
Review

Sustainable hydrothermal and solvothermal synthetic approaches for advanced carbon materials in multidimensional applications: A review

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Abstract: There is great importance and need of improving existing carbon materials fabrication methods. As such, this work proposes to offer deeper discussions of a selected and promising literature. This review will interrogate, viable hydrothermal, solvothermal, and other advanced carbon materials synthetic methods while making several other viable options. The advanced carbon materials to be interrogated will include the synthesis of carbon dots, carbon nanotubes, nitrogen/titania-doped carbons, graphene quantum dots, and their nanocomposites with solid/polymeric/metal oxide supports. This will be done with special mind to microwave-assisted solvothermal and hydrothermal synthesis due to their favourable properties such as rapidity, low cost, and green/environmentally-friendliness. Thus, these methods are important during the current and future synthesis and modification of advanced carbon materials for application in energy, gas separation, sensing, and water treatment. Simultaneously, the work will pay special cognizance to methods reducing the fabrication costs and environmental impact while enhancing the properties as a direct result of the synthesis methods. As a direct result, the expectation is to impart a significant contribution to the scientific body of work regarding the improvement of the said fabrication methods.

Keywords: carbon materials synthesis and functionalization; energy; graphene; gas separation; hydrothermal and solvothermal carbonization; microwave-assisted synthesis; nanocomposite membranes; sensing; water treatment

1. Introduction

Carbon materials are extremely versatile in terms of their applications, and as such, these materials have high and growing demand worldwide. This demand, in turn, necessitates the development of rapid, cost-friendly, scalable, and safe synthetic methods. These synthetic methods include hydrothermal, solvothermal, ionothermal, chemical vapour deposition (CVD), hard/soft templating, among other approaches [1–4]. The course, however, is changing to the direction of more favourable methods of synthesis because most of the above-mentioned methods possess several drawbacks such as contamination, lengthy reactions, the use of catalysts and toxic chemicals, among others [5]. To achieve sustainable carbon materials with enhanced properties for wide applicability, several modifications and changes need to be carried out and the [6]. The properties allowing this are solely dependent on the reaction conditions such as the precursor concentrations,

temperature, pressure, and reaction time [7]. The uses of these carbon materials have found inclusion in energy, sensing, water treatment, and gas purification.

There has been great interest generated for the development of carbon materials in the recent past. In description of the methods mentioned above, the first being the sol-gel method of synthesis[8]. This method usually involves the preparation of catalysts to serve the carbonisation (thermal treatment) of different precursors for the carbon nanomaterials to be utilised in various applications such as capacitive deionization (desalination) of saline water [9]. As such, many exciting morphologies, and chemical compositions of advanced carbon materials (and their modified counterparts) have been prepared [10].

Solvothermal synthesis employs solvents and high temperatures in the preparation of the carbon materials. In one study, a facile solvothermal carbonization of organic components for the synthesis of $\text{Fe}_3\text{O}_4@\text{C}$ as an anode material for energy applications (lithium ion batteries) was presented [11]. Of the number of challenges faced by solvothermal synthesis include the high demand of energy because of the high temperatures required to satisfy the carbonisation. Hydrothermal synthesis of materials will have the reactants or carbon source dispersed in water prior to the carbonisation under high temperatures and pressures. The benefits of this method include ease of synthesis, ease of composition control, and thus controlling the resulting particle properties such as high surface area, size, shape, and dispersion [12,13]. The advantages of these high temperature and high pressure (HTHP) methods of synthesis, also include thermal and chemical stability, and thus, mitigate the metal dissolution/leaching when metals are used as dopants to carbon [14]. As previously mentioned, one of the caveats of these methods lie in energy demand due to the high reaction temperatures. As such, other methods have been developed to reduce energy demand. These methods are low temperature hydro- or solvothermal approaches.

Low temperature solvothermal synthesis (LHS) is not a really new method because as far back as 2004, Kuang et al (2004) presented the preparation of graphene nanosheets using this approach [15]. Recently, Manohara et al (2019) prepared an aluminium-functionalised carbon-based nanocomposite using LHS for a carbon membrane, successfully removing several environmental insults in water [16]. To further address problems such as complicated procedures/equipment and environmental threats as confronted by HTHP, an even simpler method to prepare graphene nanosheets was presented by Ye et al (2020). This method used involved a one pot reaction without the use of harsh chemicals [17].

As such, this section of the book chapter aims to address the recent developments in the synthetic methods in terms of favourable, rapid, and environmentally friendly approaches for the fabrication and carbon materials. These are especially critical in the development of advanced carbon materials that will be used for energy, water treatment, sensing, and gas separation nanocomposite technologies. Because of the importance of the cost considerations of HTHP processes in this regard, low temperature and high/low-pressure synthetic methods will be interrogated with specific mind to microwave chemistry approaches. The use of sustainable carbon sources such as biomass and other carbon precursors shall also be looked at in this book chapter.

2. Short summary of the development of advanced carbon materials synthesis methods and applications

The development and growth of the solvothermal/hydrothermal methods are directly-related to the creation of nanomaterials [1]. The first study on the solvothermal process can be dated back to the middle of the nineteenth century, when micrometer-to-nanometer-sized quartz particles were used to prepare them [2]. The analysis and introduction of the hydrothermal method in material synthesis, however, lagged between the 1840s and the early 1990s because nanoscale product characterization techniques were not available and to some degree, because knowledge of hydrothermal solution chemistry was inadequate to effectively monitor crystal growth [3]. In the 1990s, hydrothermal methods were resurrected along with the revolution in nanoscale materials and the advent of

high-resolution microscopes from the 1980s [3]. At the same time, significant progress was made in understanding the chemical and physical features of hydrothermal processes, leading to the introduction of the solvothermal method in which organics were introduced as solvents in the manufacture of well-controlled nanomaterials [4]. Because of these outstanding advantages, including low process temperature, reaction efficiency in liquid environments, low energy consumption, and environmental benignity, the hydrothermal/solvothermal processes have achieved considerable success in the twenty-first century in developing nanomaterials with crystallinity, crystal phase, morphology, and size control [5].

Ever since the discovery of fullerene in 1985 by Kroto and co-workers, just one year before the discovery of carbon soot, which was synthesized for the first time in an inert atmosphere from graphite by a resistive heating process [18]. Many new allotropes of carbon were discovered. Among these are carbon nanotubes (CNTs), first discovered in the year 1991 by Iijima [19] and graphene, which is a single layer of carbon atoms arranged in a honey comb lattice, discovered in the year 2004 by Novoselov and workers [20]. Graphene is formed out of flat monolayer of carbon atoms which are densely packed in a honeycomb lattice in 2-dimensions. The carbon atoms are sp^2 hybridized; hence, they form strong intra layer bonding within the hexagonal carbon-rings, which makes graphene one of the strongest materials to be prepared [21]. This results in carbon materials finding a myriad of applications where developments have led to the discovery of a multitude of uses of carbon. Its allotropes and many structures/modified permutations have been applied in water treatment, gas separation, energy, photovoltaics, and the other above-said applications [22,23]. These include the use of carbon nanomaterials in the catalytic detection, removal, and degradation of organic compounds in water through photocatalysis, electrocatalysis, sonocatalysis and all their respective amalgamations [1,24]. Furthermore, these approaches have been included in the development of mixed matrix membranes for water treatment from microfiltration to reverse osmosis applications. In terms of the synthetic and modification methods, major approaches include hydrothermal and solvothermal techniques, with the green/er being among those gaining the recent greater interest. The use of toxic and expensive solvents is losing favour because these are difficult and costly to remove. Among such new approaches are hydrothermal and solid phase thermal methods.

3. Advanced synthetic methods and the modification of carbon materials

In the present section we would like to give a general overview of the different synthetic methods of carbon and carbon-based materials. The important role of the synthesis parameters that were demonstrated to be key factors during the growth process is also outlined. The results summarized in this work are essentially the studies from the last decade

3.1. Arc discharge method

The arc discharge method was first used by Krastchmer and Hoffman in 1990 to synthesize fullerene (C_{60}) [25]. This technique generally involves the use of two high-purity graphite electrodes i.e., anode and cathode. The electrodes are then shortly brought into contact and an arc is struck. Li et al. (2010a) synthesized N-doped multi-layered graphene in the mixing atmosphere of He and NH_3 ; this method involved the use of an electric arc oven that mainly comprises two electrodes and a steel chamber cooled by water [26]. The cathode and anode are both pure graphite rods and the current in the discharge process is maintained at 100-150 A [27]. From the TEM image in Figure 1 it is evident that they obtained large area of high purity multi-layer graphene with the size of 100~200 nm. The graphene as synthesized through this method possessed distinct characteristics and can be utilized in different applications such as electronics, gas sensors, energy storage, water treatment etc [28].

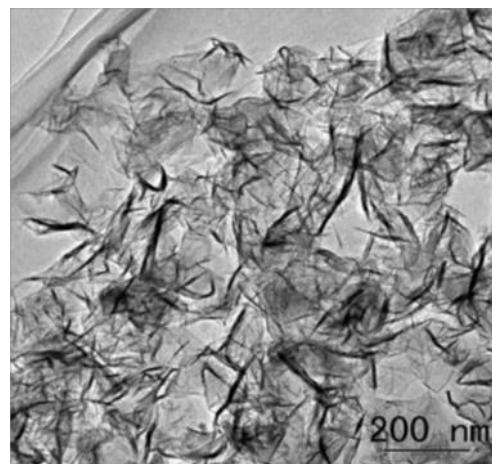


Figure 1. A TEM image of multi-layered graphene produced by arc-discharge method. (Li et al. Reproduced by permission of Elsevier Limited) [29].

In 2015, Sharma and co-workers synthesised multi-walled carbon nanotubes (MWCNTs) using arc discharge method, where an arc was produced in between the electrodes by a D.C. power supply capable to provide 100-200 Amps current voltage range of 20-30 V. The reaction environment was provided by an open vessel containing de-ionized water, carbon nanotubes (CNTs) having lesser number of layers and diameter in the range 15-150 nm was obtained. Arc synthesized MWCT's were treated with 8M Nitric acid and 8M sulfuric acid solution and it was revealed by the X-ray diffraction (XRD) that CNTs synthesised by arc discharge has good crystallinity with less impurity contents. The MWCNTs grown by this method are short, thick and curved as seen in Figure 2 and also that they gave a good yield and these MWCNTs were reported to have been used in pharmaceutical applications [27].

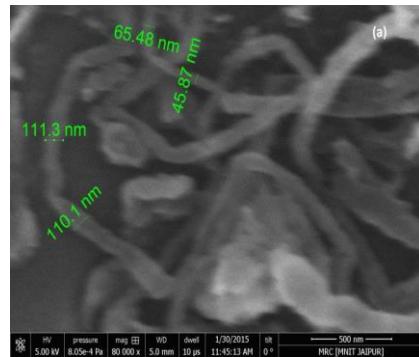


Figure 2. SEM micrograph of MWCNTs synthesized by arc-discharge method. Reproduced with permission from Elsevier Ltd [27].

Subrahmanyam and co-workers in 2009 prepared pristine graphene nanosheets with 2-4 layers by D.C arc discharge of via graphite evaporation. The reaction was carried out in a water-cooled stainless-steel chamber filled with a mixture of H₂ and He in different proportions without the use of catalysts. The discharge current was in the 100-150 A range with a maximum open circuit voltage of 60 V [30].

This method was also used to dope graphene with nitrogen (N-graphene) where relatively smaller layers were obtained as compared to pristine graphene. N-graphene has been applied in different fields but the most favoured being in photocatalysis. Sanchez et al. showed that heteroatom doped graphene give high-performance photocatalysts for the H₂ evolution with an enhanced activity in the visible range [31].

3.2. Other strategic synthetic methods of carbon-based materials

3.2.1. Bottom-up and top-down approaches

In the recent years, great progress has been made in the preparation of carbon and carbon-based materials. Depending on the carbon source used, the synthesis methods can generally be divided into top-down and bottom-up approaches [32]. Recently, Hlongwa and co-workers (2020) synthesised graphene by the reduction Hummer's method, to achieve thin, aggregated, and wrinkled nanosheets. They further used the wet chemical method to synthesise Graphene/Ni-doped LiMnPO₄ (G-LMNP), the results showed outstanding peak current intensity from electrochemical characterisation. This observation suggested an improved electrochemical reversibility; this can be ascribed to the conducting graphene layers, which provided new pathways for electron transfer thus facilitating the redox reaction [33]. The below graph (Figure 3) suggests the suitability of the G-LMNP for high power energy storage applications.

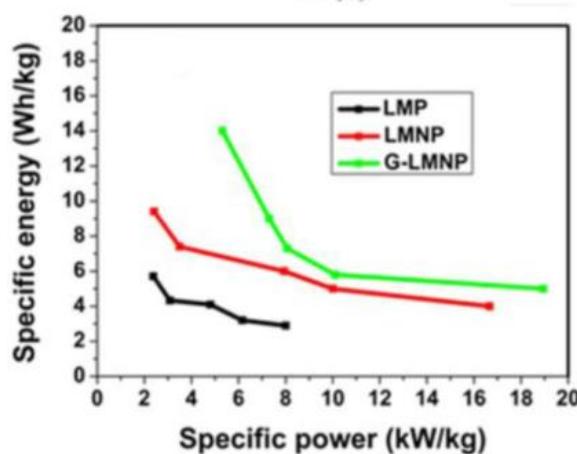


Figure 3. Displays the Ragone plots of AC//LMP, AC//LMNP and AC//GLMNP lithium ion capacitors (Reproduced by permission from Wiley) [33].

3.2.2. Sol-gel approaches for water treatment

In 2014, Mamba et al. employed a simple sol-gel method to prepare gadolinium, nitrogen and sulfur tri-doped titania decorated on oxidised multi-walled carbon nanotubes (MWCNT/Gd,N,S-TiO₂), for the degradation of naphthol blue black (NBB) in water under simulated solar light irradiation [34]. A high degradation efficiency of 95.7% was achieved in the MWCNT/Gd,N,S-TiO₂ nanocomposite, and this improved photocatalytic activity was attributed to the combined effect of improved visible light absorption and charge separation due to the synergistic effect of MWCNTs. Liu et al. synthesised fluorescent carbon quantum dots (CQDs) with quantum yield (QY) of 0.8–1.9% and diameters of less than 2 nm through the chemical oxidation method.

3.2.3. Microwave-assisted synthesis for advanced carbon materials in energy and sensing

In 2013 Jumeri et al. synthesised the ZnFe₂O₄-reduced graphene oxide nano-composite was synthesised using a microwave synthesis technique where 50ml of deionised water was used to dissolve 0.2g of NaOH [34]. They used the method by Kumar et al. to treat the wastewater samples that were evaluated by measuring the degradation of methyl blue (MB). From Figure 4 it is evident that the nanocomposite exhibited excellent adsorption and photodegradation in the first cycle of wastewater treatment although, the performance was slightly reduced in subsequent cycles, the performance still showed promising results for future use, which suggests that magnetic ZnFe₂O₄-graphene nanocomposites have potential as an alternative to existing water purification processes. The understanding of low-dimension carbon material family (CNTs, fullerenes, graphenes, and QCDs) arrived, and indicated extensively remarkable properties for various applications [21].

Hoang et al. synthesised graphene quantum dots (GQDs) by mixing 5 ml of graphene oxide, 10 ml of distilled water and 2 ml of ammonia solution together with a magnetic stirrer and sent into a Teflon container. The container was kept in a protective box and heated in a microwave oven at 700 Watts in 10 minutes [35]. The researchers further investigated performance of GQDs as an effective hole transport material in which ITO/PE-DOT:PSS/P3HT:PCBM:GQDs/Al was fabricated. GQDs assisted to lower potential difference between active layers and electrodes, this increased the short-circuit current density (J_{SC}) from 4.11 mA/cm² (no GQD doping) to 6.31 mA/cm² (2 mg GQD doping) [35,36].

Chae et al (2017) pyrolyzed the AB₂ type lysine utilizing MWAS-induced thermal polyamidation and carbonization and obtained the water-soluble CQDs with QY of 23.3% and the synthesis process took 5 min to be completed. They fabricated the CQDs with chitin nanofibers using microwave assisted hydrothermal method, which took approximately 3 min. The nanocomposite was used for drug sensing based on quenching effect. The fabricated CQDs exhibited high stability and sensitive fluorescent to *D*-penicillamine as evidenced on Figure 4 [37].

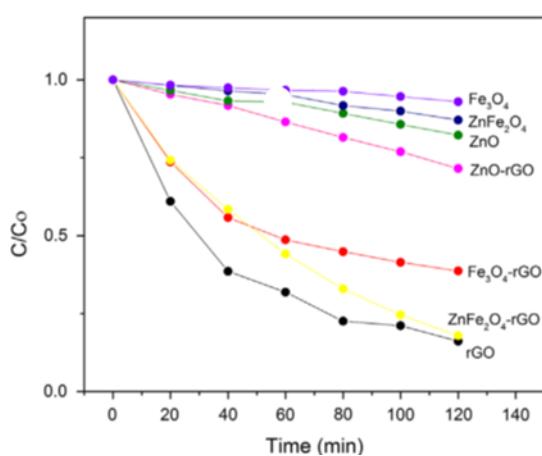


Figure 4. Comparison of photocatalytic degradation of MB by Fe_3O_4 , ZnFe_2O_4 , ZnO , ZnO-rGO , $\text{Fe}_3\text{O}_4\text{-rGO}$, $\text{ZnFe}_2\text{O}_4\text{-rGO}$ and rGO (Reproduced from Chae et al., (2017) under the Creative Commons License <https://creativecommons.org/licenses/by-nc/3.0/> by RSC [37].

Zirconium (Zr)-based metal organic frameworks (MOFs) microwave-assisted synthesis was carried out by Vakili et al., 2018 and the yield and porous properties of UiO-67 were optimized by modifying the modulator quantity (benzoic acid, BenAc and hydrochloric acid, HCl), reaction time and temperature. It was observed that an improvement in modulator quantity improved UiO-67's real surface area and pore volume due to the promotion of linker deficiency; and (ii) the involvement of modulators impaired the numbness of the surface area and pore volume. For synthesizing UiO-67 under microwave irradiation, optimum quantities of BenAc and HCl were calculated as 40 mol equivalent and 185 mol equivalent (to Zr salt), respectively. Microwave methods have encouraged quicker synthesis with a reaction time of 2-2.5 h (at equivalent temperatures of 120 °C and 80 °C for BenAc and HCl, respectively) relative to traditional solvothermal synthesis, which usually takes 24 h. In microwave-assisted synthesis, the thermal influence of the microwave is assumed to lead to the rapid synthesis of UiO-67. The efficiency of reaction mass and space-time yield indicate that the simple but highly effective preparation of Zr-based MOFs was promoted by microwave heating. In addition, UiO-67 MOFs were tested using single component (CO_2 and CH_4) adsorption from various synthesis methods i.e. microwave-assisted and solvothermal methods), showing similar gas uptakes [38]. In closed batch processes, Glover and Mu (2018) synthesized metal-organic frameworks (MOFs), which is not favorable for large scale production. Here, based on a continuous flow tubular reactor fitted with microwave volumetric heating, we report a scalable MOF

synthesis path. Under relatively mild conditions (temperature: 100–110 °C and time: 50 min), the device allowed continuous crystallization of MIL-100 (Fe) with a high space time yield of ~771.6 kg/m³/day. The MIL-100(Fe) was eventually used as a support for the preparation of Cu(I)-modified π complexation adsorbents. The adsorbents exhibited favored CO adsorption over CO₂, and the efficiency of adsorption (CO adsorption capability and CO/CO₂ selectivity) was comparable to or even greater than most Cu(I)-modified π complexation adsorbents previously mentioned [39].

4. Hydrothermal methods of preparation and modification of carbon materials.

As previously mentioned, the disadvantages of HTHP synthesis include the use of toxic reactants and the high costs accrued through the energy intensive synthetic conditions. With this knowledge, LTHP processes have generated great interest due to lower energy demands and more environmentally friendly processes. Thus, the result is wider applicability of the synthetic routes to develop versatile materials for large scale industrial use.

The LTHP approaches for carbon materials synthesis are termed hydrothermal carbonization (HTC). As a method, HTC lowers working temperatures to 150 – 350°C from the ~500°C of HTHP synthesis. The result of this can also be reduced operating pressures because these are generated by the reaction itself (as low as ~1MPa). The synthetic method to result from such low working pressures is then referred to as low temperature and low-pressure hydrothermal synthesis (LTLP). The added advantage of LTHP and LTLP are in that methods are simple, green, provide great added-value, easy to control, and are CO₂-negative [40]. It is the same study carried out just recently, presenting the facile in-situ synthesis of multi-layered graphitic carbon nanosheets while using Cu as both template and catalyst via HTC at temperatures below 300°C. Another advantage as presented by this study was the use of natural biomass, plant leaves of *Parchira aquatica* Aubl as the carbon source.

In another study, Chai et al (2019) used this method to produce graphene quantum dots (GQDs) from sugarcane bagasse through a process called hot water pre-treatment (HWP). This process mostly extracts cellulosic materials without the use of toxic or corrosive media such as organic solvents or alkalis, respectively. In this specific study, low temperatures (170°C) were used to obtain GQDs of small size at 2.26 nm. Several sugars were obtained as value-added by-products in addition to the GQDs which can be used in a number of applications such as solar cells, supercapacitors, the removal and sensing of toxic metal ions in water, and drug delivery, among others [41]. Fluorescent/photoluminescent carbon dots (CDs) have also been synthesized using a similar method for the applications in imaging, sensing, and biolabeling. This was achieved through the hydrothermal treatment of waste wheat straw where it was autoclaved at 250°C in a short duration of ten (10) hours [42]. These methods, however, are still slow even though they are environmentally friendly and cheap. This then requires the development of more rapid methods that also possess the low-cost and green factors to develop carbon materials with the required properties. These methods include, to be more specific, microwave-assisted hydrothermal/solid-state carbonization [43].

4.1. Microwave chemistry for green carbon materials

4.1.1. Hydrothermal carbonization of biomass and other sustainable carbon sources

As mentioned, microwave assisted hydrothermal carbonization is a fast method as opposed to conventional HTHP and LTLP. This is credited to the penetrative nature of microwave radiation where these waves can interact with the internal molecular structure of compatible materials. These materials do also include carbon sources such as sugars and biomass/biowastes, which are polar in nature; and thus, microwave-active [43]. These biowastes may encompass celluloses that can be derived from sugar bagasse and other plant wastes [41]. Other usable material are dairy manure as reusable wastes in the

production of graphene-like lamellar hydrochars as synthesized by Gao et al (2018) [44]. The said study reported on the shortened reaction times as required to prepare these hydrochars at the operating temperatures of 240°C with water as the media. The value-added liquid by-products (light oils) were then extracted using diethylether. Another study reported on a facile and green HTC synthesis of a hydrochar through the carbonization a sugar (glucose). This reaction took place at 200°C in deionized water over varied reaction times between 5 – 60 minutes, resulting in largely spherical microparticles after 45 minutes. These reaction times are a great improvement from the conventional heating methods where this product would be obtained after hours and hours of reaction periods. The envisaged applications of such materials include electrodes, adsorbents, and catalyst supports, among others [45].

In another interesting study, Adolfsson and co-workers presented an HTC carbonization and post-modification of solid phase polypropylene in its upcycling as a waste material. The method, as described, was one of the few in literature designed to repurpose waste plastics via microwave-assisted HTC. Furthermore, this method yielded high carbonization in water while it was incomplete in air. In addition to this, the successful modification with SiC was also carried at relatively low temperatures. These achievements are credited to the in-vessel and self-generated pressure forming favourable subcritical conditions in water [46].

4.1.2. Combinatorial MWA HTC and MWA exfoliation of GO

Several exfoliation methods have been developed recently including combinatorial approaches. Some of these would be the synthesis of GO using conventional methods followed by MWA exfoliation. To this effect, Voiry et al (2016) reported on 100% yields of highly ordered, single-layered rGO from a MWA-HTC [47]. Herein, the approach was a simple one in that the GO obtained using the Modified Hummers' method, was coagulated by a stream of a CaCl_2 solution into the reaction vessel in the presence of argon. Short bursts (1 – 2s) of MW irradiation were then introduced, leading to the reduction of GO; the formation and annealing of rGO because of the high in-situ temperatures (arcing) generated. The intended application of this annealed rGO was towards oxygen evolution reactions, however, we have already established earlier in this chapter the multitude of applications of such advanced carbon materials. Thermal annealing using microwave irradiation as a reduction approach has been reviewed by Lyu et al (2018) as requiring temperature bursts ca. 2000°C to occur [48]. Jakhar et al (2020) suggested in his review that the microwave-thermal annealing method provides superior exfoliation of GO than MWA HTC [49].

Another study recently presented a two-step preparation of N- and B-doped C-composites prepared from fir bark with ammonium tetraborate as the dopant source. The result of the doping yielded greatly changed surface morphologies and consequently, high surface areas ($955 \text{ m}^2 \cdot \text{g}^{-1}$) and enhanced capacitance retention (above 90%). These properties can be credited to the favourable synthetic method which resulted in the synergistic improvement of the said properties [50].

In another study, the microwave plasma approach to produce large-scale N-doped graphene (N-G) from simple ammonia and ethanol as the precursors. The advantage of this method was that it required no toxic solvents; it is a one-step approach, and as such, it is both cost and environmentally friendly. Furthermore, the reaction takes place at ambient conditions and results in a product possessing high electrical conductivities due to the high purity of the N-G prepared [5]. However, further developments have recently shown that the use of susceptors (supports possessing higher microwave conductivities than the sample material) can significantly enhance the exfoliation as compared to the above studies [49]. However, at this point in science, the superiority of MWA reduction and annealing of GO seems to largely apply to the exfoliation and inclusion of heteroatoms into the aromatic structure of graphenes. Thus, this development does not negate

the importance of MWA HTC in terms of the synthesis and modification of GO, rGO, and hydrochars.

5. Modified carbon materials in nanocomposites and membranes for water treatment and gas purification

5.1. Advanced carbon materials from sustainable/biomass for membrane nanotechnology in water treatment

Water is a scarce and precious resource the world over, and as such, it is critical to develop methods and materials to harness, protect, and recover it however possible. Nevertheless, climate change and environmental (air/water/soil) pollution remain an unforgiving threat to water sustainability and air quality. Current and conventional methods of addressing these challenges are not sufficient. This is where carbon-based membrane nanotechnology has become much more important in the recent years [43,45]. With this knowledge, sustainable, fast, and green methods are needed to this effect to develop suitable membranes and membrane materials. Microwave-assisted carbonization towards the synthesis of these materials are a greatly promising and exciting technologies [51].

Other than carbonization, MWAS was recently used by Ashfaq et al (2020) to hydrothermally form a polyacrylic acid (PAA) film on a GO-modified commercial TFC membrane. This reaction was also achieved in short periods of 40s, with the result being an antibiofouling and anti-scaling membrane against *H. aquamarina* (97%) and metal salts (CaCl₂ and Na₂SO₄), respectively. The membrane hydrophilicity and salt rejections were also enhanced with a decrease in permeability due to the grafting which narrowed the pore size [52]. An alternative to this method, however, would be conduct the graft polymerization of the AA to GO in-situ with the RO membrane within the MW reactor cell. With the control of parameters such as the monomer concentration and GO loading, a membrane with enhanced bioactive/antibiofouling is attainable due to the increased availability of crosslinked GO towards the active layer.

Kovtun et al presented a scalable microwave-assisted synthesis (MWAS) method of attaching layered GO to waste polysulfone (PSU) plastics and prepared a mixed matrix membrane (MMM) from the resulting PSU-GO-MW nanocomposite. The PSU-GO synthesis method was a simple (100°C), fast (45 min), green, and cheap one as no solvents were required; and only an ethanol-water solution was used for washing the product. For comparison, the same product was prepared by conventional oven heating at 200°C (PSU-GO-OV). Chemical analysis by X-ray photoelectron spectroscopy (XPS) indicated a certain degree of collapse to the molecular structure of the GO nanosheets. The PSU-GO-MW permutation, as such, presented higher Rhodamine B (RhB) and ofloxacin adsorption capacities than both the PSU-GO-OV and pristine PES membranes [53]. This indicates that the microwave chemistry approaches for advanced carbon materials yield MMMs with superior properties as compared to conventional heating.

The important discovery of MWAS-HTC has led to critical contributions towards the development of environmentally friendly synthesis methods. The research on the preparation of hydrochars has resulted in significant interest within the research fraternity of water treatment and membrane nanotechnology. One of such studies to this effect was recently carried out by Hossain et al (2020) [54]. In this work, rice husk, one of the waste biomass that continue to generate increasing research interest, was used to prepare a hydrochar as a sustainable which can be included in the fabrication of MMMs for water treatment. The authors synthesized this biochar using a temperature of 70°C over a reaction period of 20 minutes at 70 bars working pressure. As such, these reaction parameters improved adsorption capacities and catalytic efficiencies.

5.2. MWAS of carbon-based nanocomposites for gas purification

Coal gas coming directly from the bench was historically a noxious chemical soup and it was necessary to eliminate the most deleterious fractions, to increase the

consistency of the gas, to avoid exposure to machinery or premises [55]. As such, the elimination of hydrogen sulfide was assigned the highest priority level at the gas works. To remove the sulfuret of hydrogen, known as the purifier, there was a special building [56]. The purifier, if the retort-bench itself is not used, was arguably the most significant facility in the gas-works [57]. Originally, purifiers were simple lime-water containers, also referred to as lime cream or milk, where the raw gas from the retort bench was bubbled out to extract hydrogen sulfide [58]. This initial purification method was known as the process of "wet lime". One of the first real wet lime" was the lime residue left over from the "toxic wastes" process, a substance called blue billy" [59].

Recently, researchers have begun to work on redesigning synthetic methods using MW chemistry for many smart materials, have been found to be quite useful in the fields of power generation, biomaterials, nanoelectronics, and nanomedicine, among others. Researchers, scientists, and industrialists are following environmentally benign synthetic routes for the fabrication of desired goods in the age of new science and technology. Of the twelve (12) principles of green chemistry, two major criteria for MW-assisted synthetic chemistry are choice of green solvents and energy efficiency. In many systems, MW heating is seen as a more effective way to manage heating because it is less energy-intensive than traditional methods [60]. The 'Green Chemistry Monograph of the American Chemical Society' proposed the use of catalysts or MW irradiation to decrease the energy requirements for the synthesis process [61].

Membrane nanotechnology is emerging to be a critical approach in not only improving selectivity and affordability of gas sensing, fuel cells, but also gas purification [62]. Membrane nanotechnology is critical in this regard to assist in the efforts towards the mitigation of the effects of air pollution (industrial greenhouse emissions), global warming, and climate change. Carbon-based nanocomposite membranes have incorporated GO, carbon nanotubes (CNTs), and graphenes as nanofillers towards gas purification applications such as separating mixtures of CO_2/CH_4 , and the difficult removal of H_2S from biogas [63]. Furthermore, they can be used in the separation/capture/adsorption of other gases mixtures of CO_2/H_2 , H_2/CH_4 , and N_2/H_2 , among others as reviewed by Sazali (2020) [64]. In this work, the author favours the use of carbon membranes over their polymeric counterparts, citing limitations including operating temperatures, poor selectivity in terms of solubility and diffusivity for H_2 and CO_2 gases. As such, these challenges influence the design, improvement, and fabrication of such membranes by modifying them with carbon materials.

There are further synthetic methods that have been developed to this effect regarding the green hydrothermal approaches of these carbon materials towards the development of these nanocomposite membranes. One work demonstrated the nanoindentation and the further modification of vertical array C nanotubes (VACNT) via the in-situ polymerization of aniline. The facile method yielded nanocomposite membrane with a seamless deposition of polyaniline (PANI) onto the said nanotubes, achieving a nanocomposite with enhanced gas transport properties [65]. Figure 4 illustrates the synthesis route and the transmission electron microscopy (TEM) images for the resulting nanocomposite as presented in Figure 5.

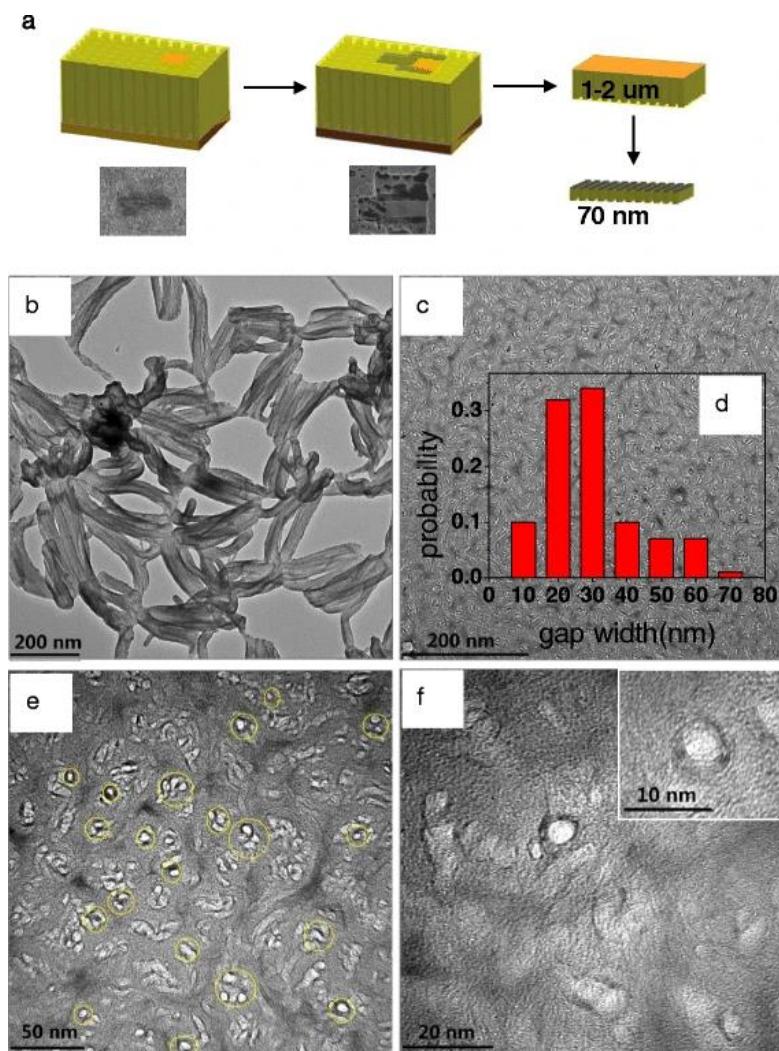


Figure 5. (a) Focused ion beam (FIB) sample preparation (nanoindentation) and TEM micrographs, (b) Cross sectional TEM images of VACNT. (c), (e), (f) TEM images of the VACNTs/PANI nano-composite membrane cross-section at different resolutions. (d) Histogram of the gap width distribution between the nanotubes (insert on (c)). Reproduced from Ding et al (2015) [65] under the Creative Commons Licence BY 4.0. Springer Nature. Copyright © 2015, Ding et al.

6. Current and future solvothermal synthetic methods for advanced carbon materials in gas purification technologies

In the envisaged satisfaction of the rising global energy demands and to simultaneously combat the environmental impacts such as global greenhouse gas emissions, it is critical to search for potential energy alternatives [66]. Natural gas is one of such vital components of the world's supply of energy that has fulfilled the previously mentioned requirements. Natural gas is a cleaner energy source compared to other fossil-based energy sources owing to its low emissions [67]. However, natural gas contains acidic gases (including CO₂, N₂, Hg, He, and H₂S), which may cause equipment corrosion and environmental damage [68]. To date, Kazmi et al., 2019, researched on amine-based absorption techniques that have been used to remove acidic gases from natural gas to reach regulated concentration limits. However, a tremendous amount of heating is required to regenerate amine-based solvents, which remains a major issue with traditional absorption-based acid gas removal units [69].

Twenty years after the first production of solvothermal reactions, it seems important to trace future developments, taking into account their potential and the various economic constraints, through the current research activities [70]. Solvothermal reactions have been

used primarily in the processing of micro- or nanoparticles of various morphologies over the last twenty (20) years. Such a presentation would only concentrate on the potential of solvothermal reactions in material synthesis, considering the importance of disposing of new materials towards the production of either fundamental science or industrial applications [71]. Researchers have investigated future materials that will be prepared by solvothermal methods, an example of this was illustrated in the work by Pahinkar and Garimella (2018) [72]. The authors of the said work discovered a novel TSA-based gas separation cycle using a microchannel monolith coated along the inner walls of each microchannel with a hollow polymer-adsorbent matrix was investigated. By passing impure feed gas through the microchannels, CO_2 is eliminated from CH_4 , followed by a concurrent flow through the same microchannels of desorbing hot liquid, cooling liquid, and purging gas. Owing to the intimate interaction with the transport fluid and the adsorbent sheet, this configuration is supposed to improve the heat and mass transfer to the adsorbent, and thus decrease the total device size because of the flow into the same microchannels of the operating and coupling fluids. Computational models are built in this part one of a two-part analysis to study the related fluid dynamics, heat transfer and mass transfer in each phase. Parametric experiments are done to determine the optimal geometry of the microchannel and components for adsorbent and heat transfer fluid (HTF). In contrast with bed-based designs, the process is supposed to purify up to two orders of magnitude higher gas throughput. A detailed process efficiency chart and optimization of energy needs for the process are addressed in the accompanying report.

Zhu et al., 2019 studied the environmental purification and engineering because of the importance of effective yield of reactive-oxygen species (ROS). In their study, the perfected p-conjugated g-C₃N₄ (PNa-g-C₃N₄) photocatalysts were constructed at the vacancy structure of tri-s-triazine polymer for ROS evolution and HCHO and NO removal by co-ordination between 3p orbitals of Na and N 2p lone electron. The structured p-conjugated structure increases the ability to absorb visible light, enriches active O₂ activation sites, and promotes the directional charge transfer from N 2p of C₃-N to Na and C. Superior operations, including the evolution of O₂ (35 mmol.L⁻¹) and H₂O₂ (517 mmol.L⁻¹) over the photocatalyst PNa-g-C₃N₄, have therefore been accomplished. Consequently, PNa-g-C₃N₄ photocatalysts display high performance removal efficiency of NO (53% over 6 min contact time) and HCHO (almost 100% over 55 min). The findings may provide a promising strategy for developing an effective photocatalytic device to produce ROS for environmental purification [73]. Wiheeb et al (2013) investigated hydrogen sulfide (H₂S). Hydrogen sulfide includes biogas, natural gas, and synthesis gas from coal gasification, which is extremely poisonous to humans and corrosive to devices. Prior to utilization, H₂S must be separated from fuel gases. The goal of Wiheeb et al., 2013 was to equate the use of commercial and alkaline impregnated activated carbons to the adsorption of H₂S. The commercial and alkaline impregnated activated carbons were tested for adsorption of H₂S at 30 °C and 550 °C by the temperature program. Alkaline activated carbons adsorbed H₂S much higher than commercial activated carbon at elevated adsorption temperatures (3-29 times higher depending on the process of modification). In addition, the concentration of H₂S in the outlet gas after the KOH and Na₂CO₃ impregnated activated carbons were treated was less than 30 ppm, which was safe for mechanical and power engine use [74].

Solvothermal carbonization (STC), as previously mentioned, require the use of solvents during the carbonization of carbon precursors. The solvents commonly used in this approach are usually ionic (and toxic) in nature, with some examples being *p*-toluene sulfonic acid, *o*-dichlorobenzene, and 1,2,4,5-tetraaminobenzene, dimethylformamide (DMF), among others [17,75]. In one study, using DMF as solvent in a solvothermal method, a graphene/metal-organic framework was prepared and it yielded high adsorption capacities for nitrogen gas and benzene [76]. Furthermore, this approach is will often require the use of high reaction temperatures, another unwanted reaction parameter as it contributes to high costs. However, there has been several developments to mitigate or eradicate the use of high temperatures and toxic solvents. These solvents can also be

expensive and as such, their negative impacts on the environment need to be reduced. Nevertheless, many works have reported on the use of ethanol as a green solvent, and the carbon source being biowastes [77]. An example of such an investigation was conducted by Jin et al (2017). In this work, the authors synthesized a magnetic nanocomposite material ($\text{Fe}_3\text{O}_4/\text{C}$) from keratin-rich chicken feathers as beginning biowaste in the presence of ethanol [78].

Habartová et al., 2013 worked on chloroform (CHCl_3) and water vapor gas-phase treatments that have been used to extract metal impurities (MIs) from as-prepared multi-walled carbon nanotubes (AP-MWCNTs), which are a non-destructive means of processing highly pure CNTs with exceptionally low MI content and CNT property preservation. The MIs in the AP-MWCNTs decreased dramatically to 12 ppm after purification using CHCl_3 , reflecting a purification efficiency of 99.8%. This method of purification, applicable with various AP-MWCNTs with a high content and different MI compositions, is more efficient than acid-based liquid-phase purification and does not affect the structure and morphology of the CNT. A mixture of factors is responsible for this mild purification. Chlorine radicals and hydrochloric acid from the thermal decomposition of CHCl_3 react to form metal chlorides that sublime at high temperatures with MIs encased by graphitic carbon layers. During the forming of the metal chlorides, hydrogen, oxygen, and water vapor create etch graphitic carbon layers and lead to the formation of new pores and cracks that provide quick reaction and diffusion pathways. The MWCNT surface becomes lightly covered with chlorine or chlorinated carbon during metal purification and is extracted using water vapor from the surface post-treatment [79].

Choudhury et al., 2017 investigated one of the pollutants to be nitric oxide (NO) from anthropogenic pollution, which creates multiple environmental issues. An alternative technology for reducing NO is provided by microbial fuel cells (MFCs) with a gas diffusion cathode. In this work, pure NO was confirmed as the single electron acceptor of gas diffusion cathode (NO-MFC) MFCs. The overall power density of the NO-MFCs was $489 \pm 50 \text{ mW/m}^2$. The columbic performance improved from $23.2\% \pm 4.3\%$ (Air-MFCs) to $55.7\% \pm 4.6\%$ (NO-MFCs) relative to MFCs using O_2 in air as an electron acceptor (Air-MFCs). The rate of NO elimination was $12.33 \pm 0.14 \text{ mg/L/h}$ and the principal reduction product was N_2 . The dominant route of NO conversion in NO-MFCs, including abiotic electrochemical reduction and microbial denitrification process, was cathode reduction. In the anodic microbial culture, the prevalent genera modified from exoelectrogenic bacteria in Air-MFCs to denitrifying bacteria in NO-MFCs and effected the power generation [73].

Because of the problems associated with the release of CO_2 to the environment, Liu et al (2017) presented a solvothermal method for the preparation of boron and nitrogen-doped 3D graphene aerogels for carbon capture. This synthesis was carried out at working temperatures of 180°C over a reaction time of 6h [80].

7. Solvothermal and hydrothermal approaches to synthesis of carbon nanodots for multiple applications

7.1. The sustainable synthesis of carbon nanodots

This section further discusses carbon nanodots and their synthetic routes as per initially introduced in the previous sections. This is because of their rising importance over the years due to their versatility. Carbon nanodots (CDs) refer to a class of zero-dimension carbon nanoparticles such as carbon quantum dots (CQDs), graphene quantum dots (GQDs), carbonized polymer dots (CPDs), carbonized polymer dots (CPDs) and various carbogenic nanodots (CNDs) [81,82]. Their carbon cores is usually sp^2 hybridized with different functional groups such as amino group, epoxy, ether, carbonyl, aldehyde, hydroxyl, and carboxylic acid functional groups on the surface [81,83]. They are quasi-spherical, amorphous to crystalline in nature with size less than 10 nm as shown in Figure 5 [81]. These possess unique optical properties (photoluminescence) and differing physico-chemical properties [81]. These nanomaterials and their nanocomposites are

characterized by facile synthetic methods, water solubility, low cost, biocompatibility, low toxicity, and chemical inertness. Furthermore, CDs are abundant because of the use of inexpensive precursors resulting in sustainable synthesis [84,85]. As a direct result of this, materials have found widespread applications in anti-counterfeiting, sensing, bioimaging, optoelectronic, energy-related fields, and even wastewater treatment [84–86].

Various synthesis methods have been developed for fabrication of CDs where these include electrochemical exfoliation of a graphitic source [82]; the incomplete combustion of carbon soot [84]; the carbonization of polymerized resoles on silica spheres [87]; the thermal oxidation of suitable molecular precursors [88]; and also the dehydration of carbohydrates [89]. Most of these methods often require complex synthetic controls which may cause adverse degradation of the required CD properties such as poor crystallinity, introduction of impurities, extensive post-treatments techniques, complicated purification and separation procedures [90]. Previous reviews have detailed synthesis strategies and different applications of CDs in bioanalysis, bioimaging, and energy conversion. Such collated knowledge greatly improved our level of understanding and promoted the development of CDs in works that followed [90]. Nevertheless, to obtain CDs with high purity and better physico-chemical properties is still faces high challenges due to the complicated purification and separation procedures [90].

7.2. *Synthesis of CDs through solvothermal synthesis*

Commonly, the synthesis method is categorized as “top-down” and “bottom-up” as per Figure 6. In the top-down approach, large carbon structures are converted into quantum-sized and fluorescent carbon quantum dots [85]. In the bottom-up method, the CDs are obtained from carbonizing small molecules as precursors [85,91]. These include electrochemical exfoliation of a graphitic source [82], incomplete combustion of carbon soot [84], carbonizing polymerized resoles on silica spheres [87], thermal oxidation of suitable molecular precursors [88], and the dehydration of carbohydrates as previously noted [89]. Studies of these synthetic methods indicate that the obtained CD structure and compositions is closely related to the synthetic methods and the nature of carbon sources or the molecular precursors [83].

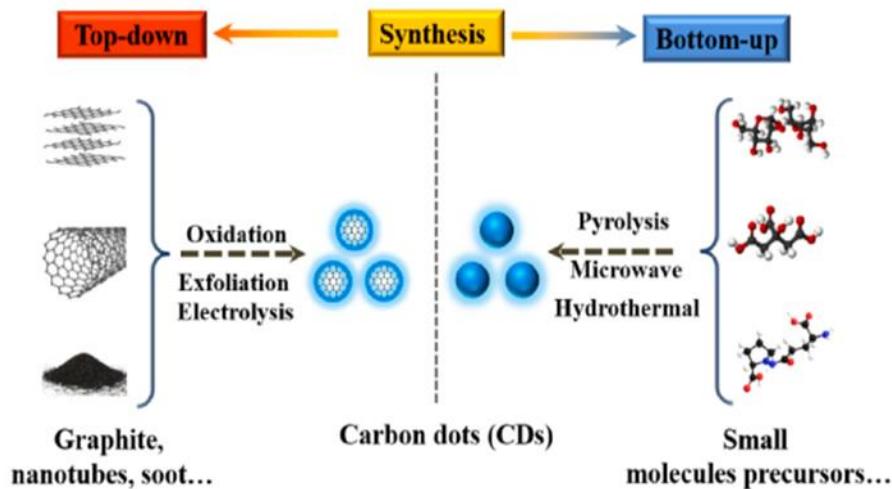


Figure 6. Different Synthesis methods of CDs courtesy of Long et al [86].

In the past few years, there have been several studies and reviews on the development of facile synthetic methods that generate enhanced physicochemical properties and surface functionalization for various applications [85]. From these methods hydrothermal/solvothermal synthesis have continued to gain popularity [90]. These methods involve the use of inexpensive precursors, simple synthetic processes, environmentally friendly approaches, large instruments, and non-toxic routes [85]. Since most of the

prepared CD-based materials already possess a mass of hydrophilic functional groups, no additional modification treatment is required to impart hydrophilic properties and reactivity to the CDs [85]. An example of this was presented by Zhu *et al.* [92] where they developed a simple microwave-assisted method to synthesize new types of CDs. In that work, a carbohydrate was used as a carbon source and polyethylene glycol (PEG200) employed as both solvent and coating agent. The reaction gradually changed from colorless to dark brown solution when under 500W microwave irradiation for a duration ranging 2~10min. The product was diluted with water to attain fluorescent CDs. The obtained particle size and the quantum yields of fluorescent CDs were observed to depend on the reaction time [92].

Recent studies indicate that short external heat pulses can contribute to the chemical oxidation and carbonization of organics and turn them into CDs. Microwaves with frequencies ranging from 300 MHz to 300 GHz provide sufficient energy to break the chemical bonds in the raw materials [85]. The microwave-assisted hydrothermal/solvothermal synthesis provide uniform heating effectively reducing the reaction time, so that the particle size distribution of CDs is small. Additionally, MWAS does not require hydrothermal reactor for the sealing and reaction of the organic precursor at high pressure, high temperatures, and long reaction times compared with conventional synthesis [93].

7.3. Carbon nanodots composites synthesis through hydrothermal synthesis

Although CDs have various advantages, they also suffer from problems associated with aggregation of pristine CDs in solid state. This often leads to property change such as luminescence quenching, surface defects, and decreasing surface areas [81]. To mitigate these unwanted phenomena, and to further optimize their optical and electrical properties, various solid supports such as polymer matrices, inorganic salts and porous materials (PMs), etc., have been used to support CDs [94,95]. To prepare such nanocomposites, solvothermal and hydrothermal synthesis techniques are in the forefront in establishing various modified CDs. Typically, for CD nanocomposites, two main synthetic approaches have been proposed, i.e., a one-step method and a two-step method [83].

The one-step method means the simultaneous generation of the CDs into the supporting matrix in the same reaction is carried out. The two-step method means that the CDs are first prepared using the top-down/down-top route and then embedded in the host matrices via chemical or physical methods [83]. A good example of the latter was demonstrated by Ming *et al* [90] where a novel photocatalyst (TiO₂/CD) by combining CD with TiO₂ through an easy hydrothermal method. The obtained TiO₂/CDs exhibited excellent visible-light photocatalytic activity. The CDs were initially fabricated through electrochemical exfoliation of a graphitic source as follows; dropwise addition (1 mL min⁻¹) of Ti-[OCH(CH₃)₂]₄ (1 mL, dissolved in absolute alcohol with a ratio of 1:19) into CDs solution (55 mL, 0.1 mg mL⁻¹). After continuous stirring of the mixture for 4 h, a colloidal solution of TiO₂/CDs nanohybrids then formed. The resulting solution was sealed into a Teflon-lined autoclave, followed by hydrothermal treatment at 180 °C for 48 h. The obtained gray solid TiO₂/CDs was washed with water and ethanol, and dried in a vacuum oven at 80 °C.

The direct in situ incorporation of CDs into the host matrix is somewhat more difficult with very few literature examples [83]. This is mostly due to difficulties in controlling the simultaneous generation of CDs in one system and the requirement of a strong driving force to co-assemble the guest CDs into the host matrix [96]. Nevertheless, Wang *et al* [97] recently synthesized luminescent CDs@zeolite and CDs@AlPO nanocomposites through direct in-situ incorporation of luminescent CDs into the host matrix using the solvothermal approach. In this method, triethylamine was utilized as the template and triethylene glycol as the solvent to form uniformly embedded CDs (\approx 3.7 nm) in AlPO-5 crystals as shown in Figure 7.

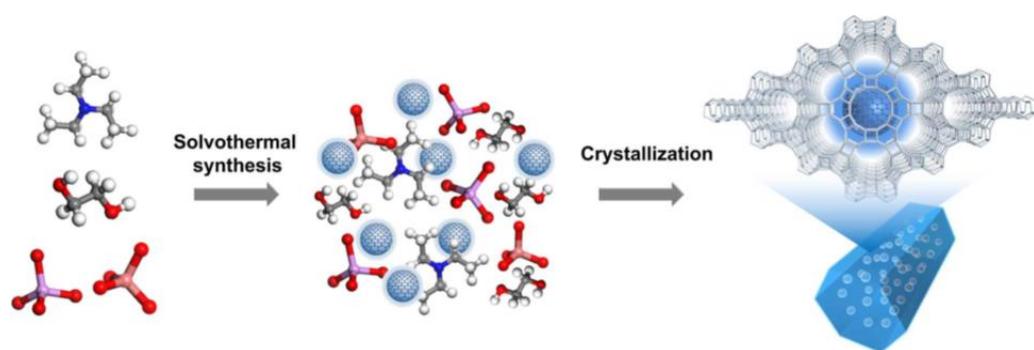


Figure 7. Schematic illustration of one-step synthesis. a) CDs@AlPO-5 composite via solvothermal synthesis. Reproduced from Zhang *et al* with permission from Wiley & Sons [81].

The successful one-step synthesis of CDs@zeolite composites was credited to the facile solvothermal synthetic method. The end-result was the highly dispersed CDs due to the well-confined nanospaces and high stability of zeolites. In this case, the organic species (i.e., templates and solvents) used in the synthesis of zeolites provide the source materials for CDs and the simultaneous formation of CDs and zeolites can further be achieved by varying certain synthetic conditions [83]. The use of one-step reaction processes not only simplify the preparation procedure compared with the multistep preparation method, the prepared CDs also indicate enhanced fluorescence, crystallinity, and uniform size [98]. Different CDs with varying properties can be achieved by choosing different solvents (carbon source) [98].

So far, a variety of PMs (zeolites, MOFs, mesoporous materials, and other disordered porous nano-carries) have been used as host matrix for CDs [81]. Given the diversity and inherent features of PMs and CDs, and the capability of solvothermal and hydrothermal synthesis. A synergistic approach using a mixed synthesis approach of solvothermal synthesis is therefore possible [81]. In another work, Liu *et al* [99] used a multi-step synthetic approach to synthesize CD-zeolite by carbonizing CDs in-situ, encapsulating the CDs into zeolite crystals produced by hydrothermal crystallization (Figure 8). This strategy allowed CDs to be tightly confined in the interrupted zeolite framework and form abundant H-bonds. This resulted in the restricted vibration/rotation of functional groups of CDs, and thus protected the triplet excitations. The produced composite indicated unique thermally activated delayed fluorescence (TADF) emissions. In contrast, no TADF was observed for pure CDs isolated from the synthetic mother liquid [81].

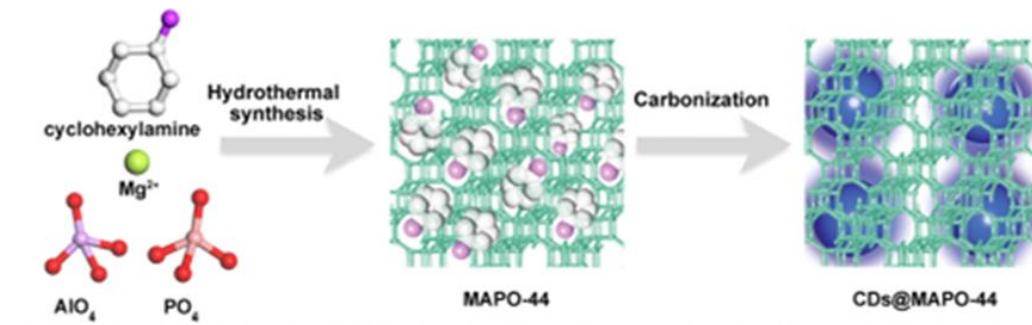


Figure 8. The multi-step synthetic route for the preparation of CDs@MAPO-44 where the final product shows CDs confined in MAPO-44 (CHA) via the carbonization of the organic template. Reproduced from Zhang *et al* with permission from Wiley & Sons [81].

Pyrolyzing organic solvents or guest molecules confined in MOFs (CDs@MOF nanocomposites) can also be feasibly prepared. Unlike zeolites, the carbonization of MOFs is usually conducted below 200°C due to their inferior thermal stability. In addition, the one-step synthetic method used for synthesis of CDs@zeolites is generally not possible. This is

because the precursors of CDs influence the crystallization of MOFs and the synthetic temperatures required for the preparation of MOFs is also much lower than the carbonization temperature of CDs [81,100]. This means that the most suitable synthetic routes for carbon-modified MOFs are the LTHP or LTLP approaches as discussed in subsection 4.1.

8. Conclusions.

The importance of the synthetic methods as applied in the preparation of advanced carbon materials was discussed in this book chapter. These synthesis methods were disseminated in terms of their developments in terms of the current developments from conventional to sustainable materials and environmentally friendly hydrothermal and solvothermal carbonization approaches. As has been discussed, the use of green solvents and sustainable carbon sources has drawn great attention. Water and ethanol are favored as green solvents where solvents, biomass or biowastes have proven to be sustainable carbon-negative materials as carbon precursors. Special attention was also paid to the use of microwave-assisted hydrothermal and solvothermal carbonization (MWAS HTC and STC). The studies, as discussed, show that the latter methods can be applied during the synthesis of advanced carbon materials, yielding different morphologies and physico-chemical properties. These properties allow for the (future) application of these materials in the fabrication of nanocomposites in energy, sensing, photocatalysis, electrocatalysis, and water treatment. These can be further be indiscriminately subdivided to fuel cells, photovoltaics, the degradation/adsorption of in-/organic environmental insults; and in membrane nanotechnology for gas separation/storage/adsorption; and water purification.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used “Conceptualization, L.N., N.R., software, L.N., H.O.O.; validation, L.N., M.M.M., and B.B.M.; resources, B.B.M.; writing—original draft preparation, L.N., N.R., H.O.O., M.D.; writing—review and editing, L.N., M.M.M.; visualization, L.N.; project administration, L.N., M.D., M.M.M., B.B.M.; All authors have read and agreed to the published version of the manuscript.

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