Graphene: a catalyst for the carbon age

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Ever since the discovery of graphene a decade ago by Andre Geim and Konstantin Novoselov, it has sparked the imagination of scientists around the world.

Graphene is an atom-thick two-dimensional allotrope of carbon that has exceptional physical, optical, electrical and chemical properties. For example, graphene is both the thinnest and strongest material ever discovered, and it has a higher electrical and thermal conductivity than any other material. In addition, graphene is remarkably flexible, transparent and impermeable. Graphene also exhibits promising chemical characteristics, such as high chemical stability, large surface area, high porosity, biocompatibility and non-toxicity. These properties make graphene a promising material for a range of chemical applications – from hydrogen storage and nanosensors, to chemical catalysis. These applications are at different stages of realisation, and it is difficult to predict which ones will have a broad industrial impact. Nevertheless, graphene research is already attracting massive investments from universities, industry, and governments around the globe; for example, last year, the European Commission pledged a sum of €1 billion for the fabrication of graphene, and investigation into its potential applications.

Due to its two-dimensional structure, high surface area, and unique electronic structure, graphene is emerging as a powerful catalyst (and catalyst support) for a variety of chemical processes ranging from organic synthesis to polymerisation reactions. Graphene-based heterogeneous catalysts provide eco-friendly alternatives for traditional homogeneous catalysts, such as metal-based and Brønsted/Lewis acid catalysts. This has significant industrial implications since heterogeneous catalysts (that is, catalysts that are insoluble in the reaction mixture) are much easier to separate and re-use compared with homogeneous catalysts (that is, catalysts that are soluble in the reaction mixture). Graphene-based materials are also attracting increasing attention due to the ease by which they can interact with polymers, organic dyes, enzymes, and proteins through covalent and non-covalent interactions. New catalytic applications of these materials are continuously being reported in the literature. This essay briefly summarises some of the recent developments in the catalytic applications of graphene-based materials in the imminent 'carbon age'.

Graphene oxide is an oxidised form of graphene that is produced from graphite via relatively low-cost processes. Graphene oxide (and graphite oxide) can function as a green oxidant or solid acid catalyst due to the presence of oxygen-containing functional groups. These functional groups can catalyse a range of oxidation reactions, most notably the selective oxidation of:

- alcohols to aldehydes or ketones
- thiols to disulfides
- sulfides to sulfoxides
- olefins to diones.

Graphite oxide has also been shown to catalyse polymerisation reactions; for example, the polymerisation of olefins and the ring-opening polymerisation of cyclic lactones and lactames. In addition, graphite oxide catalyses the synthesis of biologically important chalcones from alkynes and alcohols. Remarkably, in this process, graphite oxide catalyses three reactions (oxidation, hydration and aldol coupling) in a single reaction mixture. Thus, graphite oxide circumvents limitations inherent to the traditional synthetic approaches, and enables a metal-free synthesis of chalcones.

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Graphene-based materials are also emerging as promising catalyst supports. For example, it has been found that a platinum/graphene composite can catalyse methanol oxidation and oxygen reduction reactions in fuel cells. Similarly, it has been found that palladium and gold nanoparticles dispersed on graphite oxide can catalyse the Suzuki cross-coupling reaction. This coupling reaction is among the most widely used for the formation of carbon–carbon bonds. As a side note, it is worth mentioning that Akira Suzuki received the Nobel Prize in Chemistry in 2010, the same year Andre Geim and Kostya Novoselov received the Nobel Prize in Physics for the discovery of graphene.

Parallel with the increased experimental research into new catalytic applications of graphene-based materials is the increase in computational modelling of their chemical properties. Computational chemistry is a branch of chemistry that attempts to model chemical processes as accurately as possible by using calculations rather than experiments. Computational chemistry is widely used in investigating and designing new catalysts since it is often easier (and cheaper) to computationally model these systems rather than synthesise them and conduct experiments in the lab. With the advent of theoretical methods and high-performance computing facilities (such as the National Computational Infrastructure supercomputer in Canberra), computational chemistry provides a powerful means for exploring currently unknown chemistry.

In my computational chemistry lab at the University of Western Australia, we are using sophisticated quantum chemical simulations to design efficient catalysts and other functional molecular systems. We are currently exploring the use of single-layer graphene sheets for catalysing reactions through π–π interactions, which are attractive forces between aromatic sub-units of molecular systems. These non-covalent interactions are of broad importance in nature; for example, they play a major role in protein folding, and in determining the structures of DNA and RNA.

Recently, we have found that nano-sized fragments of graphene can efficiently catalyse a range of chemical processes via π–π interactions. These processes include the:

- bowl-to-bowl inversion of curved aromatic molecules (for example, corannulene)
- 'flip-flop' inversion of helicenes (for example, benzo[c]phenanthrene)
- rotation processes in substituted biphenyls.

We have shown that a graphene-like catalyst accelerates the rates of these reactions by several orders of magnitude, due to the strong π–π interactions between the catalyst and the aromatic substrates involved in these reactions. This work illustrates for the first time that graphene-like structures can catlayse chemical reactions via π–π interactions, and paves the way for exploring other reactions that may be catalysed by graphene via non-covalent interactions.

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