The Invisible Matter: Nanomaterials

Disha Bandyopadhyay
3rd year MEng Materials with Nuclear Engineering

Despite a nanometre being just a billionth of a meter, materials with features on this scale are much more reactive and dynamic than their bulk counterparts. Just the basic components of matter – elements and their electronic densities are fused in together in a smaller area in a nanomaterial such that most of the electron density spews on the surface, ready to react with other materials. Their widespread use in industry allows nanoparticles to be either engineered with a specific purpose or be an incidental by-product that could cause multitudes of problems. Therefore, the study of nanomaterials has two great benefits: understanding the pollutants and toxins and using the same science to trap and reduce pollution. Although their high reactivity and small size makes them unpredictable and difficult to control, the Department of Materials at Imperial College London studies them so that their properties can be harnessed for the good: healthcare, sporting goods, cosmetics, food, consumer electronics, computing, environmental remediation among others in various forms of unique particles or thin films.

There have been growing concerns since the early 2000s about nanotoxicity, leading up to the much-debated nanomaterial paradox. What gives nanomaterials their huge potential benefits, (their large surface area to volume ratio) is also the same property that makes nanomaterials so dangerous.

Owing to their small size, not a lot of material is required to make these structures, but typical nanoparticles are made of inorganic materials such as cadmium selenide and tellurium which are mostly toxic. They are also capable of entering animal and plant systems easily. Zinc oxide nanoparticles from cosmetics enter through oral or dermal routes, nanoparticles from cigarette smoke enter the system via inhalation while some nanoparticles are intentionally injected intravenously for medical treatments. When these particles enter any living species, they cause an inflammatory biological and ecological response. They produce reactive oxygen species which alters cell potential causing acidification, killing, and compromising healthy cells. Even inert nanoparticles can interact with the environment by forming physical coatings around organisms, interfering with their growth and natural behaviour. In the third-year nanomaterials option we study this phenomenon, particularly how the core and surface structures affect nanomaterial properties. Stability of any suspension of nanoparticles is achieved by controlling basic parameters such as pH, temperature, dissolution/redox behaviour, and surface agitation. The ability to translocate barriers and intoxicate flora and fauna is controlled by the effective dose or the concentration of the particles, clearance time

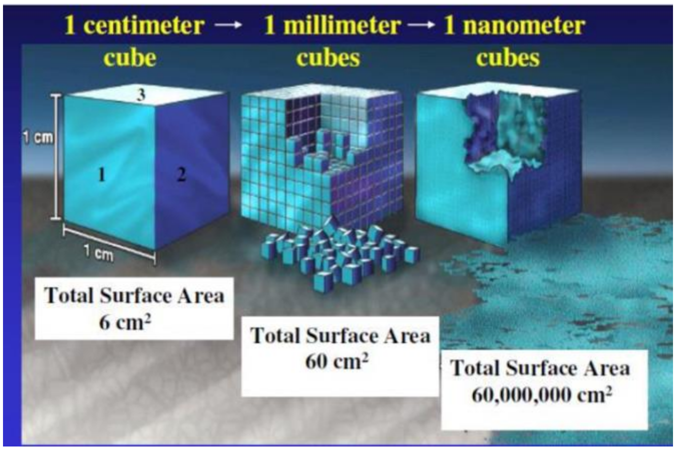

Figure 1: How nanoscale features result in increased surface area. From [1]

and how easily accessible cells and organelles are in the ecosystem. All of this is ultimately a function of materials processing which controls the shape, size, surface area and surface reactivity. Due to their tiny size, synthesising a batch of nanoparticles to be monodisperse and homogenous can be challenging, albeit not impossible.

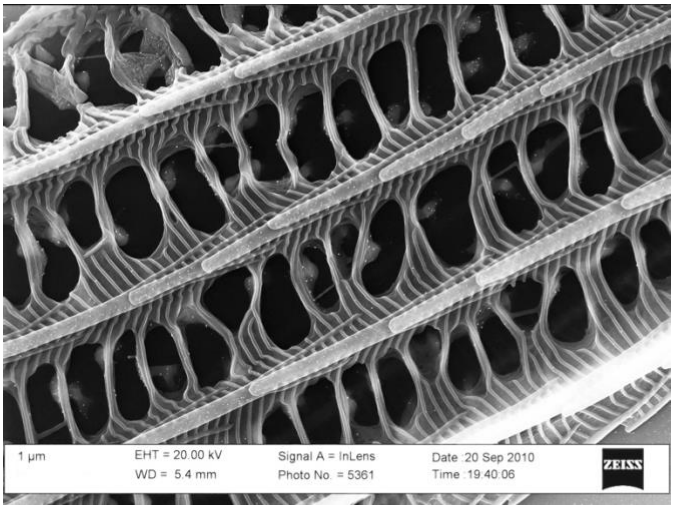

Figure 2: SEM image of the fibrils on a morpho moth wing. The spacing of the fibrils allow constructive interference of about 450nm waves resulting in the blue colour of the wings. From [2]

Man-made nanoparticles often end up in landfills, wastewater systems and biosolids, as they emerge from the production of raw materials, manufacture of products and the end of product lifecycles through wear and tear and corrosion. Naturally occurring nanomaterials exist and are randomly structured and distributed. They're formed by volcanic ash, ocean spray, bacteria, mineral composites and much more. Whether these nanoparticles attack or protect species depends on whether the particles are stable in their tiny form or if they deposit themselves onto surfaces, or aggregate and transform themselves into more complex arrangements. Some of these nanoparticles set themselves into useful arrangements such as the sharp conical spikes on a cicada wing which gives them antimicrobial properties, nanoscale fibrils in the wings of the morpho moth which give it a brilliant blue colour, or into thin films on aquatic plants like water lilies which make them superhydrophobic and an inspiration for artists like Monet.

Nanoparticles are small enough such that the bulk material properties do not apply to them. And they aren't singular particles either, so quantum mechanics doesn't define them. Hence, nanomaterials form a bridge between modern and classical physics, expanding our understanding of what matter is and all its capable of. The confinement of electron densities results in smaller nanoparticles being good absorbers, while the larger ones are better scatterers of light.

Due to their highly sensitive surfaces, nanomaterials work as effective gas sensors. This works on the basis of how the interaction with specific gas molecules can rearrange the surface electron densities, affecting the overall conductivity of the material. Each type of nanoparticle changes its conductivity in a set way in the presence of the gas molecule, which is documented. For example, a graphene coated with a polymer nanoparticle has high sensitivity to nitrogen dioxide levels and is used as a gas sensor for the same. In environmental applications the presence of hydrogen peroxide is a good indicator of whether a degradation process is taking place and judging by the rate of change of conductivity, the rate of the degradation process can be determined. The same principle can be used to synthesise various other sensors which can be used to efficiently detect when air toxicity is increasing or if there has been any leak in manufacturing processes, particularly when hazardous gases are used in synthesis routes. These particles also double as buffers to help maintain healthy compositions.

Nanomaterials allow for another great sensing application which works with solvents. Specialised functional groups attached to nanoparticles bind with the target molecule that is wished to be detected. Once this bonding happens, the size of the particle changes and therefore so does its absorbance capability, which can easily be detected by UV-vis spectroscopy and dark field microscopy. This makes it a quick and relatively easy testing technique for detecting toxin levels in rivers and lakes. The same idea is also used when nanoscale zero valent iron is used to immobilise metals, detoxify pesticides, and transform fertilisers. The use of magnetic nanoparticles in this way also helps clean-up carcinogenic dyes released from the textile industry [3]. Furthermore, since nanoparticles are typically inorganic substances they don't bleach over time and it's a lot easier to use them than their organic competitors. Both the detector and marker can be made of the same material, just a different size/morphology, so they're easier to make. Essentially, just the processing time can be changed and the product changes from one function to another.

The primary challenge with dealing with nanoparticles is how tiny they are. It isn't possible to have a wide beach clean-up with them as we do with plastics (instead, they're used for the clean-up), so targeted and specific solutions must be engineered. This is where nanoporous structures are making headlines as saviours where one nanoscale structure immobilises the more harmful nanostructure. The tailoring of pore number, size, and charge in a nanoporous material aids the removal of organic solvents, heavy metals, bacteria, and aerosols from the environment and so environmental remediation remains an immense arc of applications. Nanomaterials have been used in water filtration where a bottle with two necks and a membrane in the middle is manufactured. The inlet water contains many particulates and pollutants. The other side of the membrane creates an osmotic pressure by the presence of nanoparticles. The nanoparticles help segregate the pollutants to one side of the membrane so clean water can be poured out. And a nifty magnet at the top and none of the nanoparticles can enter the useful water stream.

Nanoscience is not a new field. In fact, historic artefacts such as the Lycurgus cup made by the Romans in the fifth century AD harnessed orientation dependent scattering effects of nanoparticles to produce luminescence in different colours. It is likely they didn't understand the science behind this colour change, but pairing known applications with our current technological advancements, we can engineer better and highly functional structures with nanotechnology. It is becoming easier to synthesise nanoparticles now whether this be by modelling them with greater

Figure 3: The Lycurgus cup, currently in the British museum, that changes colour depending on direction of incident light. From [4]

accuracy or synthesising the modelled structures via sputtering techniques or sol gel processing. We can ultimately visualise them with advanced microscopy techniques such as SEM and TEM, as well as FIB which allows in situ imaging to potentially show the reaction taking place in live time. With these possibilities, even more permutation and combinations of materials and structures can be studied, combined, and implemented for applications with a greater impact and chance of success.

Evidently, nanoparticles have a variety of applications and their contribution to advanced sensing technologies have brought breakthroughs in efficient detection systems. The challenge for the scientific community now lies in making safe nanomaterials and harnessing the power of their unique properties to address the challenges of ecological disaster. The question of whether nanomaterials are safe in their current form for the ecosystem remains largely unanswered, and with lots of inconclusive results. However, it can't be denied that their widespread use and successful integration has been an indispensable tool, making it clear that nanomaterials need to be further explored. They have the potential to change and revolutionise our world, but in which direction exactly is yet unknown. So, there's only one way to find out – continual research and study!

References:

[1] Ryan, MP 2020, Lecture 4: Nanotoxicology, lecture notes, MATE96007 Nanomaterials 1, Imperial College London, delivered December 2020.

[2] Nisenet.org. 2021. Scientific Image - Nanoscale Structures on a Blue Morpho Butterfly Wing | NISE Network. [online] Available at: <https://www.nisenet.org/catalog/scientific-image-nanoscale-structures-blue-morpho-butterfly-wing> [Accessed 15 May 2021].

[3] Sara Ryding, B., 2021. Using Nanoparticles for an Environmental Cleanup. [online] AZoCleantech.com. Available at: <https://www.azocleantech.com/article.aspx?ArticleID=945#:~:text=Applications%20of%20Nanoparticles%20to%20Environmental%20Cleanup&text=By%20injecting%20it%20to%20the,transform%20fertilizers%2C%20such%20as%20nitrates.&text=Similarly%2C%20nanoparticles%20have%20been%20successfully,the%20removal%20of%20toxic%20metals.> [Accessed 15 May 2021].

[4] British Museum (2019) [Twitter] 26 March. Available at: https://twitter.com/britishmuseum/status/1110566063245271040