HYDROTHERMAL FLOW FOR 2D MATERIALS

Suela Kellici

Materials World magazine

29 Aug 2019

Hydrothermal flow synthesis has been used to make new 2D materials at London South Bank University.

Two-dimensional (2D) materials have attracted interest due to their wealth of remarkable properties that are a consequence of their atomic level of thickness and lateral dimensions. Examples of such materials include graphene (G), molybdenum disulphide (MoS2), boron nitride (BN) and MXenes (Mn+1Xn, where M is an early transition metal, X is carbon or nitrogen, and n equals 1, 2, or 3).

Their extraordinary properties include a high surface area, high Young modulus, chemical stability, transparency and quantum confinement.

However, these 2D materials alone do not possess the diversity of properties required to allow facilitation and integration into a range of technological applications, for example, as components for the next generation catalysts, biosensors, energy storage and production, computing, or water treatment. The fundamental requirement for such applications is the ability to produce and modify the 2D functional material in high-quality, with minimal defects in a controlled manner using a target-orientated approach in regard to their chemical and physical properties including composition, structure, particle size and morphology.

Tuneable properties

The flexible and robust nature of these 2D nanosheets allows for the design of 2D-based functional materials with new tuneable properties. This can be achieved via top-down and bottom-up approaches and or in combination with structural functionalisation. The top-down approach involves the exfoliation of the corresponding 3D material reduced to give a single atom thick monolayer 2D sheet. The bottom-up approach employs chemical synthesis via atom-by-atom growth. Design routes may include:

Functionalising, doping or decorating the 2D with highly crystalline inorganic nanostructures, for example homo or hetero metal oxides

Coupling with an alternative 2D material, for example, graphene and MXene, forming nanocomposite materials

Substitutional doping with various atoms, including heteroatoms such as boron (B), nitrogen, phosphorous or sulphur or metals such silver (Ag), iron and cobalt, or

Cutting the atomic sheets to smaller sizes of less than 10nm zero dimensional quantum dots.

A single-step process

Despite extensive research efforts and the notable advantages offered this far, current processes for synthesis of 2D materials show shortcomings in terms of their complexity, performance and cost. Further improvements to keep up with increasing demands for new outstanding functional materials are required. The economic viability and applications of 2D materials strongly depends on better synthetic routes that reduce costs, provide consistency in the materials performance and durability. While these factors will improve as technology matures, radically new approaches for the production of the materials are desired.

Nano2D Lab uses continuous hydrothermal flow synthesis (CHFS) that enables a change in cost, performance and durability. CHFS is a single-step process that involves mixing a flow of superheated water in a bespoke reactor with a flow of water-soluble precursors to give highly controlled, continuous and synthesis of a variety of nanomaterials within seconds.

A significant feature of this synthetic approach is the mode of which the properties of water such as density, dielectric constant and diffusivity, change considerably around the critical temperature and pressure settings of 374°C, and 22.1MP, leading to its use as controllable reaction solvent or medium. Also, CHFS offers fine controls such as temperature, residence time, pressure and reactant concentration, that allows a high degree of tailoring and functionalisation of the 2D materials. These include oxidation, composition and surface area in their design before desired fit-for-purpose application.

Based on the searchable items on the ISI Web of Science database, less than 1% of hydrothermal methods reported use CHFS as a route to material synthesis. The synthetic approach is advantageous in that it is a continuous process, restricts the use of harmful or toxic chemicals by using metal salts or biomass derivatives, and uses supercritical water. It reduces the synthetic timescale from hours to minutes – offering reduced energy consumption – and is readily scalable. It is highly controllable and due to fast nucleation and growth rates, the materials are produced with well-defined and tailored properties including particle size, morphology, composition and surface area.

The laboratory has contributed to scientific CHFS advances, with recent published developments that foster innovative CHFS approaches in producing high quality 2D reduced graphene oxide, with tuneable thickness and surface functional groups exhibiting superior antibacterial properties, the first in the CHFS field. This was reported in A single rapid route for the synthesis of reduced graphene oxide with antibacterial activities, published in RSC Advances. Another is adding new functionalities to the 2D substrate via surface modification with various nanoparticles, for example ceria-zirconia, or tin oxide, to form nanocomposite catalysts that exhibit excellent catalytic properties for the conversion of CO2 into valuable products.

Nano2D Lab’s materials portfolio includes the first development of directly printed graphene-based 3D structured nanocatalysts for industrially relevant reactions for CO2 utilisation, as well as making silver (Ag) nanoparticles embedded on graphene, giving antibacterial properties superior to Ag alone and in selected cases outperforming antibiotics.

Furthermore, the laboratory developed synthetic routes that enable hydrothermal fragmentation of graphene sheets to produce water-soluble zero-dimension graphene quantum dots (GQD) less than 10nm with excellent tuneable optical properties in useful quantities. The team engineered the particle size and consequently their optical properties via a range of molecular capping tools to confine hydrothermal growth of the GQD, and using cross-flow ultrafiltration – commonly used in industrial processes for separation – to enhance further control and isolation of discrete particle sizes. They have also designed 2D MXene for the first time with new morphologies, crumpled sheets, spheres and scrolls, providing access to a variety of properties that are typically useful for energy storage applications.

These examples illustrate that CHFS can deliver world-class material engineering by creating a gold access route to the utilisation of advanced 2D functional materials in a wide range of applications. It does so by introducing key transformations in materials engineering including:

Changing and reducing the processing steps required to make such functional 2D derivatives from multi-step to a rapid single step

Giving instant independent control over reaction parameters and hence particle properties

Using materials with a 2D plate-like structure as an attractive substrate for deposition of nanostructures and 2D surface functionalisation via a rational design approach to form novel, highly dispersed nanocomposites with unique properties, and

To transform and adapt this process to high throughput methods for synthesis of materials in a relatively short timeframe, thus, allowing rapid production and evaluation of new nanocomposites.

The CHFS route covers an array of 2D materials across a range of potential applications. These include energy storage, such as electrodes for lithium-ion batteries, supercapacitors and solar cells, reduction of CO2 and other environmental pollutants, including catalysts and absorbers, and biomedicines like antibacterials, biosensors and bio-tagging.