glass-like appearance and mechanical break, excellent for optical uses.



Between 1857 and 1863, organic-inorganic hybridization took a step due to the then-recent confirmations made by chemists Friedrich Wöhler, C. Friedel, and J.M. Craft. [6] After the discovery of silicon tetrahydride (SiH<sub>4</sub>), compounds characterized by a carbon-silicon bond were established by reacting the first organosilicon compound, the tetraethylsilane, with silicon tetrachloride and diethyl zinc which will then be pursued 20 years later by German chemist A. Ladenburg. He investigated the hydrolysis of Et3SiOEt (Et = C2H5) to form triethylsilanol (Et3SiOH), the first "silanol" or "oil" which is stable at high temperatures. [6]

Nonetheless, there were many notable failures that turned into successes. One such example includes the formation of English chemist F. S. Kipping's silicones. [6] He first utilised Grignard's reagents to synthesize a variety of novel organo- and chlorosilanes and then hydrolysed it to form "sticky messes" known as silicones. By 1940, J. F. Hyde at Corning Glass Works realized that this "failure" might just be a blessing for the glass industry as coupling agents. [6] Due to its high thermal resistance and electrical resistivity, businesses continued to mass produce this product in hopes of competing with rival industries. Since then, they have been used to produce supplies for the military and commercialised for textile, flame retardant, and paper products. [6]

### C. Modern Hybrids

From the 1940s to the end of the 1970s came the development of mixed organic-inorganic materials. Initially, as demonstrated by Gieseking and Hendricks in the early 1940s, organic-inorganic hybrids were produced by exchanging interlayer inorganic cations or layered clay minerals such as smectites with organic cations. [6] Then, Bradley and MacEwan started to intercalate a wide variety of organic molecules with different characteristics and functions in the same type of clay minerals. [6] In this manner, this mechanism can be applied to other diverse 2D solids, encouraging the growing discoveries of organic-inorganic hybrid materials.

While clay-organic hybrids proved to be advantageous previously, their extensive use has brought about a decrease in supply, pushing industries for the discovery of new, cost-efficient organic-inorganic hybrid materials such as alkaline layered silicates, derived layered silicic acids, transition-metal chalcogenides, and hydrated vanadium pentoxide. These developments are now responsible for the manufacturing of organoclays in recent years, most of which have led to the production of polymer-clay nanocomposites (PCN), nano architectures ranging from structured clay layers to completely delaminated materials. Officially patented by 1998, researchers in the Toyota Central R&D Labs reported that by intercalating polyamides like Nylon, they were able to synthesise these novel composite materials featuring high mechanical strength, excellent high-temperature properties, and electrical conductivity. As time passed, various results were heavily doubted. For instance, the first formation of organic derivatives of silicates by Deuel in 1952. [6]

In general, this period featured a wide variety of materials such as clays, zeolites, and polymers that had their "basic compounds" mixed with complementary components of a different nature (organic with inorganic or inorganic with organic) to create new structures and modify existing physical properties. For instance, inorganic nanofillers were added or in-situ generated by

sol-gel chemistry to produce polymers in order to hybridize clay by intercalation of organic components or synthesise new zeolites by using organic cationic templates.

#### D. Current Applications

In more recent years, from the 1980s to the present day, there was a significant development in the applications of hybrid nanomaterials, whether it be in the household or the medical field (see Figure 2). But how did it improve on such a large scale? While it is very important for us to acknowledge its findings through the hard work of all scientists in their research of academic papers, it is through the impacts of market competition that they were truly globalised. The number of general economic, technical, practical and regulatory requirements can be fulfilled easily.



As businesses or institutions start to compete with one another, pressure for these hybrid materials to feature the best quality while maintaining reasonable costs is expected. However, it is to be noted that the development of modern hybrid materials relies upon the same kind of compromise: cost versus efficiency.

In the early stages of hybrid nanomaterials, raw materials easily found in nature such as clay or silicates tended to be utilized, forming robust products via well-known "manufacturing" processes.

Figure 2: Examples of commercial applications. [6]

On the other hand, modern hybrid materials generally depend on their economic viability as they are usually less costly and can easily be mass-produced at the industrial scale. Further emphasis is also placed on their compatibility with the industry they're produced for, physical improvements compared to previous products, and safety through countless regulations. A great example of how these parameters have affected innovation is well-portrayed by the founding of aerogels. First identified by Kistler in around 1931-1932, they were synthesized through the acidification of water glass (Na2SiO3) solution with HCl, involving various steps such as washing, replacing water solvent with ethanol, and supercritical drying. [6] After being mass-produced by Monsanto Chemical Corporation, it was commercialized as a flatting agent for paints and varnishes, a thermal insulator, or a filler in silicone rubber. However, their high expenses led to rising competition with a more inexpensive substitute, "fumed" silica, which eventually led to a halt in their production. [6]

In an attempt to improve safety related to the dangers of supercritical drying including extreme conditions such as high temperatures (230°C), technical developments were made in the 1980s. By replacing the flammable ethanol before supercritical drying with liquid  $CO_2$ , a nonflammable



solvent, lower temperatures (31°C) could be used. Finally, a new and improved drying procedure that can be carried out in ambient conditions (ambient pressure, 50 °C), hence its name, ambient drying was developed through prior aerogel hydrophobization in the 1990s.

Nowadays, both supercritical and ambient drying remains used to produce various aerogel-based materials commercially. For example, composite materials by Aspen Aerogels® and translucent hydrophobic silica-based aerogels granules by Cabot Corporation. Nonetheless, various tools such as Technology Readiness Levels (TRL) and Demand Readiness Levels (DRL) have also been developed to assess the technological performance and market demand for these products. Only through these assessments, will materials be approved for industrial production. [6]

## SYNTHESIS PATHWAYS

A. Sol-gel Method

Mainly used to synthesise silica nanoparticles, this method involves the hydrolysis and condensation of metal alkoxides or inorganic salts using mineral acids or bases as a catalyst. Considering its alterable properties, this method tends to be used in situations where specific reactions have to be controlled in order to synthesize a certain product. Specifically, the temperature, stirring speed, or concentrations of reactants. For instance, Stöber et al. hydrolyzed TEOS under ethanol, water and ammonia to form silica tetra hydroxide which eventually undergoes polycondensation to develop spherical and monodisperse silica NPs. [3]

Similarly, further research has discovered another method which utilizes amino acid catalysts to produce an improved, uniform version of current silica NPS that require milder reaction conditions. By simply using water, a green solvent that does not require the use of further chemical solvents, scientists can now promote an eco-friendlier approach. [3]

B. Microemulsion

Owing to their unique physical and chemical properties, microemulsion has always been a sought-out method in both research and industry. With their great thermodynamic stability and ability to solubilize immiscible liquids as well as mend particle properties like morphology and



homogeneity, their uses and applications are invaluable. [7]

First reported by Hoar et al., microemulsions are made up of liquid mixtures of water, oil, surfactant and co-surfactant molecules that arrange themselves to form a continuous phase of spheres (see Figure 3). [3] Generally used for the synthesis of ultrafine silica NPs, these water-in-oil microemulsions, or reverse micelles, have used the catalyzation of base-assisted hydrolysis

Figure 3: Structure of a reverse micelle. [3]

of silicon alkoxide to allow the silica NPs to grow inside the water-droplet of a water-in-oil microemulsion. Nonetheless, some of its limitations include expensive costs and difficulty separating surfactants from final products. [3]

C. Hydrothermal Synthesis

Hydrothermal synthesis was founded on the basic principle that all inorganic substances will dissolve in water at elevated conditions, such as high temperature and pressure. Hence, the water will evaporate which causes the dissolved substance to form crystals. This method has been used numerously in the production of silica-supported nanomaterials. Known for not requiring controlled temperatures or environments, this technique is extremely beneficial when needed to prevent re-clustering and contamination. This is particularly useful for the synthesis and post-synthetic treatment of specifically mesoporous silica NP. As its name suggests, it consists of a great amount of uniquely ordered pores, specific surface areas, and a broad range of morphologies. [8] It can be synthesised via techniques including the one-pot hydrothermal suppressed-growth strategy, in which silica NP growth can be controlled by the addition of formaldehyde to form products with higher hydrothermal stability, improved mesoscopic regularity and high pore size. [3]

D. Agricultural Wastes



Figure 4: Graphical abstract on how agricultural waste can be transformed and utilised as a silica NP. [9]

We are not foreign to the disastrous impacts that increasingly unavoidable agricultural activities have brought upon society. From air pollution to the serious health risks it poses, scientists have been trying to eradicate or minimize their negative impacts. One such result includes managing a substantial amount of agro-waste worldwide to create value-added products such as organic fertilizers in agriculture and biogas via the use of nanotechnology in synthesizing silica NPs (see Figure 4). [9]



## 1. Bio-Based Methods

Multiple studies have verified the possibility of producing silica NPs using organic biomass. They secrete significant enzymatic levels that enable the optimal conditions needed to fermentise products like corn cob husks by applying Fusarium culmorum which could produce spherical silica NPs. This is proven by a success rate of 47% as Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was carried out which shows the presence of siloxane bonds and O-Si-O bonds in the post-biotransformation fluid. Therefore, results indicate that the application of fungi as biocatalysts is advantageous as it is easy to process and isolate the biomass, only simple procedures are needed, and economic viability is attainable.

Similarly, a greener bio-based approach involves the usage of a thermophilic bacterium (BKH1) as a biotemplate. Since BKH1 can secrete an enzyme, bioremediase, which enables the release of silica from the silicate phase of inorganic and organic precursors like magnesium trisilicate, it will be able to fabricate the synthesis of silica NPs with the help of Actinobacter sp. bacterium. It has the ability to further release reductases and oxidizing enzymes, leading to silica NP production while not exhibiting any cytotoxicity to human skin cells. [10]



2. Microwave-Assisted Synthesis

Figure 5: Synthesis of silica NPs from agro-wastes via green luminescent fabrication. [10]

While the use of microwaves to produce nano-silica hollow spheres is still a relatively novel approach, it displays outstanding capabilities. For example, the ability to create a hollow, uniform, porous morphology. Tested for their potency as drug ibuprofen carriers, these silica NPs have proven that they have high reaction efficiency, low energy consumption, and short reaction times. Additionally, after the application of the surfactant-free microwave-assisted synthetic method, it was reported that the choice of solvent, silicic acid precursor, catalyst, and microwave irradiation time could influence silica NP size. In a study involving the usage of an inexpensive agro-waste silicon precursor, rice husk, it was reported that refined fluorescent efficiency with the NPs display significant green fluorescence, strong storage stability and photostability, and continuous luminescence for over 48 hours under UV irradiation (see Figure 5). When mixed with produced red and blue luminescent silicon NPs, results demonstrate that it's highly suitable for energy-efficient white light production, much better than its commercial compact fluorescent lamp counterpart. [10]



E. Graphene Oxide Functionalized Organic-Inorganic Hybrid (GO–Si–NH2–PMo)

GO–Si–NH2–PMo is a catalyst formed from the ionic immobilization of two catalysts, heteropoly acids (HPAs) and graphene oxide (GO). These catalysts are desired due to their unique sets of properties such as simple recovery, high rates of recyclability, and biochemical compatibility. When combined, they form a catalyst with astounding separation efficiency and a relatively high surface area to maximize catalyst activities. To synthesise GO–Si–NH2–PMo, there are 3 overall steps including the synthesis of GO from graphite, synthesizing amino-functionalized graphene oxide (GO–Si–NH2), and forming GO–Si–NH2–PMo with the help of ethanol.

While using organic solvents such as acetic acid are conventionally used, they pose a couple of disadvantages by causing the procedures to be highly complicated, have harsh reaction conditions, difficult catalyst separation, and a low product yield. Hence, based on this information, the Hummers method is the most efficient solution as compared to its other alternatives. It is clean, environmentally sustainable, and high-yielding which makes it highly desirable. [11]

## CATALYTIC APPLICATIONS

- A. Biomedical Applications
- 1. Drug Delivery

While other silica NPs like those that are mesoporous have great potential for applications as a drug delivery system (DDS), given their desirable properties such as high surface area and biocompatibility, their synthesis requires chemicals that may be harmful to humans and are energy-intensive to synthesise. On the other hand, biosilica, its most viable alternative, can be formed efficiently using harmless marine resources. [12] Additionally, its promising pore size causes a suitable balance between stability and degradability, showing great potential to function as a DDS. An ideal system was first introduced by Pack and coworkers. [10] They created a dual-drug delivery system (dDDS) using R5 peptide-fused ferritin (R5FT). Due to the mediation of biosilica deposition on the ferritin surface (SiO2/R5FT) using a fused R5, 2 types of molecules can be inserted into the core (ferritin cage) and the outer shell (biosilica matrix). For instance, an anticancer drug, Doxorubicin (Dox), was inserted into the ferritin cage and along with the reassembly of R5FT formed R5FT(Dox). Next, another anti-cancer drug, paclitaxel (PTX), was captured by biosilica matrix formation to form SiO2(PTX)/R5FT(Dox). This system can then be applied to different combinations of drug delivery. [10]



2. Tissue and Implant Engineering



**Figure 6**: Systematic process of supplying hMSCs embedded in alginate with biosilica and olyp into a fracture zone. [10]

Biosilica-based materials are typically ideal for on-site bone repair. They are stable, compatible with biomolecules, and morphogenetically active which helps osteoblast-like cells (SaOS-2) to mineralize. A study by Wang et al. uses biosilica (BS) and polyphosphate (olyp) to show and study morphogenetic effects on osteoblasts, human multipotent stromal cells (hMSC), and mesenchymal stem cells which were encapsulated into biocompatible plant polymer alginate beads (see Figure 6). [10] Results show that both biosilica and olyp caused an improvement in the mineralization of osteogenic cells, increasing their alkaline phosphatase (ALP) expression and bone morphogenetic protein 2 (BMP2). Hence proving that when supplied with biosilica and olyp, an inert alginate polymer is morphogenetically active and can be used in the 3D tissue printing of hMSCs as well as delivering hMSCs in fractures. [10]

- **B. Industrial Applications**
- 1. Oil Recovery

Increasing levels of oil recovery due to the applications of silica NPs have become even more popular. These NPs are first injected into various core plugs taken from carbonate reservoirs which are major oil and gas sources, affecting their viscosity, interfacial tension, and wettability. [14] Thus, making it easier to recover oil. For instance, Abed and Ali. synthesized environmentally responsive surface-modified nanoparticles using silica NPs that were coated with polyethylene glycol (hydrophilic agent) and propyl (hydrophobic agent) chains, ensuring oil–water interfacial tension and water surface tension are decreased. [15] As a result, the removal of oil via the flooding process as well as the oil drop mobility becomes much more efficient. [13] This demonstrates that these surface-modified silica NPs considerably improve oil recovery and wettability alteration, showing promising results as an alternative for chemical surfactants in oil industries. [15]



## 2. Food Preservation

Applications of the synthesis of silica-based hybrid films have been garnering widespread attention from scientists globally due to their ability to increase shelf life and preserve food for longer periods of time. Silica-based hybrid films can be formed using decylethyldimethoxysilane (C10EtDMS) and didecyldimethoxysilane (2C10DMS). [16] After undergoing a series of processes such as the breaking down of chemical substances via co-hydrolysis, polycondensation with tetramethoxysilane (TMOS), and spin-coating, these films are formed. [3] Scientists like Mirzadeh et al. have confirmed through their research that after fruits such as Longan were coated with a film, there were reduced weight loss and browning effects. [15] Similarly, another research using the same film coating on Loquat showed enhanced enzymatic activity and reduced sugars.

### 3. Water Purification

Silica NPs, given their ability to remove heavy metals from aqueous solutions, have always been used to purify wastewater, especially those generated by industries. This is achieved by decreasing biological oxygen demand (BOD). Similarly, a study by Park et al. tested the antimicrobial strength of synthesized silver nanoparticles coupled with silica NPs using 2 pathogen viruses, bacteriophage and murine norovirus, which can be found in the ground, tap, and various deionized water samples. [15] Results show that there was greater antiviral strength when the coupled silver-silica-nanoparticles (Ag-SNPs) were added to murine norovirus as compared to bacteriophage for all samples. Hence, proving that silica-coupled NPs have the ability to eliminate viruses in wastewater.



Furthermore, another study showed the oil recovery capability of silica NP-based films, coated with PDMS. This type of film is synthesized through a chemical vapor deposition (CVD) process where a substrate is exposed to volatile precursors and forms a thin film deposit to produce a polydimethylsiloxane (PDMS) thin film on silica NPs. Since PDMS is hydrophobic, it was able to separate oil-water mixtures. The results demonstrated that in the case of environmentally detrimental oil spillage or diffusion, these films could be used to alleviate it.

# Figure 7: Oil Recovery Factor. [15]

Correspondingly, a study by Fan et al. was able to compare the oil recovery factor for polymernanosilica, polymer and water flooding. [15] As shown in Figure 7, the oil recovery factor which is the overall proportion of oil expected to be extracted from using polymer-nanosilica was the highest at 65% as compared to polymer with 55% and water flooding at 50%. Therefore, we can conclude that the use of silica NPs is highly effective for enhanced oil recoverability.



#### FURTHER RESEARCH

While a significant amount of effort has been placed into researching the synthesis pathways and applications of silica NPs, many aspects have yet to be fully exploited and can be further investigated in various ways. Firstly, in their synthesis using agricultural waste, there is a risk of harming the environment and human life. To obtain silica NPs, the organic compounds in the waste need to be removed through burning. Hence, releasing greenhouse gases and excessive tiny particulate matter that is detrimental to humans when inhaled [9]. Similarly, when a pure version of the silica NPs is needed, strong acids need to be used as reactants which is dangerous because these acids may react violently with the surrounding water and cause harm. [15]

Furthermore, as for the catalytic applications of silica NPs, additional research regarding its capabilities when entrapping colorless and water-insoluble drugs is necessary for more targeted delivery in DDS. Likewise, when silica NPs are coupled with other substances, there is room for improvement in terms of selecting particular types of seeds that can develop antifungal properties as well as different types of aminosilanes that can efficiently remove dye or other chemical pollutants from wastewater. Finally, as proven by the increased shelf life of loquat fruits when exposed to silica hybrid films, there is a possibility that more fruits can develop this feature, thus motivating more research. [15]

#### CONCLUSION

Over the years, silica NPs have contributed a great deal towards the development of nanotechnology and scientific discovery. From the times of prebiotic chemistry to our modern hybrid nanomaterials, scientists haven't ceased development, with each stage becoming even more viable both economically and scientifically. Nowadays, these nanomaterials can be easily mass-produced and commercialized for a diverse group of industries. Whether it is silica NPs or graphene oxide, they each have their own unique properties that make them valuable. For instance, their high surface area, versatile morphology, and biocompatibility allow them to be advantageous in their multifaceted applications including water purification and drug delivery systems. As for their synthesis pathways, some are much more commonly used than others. For instance, due to the simplicity of the sol-gel method, it tends to be favoured as compared to the methods using agricultural wastes. Nonetheless, these nanomaterials have proven to be a step forward towards a sustainable and green future as they enable benign catalytic processes and are environmentally friendly. As a result, they might just be one of our leading solutions to solving the growing threats of global issues like global warming and climate change.



#### REFERENCES

- 1. IPCC intergovernmental panel on climate change. (n.d.). https://www.ipcc.ch/site/assets/uploads/2018/05/SYR\_AR5\_FINAL\_full\_wcover.pdf
- 2. IPCC intergovernmental panel on climate change. (n.d.). https://www.ipcc.ch/site/assets/uploads/2018/03/SREX-Chap3\_FINAL-1.pdf
- Sharma, R. K., Sharma, S., Dutta, S., Zboril, R., & Gawande, M. B. (2015). Silica-nanosphere-based organic-inorganic hybrid nanomaterials: Synthesis, functionalization and applications in catalysis. *Green Chemistry*, *17*(6), 3207–3230. https://doi.org/10.1039/c5gc00381d
- 4. Rodrigues, T. S., da Silva, A. G., & Camargo, P. H. (2019). Nanocatalysis by noble metal nanoparticles: Controlled synthesis for the optimization and understanding of activities. *Journal of Materials Chemistry A*, 7(11), 5857–5874. https://doi.org/10.1039/c9ta00074g
- 5. Akubude, V. C., Nwaigwe, K. N., & Dintwa, E. (2019). Production of biodiesel from microalgae via nanocatalyzed transesterification process: A Review. *Materials Science for Energy Technologies*, 2(2), 216–225. https://doi.org/10.1016/j.mset.2018.12.006
- Faustini, M., Nicole, L., Ruiz-Hitzky, E., & Sanchez, C. (2018). History of organic-inorganic hybrid materials: Prehistory, art, science, and advanced applications. *Advanced Functional Materials*, 28(27), 1704158. https://doi.org/10.1002/adfm.201704158
- Malik, M. A., Wani, M. Y., & Hashim, M. A. (2012). Microemulsion method: A novel route to Synthesize Organic and inorganic nanomaterials. *Arabian Journal of Chemistry*, 5(4), 397–417. https://doi.org/10.1016/j.arabjc.2010.09.027
- 8. Hanrahan, J. P., O'Mahony, T. F., Tobin, J. M., & Hogan, J. J. (n.d.). *Mesoporous Silica and their Applications*. https://www.sigmaaldrich.com/ID/en/technical-documents/technical-article/environmental-testing-and-industrial-hygiene/waste-water-and-process-water-testing/mesoporous-silica
- Sarkar, J., Mridha, D., Sarkar, J., Orasugh, J. T., Gangopadhyay, B., Chattopadhyay, D., Roychowdhury, T., & Acharya, K. (2021). Synthesis of nanosilica from agricultural wastes and its multifaceted applications: A Review. *Biocatalysis and Agricultural Biotechnology*, 37, 102175. https://doi.org/10.1016/j.bcab.2021.102175
- 10. Shafiei, N., Nasrollahzadeh, M., & Iravani, S. (2021). Green synthesis of silica and silicon nanoparticles and their biomedical and catalytic applications. *Comments on Inorganic Chemistry*, *41*(6), 317–372. https://doi.org/10.1080/02603594.2021.1904912
- Ataie, F., Davoodnia, A., & Khojastehnezhad, A. (2019). Graphene oxide functionalized organic-inorganic hybrid (go-si-nh2-pmo): An efficient and green catalyst for the synthesis of tetrahydrobenzo[b]pyran derivatives. *Polycyclic Aromatic Compounds*, 41(4), 781–794. https://doi.org/10.1080/10406638.2019.1622137
- 12. *Mesoporous silica nanoparticle: Encyclopedia Mdpi*. Encyclopedia. (n.d.). https://encyclopedia.pub/entry/history/compare\_revision/69025/-1
- Behzadi, A., & Mohammadi, A. (2016). Environmentally responsive surface-modified silica nanoparticles for enhanced oil recovery. *Journal of Nanoparticle Research*, 18(9). https://doi.org/10.1007/s11051-016-3580-1
- 14. Olayiwola, S. O., & Dejam, M. (2020). Effect of silica nanoparticles on the oil recovery during alternating injection with low salinity water and surfactant into carbonate reservoirs. *Day 2 Tue, October 27, 2020.* https://doi.org/10.2118/201586-ms



- Akhter, F., Rao, A. A., Abbasi, M. N., Wahocho, S. A., Mallah, M. A., Anees-ur-Rehman, H., & Chandio, Z. A. (2022). A comprehensive review of synthesis, applications and future prospects for silica nanoparticles (snps). *Silicon*, *14*(14), 8295–8310. https://doi.org/10.1007/s12633-021-01611-5
- Umeda, N., Shimojima, A., & Kuroda, K. (2003). Synthesis of multilayered silica-based hybrid films from difunctional organosilanes by co-hydrolysis and polycondensation with Tetraalkoxysilane. *Journal of Organometallic Chemistry*, 686(1-2), 223–227. https://doi.org/10.1016/s0022-328x(03)00619-3