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Coal-Based Carbon Nanomaterials: En Route to Clean Coal Conversion toward Net Zero CO_2

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As the world is committed to reach carbon peak by 2030 and net zero by 2050, the use of coal as an energy source is facing unprecedented challenges. According to the International Energy Agency (IEA), global annual coal demand is estimated to drop from more than 5640 million tonnes of coal equivalent (Mtce) in 2021 to 540 Mtce in 2050 under the net zero emission scenario, mostly being replaced by renewable energy such as solar and wind. Therefore, the coal industry is vigorously seeking alternative applications to keep it thriving, and nanotechnology can be one of the contributors. Herein, the challenges to coal-based carbon nanomaterials syntheses are outlined, along with a path toward commercialization. Coal-based carbon nanomaterials can be promising contributors to the concept of clean coal conversion, initiating its migration from an energy source to a high-value-added carbon source.

1. Introduction

Coal has played an important role in human progress since the Industrial Revolution in 1700s through its combustion to provide energy. Coal continues to be the primary energy source for some of the world's largest economies today.[1] Coal was first used for heating, fuel, and metallurgy, and later it was mainly used for generating electricity and producing chemicals.[2] The dominant role of coal as a primary energy source was first challenged by oil in the 1970s because of the mass production of automobiles. The trend was further enhanced in the past few decades by the development of oil and gas technologies, especially the boom of large reserves of unconventional oil and gas. As the world proceeds to combat climate change in the 21st century, most developed countries are starting to further decrease the share of coal in their energy portfolios in order to minimize greenhouse gas emissions.[3] In 2015, the Paris Agreement set the goal of achieving net-zero CO_2 emissions by 2050, hence more countries have sought an array of domestic strategies.[4] Coal is often the first hydrocarbon to be slated for reduced use due to its low H/C ratio compared with oil and gas, which means more CO_2 emissions for the same amount of energy generation. According to the International Energy Agency (IEA), in 2021, the global coal reserves reached 1075 billion tonnes while the global coal demand is estimated to drop from more than 5640 million tonnes of coal equivalent (Mtce) in 2021 to 540 Mtce in 2050.[5] The question then rightly arises, what might be done with the enormous coal reserves and the jobs and infrastructure in that industry? One viable and well-accepted concept is to find a way to switch the role of coal from an energy source to a feedstock for producing gases, liquid chemicals, and coke. More importantly, it is imperative to develop high value-added products and alternative applications for coal if that industry is to remain.

The structure of coal is complex. Its composition and properties vary with different coalification levels such as anthracite, bituminous, and lignite, and from different locations.[6] With continuous effort and study performed by researchers, several structure models have been proposed in the past few decades.[7] It is well established that coal contains nanoscale aromatic crystalline carbon domains connected by bridging bonds like aliphatic chains or ether bonds. Unlike coal's other allotropes such as graphite, graphene, and fullerenes, which have large crystalline sp^2-carbon domains that endow them with superior electrical, thermal, and mechanical properties, these properties from coal research were rarely explored due to coal's complex composition and small crystalline domains. Hence, coal's applications were mainly focused on power generation, heating, metallurgy, and chemical processing. In recent years, clean and efficient conversion of coal into high value-added products became desirable. The formation of coal-derived carbon nanomaterials has been the topic of increased recent research efforts. This includes the synthesis of carbon dots (CDs),[8] graphene,[9] fullerenes,[10]

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Figure 1. Coal-based carbon nanomaterials and their applications.

nanodiamonds (NDs),[11] carbon nanotubes (CNTs),[12] carbon nanospheres,[13] and more. These carbon nanomaterials have been used in batteries, solar cells, capacitors, illumination devices, displays, bioimaging systems, drug delivery, anticounterfeiting, and composites, among others,[14,15] as shown in **Figure 1**.

In the following sections, we will briefly discuss coal-based carbon nanomaterials in three parts, categorized by the technology readiness level (TRL).[16] First, we introduce the progress of coal-based CDs, with TRL 7–8 in certain applications. Second, flash graphene (FG) from coal with TRL 7 is presented. Finally, the development of other coal-based nanomaterials with TRL 1–3 are discussed, including fullerenes, NDs, and CNTs. Perspectives on the way forward for these coal-based carbon nanomaterials are also provided in each section.

2. Coal-Based CDs

CD is a general term for carbon nanoparticles with photoluminescent characteristics, including graphene quantum dots (GQDs), carbon quantum dots (CQDs), carbon nanodots (CNDs), and polymer dots (PDs). Compared with other carbon nanomaterials, CDs have tunable photoluminescence emissions, good biocompatibility, unique photoelectron transfer properties, abundant surface functional groups that are promising for many applications like permanent and unique identifying tags for anticounterfeiting, bioimaging systems, photocatalysis, ion detection, illumination devices, displays, and more.

The synthesis methods and applications of CDs from various carbon sources, including coal, have been extensively reviewed in recent years.[17] In the top-down approach, coal is a superior carbon source when compared with other carbon allotropes, due to its unique polycrystalline nanostructure.[8] These polycrystalline nanostructures are quasi CDs that are connected by the bridging bonds, so CDs can be readily extracted from coal by breaking the bridging bonds. The bridging bonds, such as benzylic systems, C–O–C and C(O)O, have lower disassociation energy than sp^2-carbon; oxidation reaction prefers to break the weaker bridging bonds and leave the polycrystalline domains intact, resulting in CDs with different functional groups. Coal-based CDs were first produced by an oxidation method in HNO_3 and H_2SO_4 mixture[8] (see **Figure 2**a). This method produced CDs at a yield of 20–25% with good water solubility. Bandgap engineering of CDs was tailored by changing the reaction temperature, followed by cross-flow ultrafiltration separation[18] (see Figure 2b). To meet the needs of different applications, surface modification of CDs is necessary, for example, poly(ethylene glycol) (PEG) functionalization on CD surfaces is feasible due to their rich oxygen containing edges[19] (see Figure 2c). Figure 2d shows a typical transmission

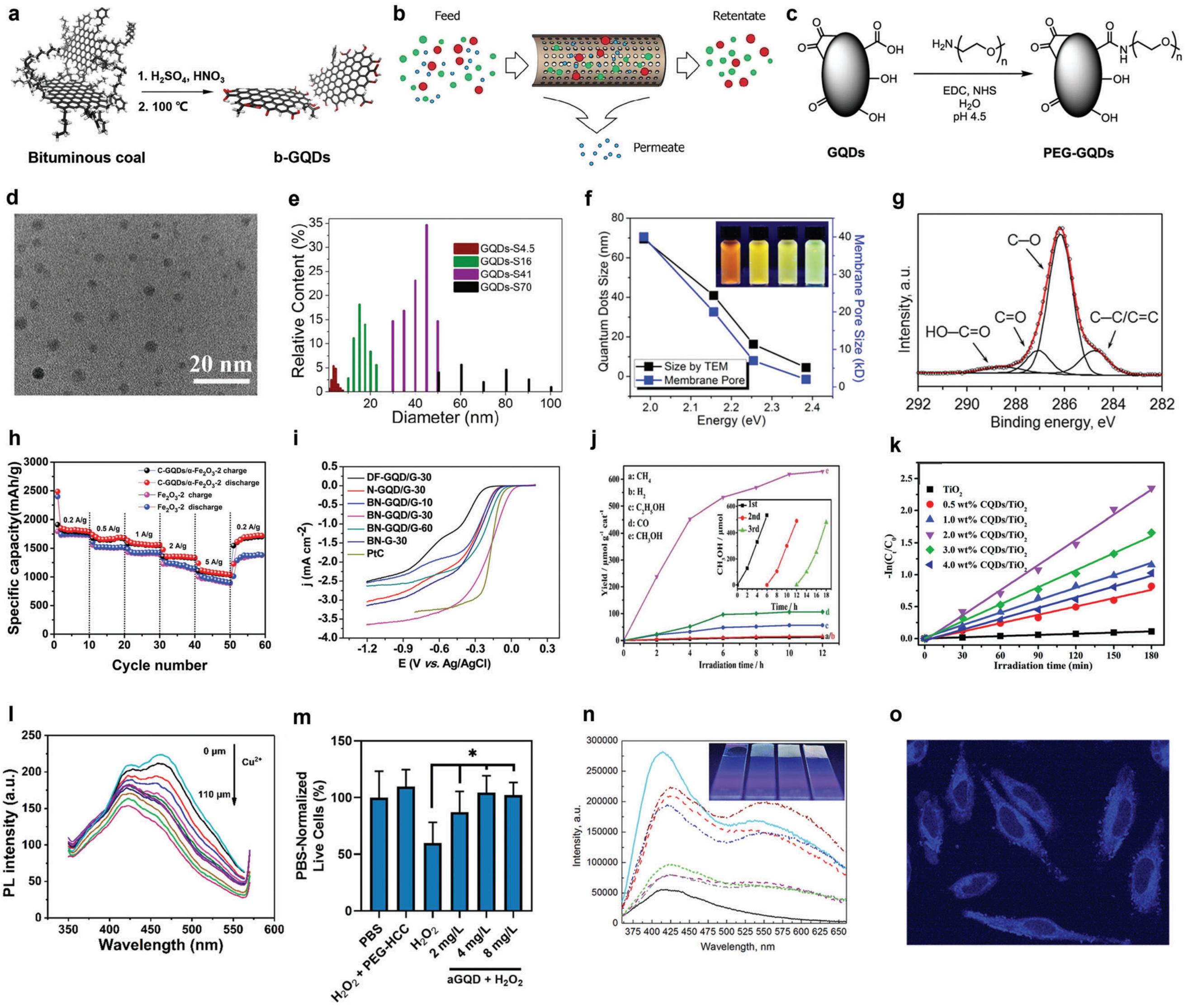

Figure 2. a) Schematic illustration of the synthesis of CDs from coal. b) Schematic illustration of the separation of CDs using cross-flow ultrafiltration. c) Synthesis of PEG-CDs. d) TEM image of CDs. e) The size distributions of CDs from (b). f) Relationship between the bandgap and size of CDs. The inset shows the corresponding fluorescence photo. g) High-resolution XPS C 1s spectra of PEG5000-CDs. h) Rate performance curve of CDs/α-Fe_2O_3-2 composite. i) Rotating disc electrode (RDE) linear sweep voltammograms of the ORR on different CDs VS Pt/C on a RDE at a rotating speed of 900 rpm and scan rate of 5 mV s^{-1}. j) CDs' photocatalytic conversion of CO_2 to hydrocarbons (the inset shows the change in CH_3OH yield produced by using CDs for three cycles.) k) Photodegradation test results of CDs. C_0 represents the initial concentration of Rhodamine B; C_t corresponds to the real-time concentration of Rhodamine B. l) Fluorescence emission spectra of CDs at Cu^{2+} concentration ranging from 0–110 μM. m) Live cell test of PEG-modified CDs as antioxidants. n) Fluorescence spectrum of CDs/PVA composite film. o) CDs used for cell imaging. a,d) Reproduced with permission.[8] Copyright 2013, Springer Nature. b,e,f) Reproduced with permission.[18] Copyright 2015, American Chemical Society. c,g,m) Reproduced with permission.[19] Copyright 2019, American Chemical Society. h) Reproduced with permission.[20] Copyright 2019, Elsevier. i) Reproduced with permission.[21] Copyright 2014, American Chemical Society. j) Reproduced with permission.[22] Copyright 2018, Royal Society of Chemistry. k) Reproduced with permission.[23] Copyright 2019, Royal Society of Chemistry. l) Reproduced with permission.[24] Copyright 2019, American Chemical Society. n) Reproduced with permission.[25] Copyright 2015, American Chemical Society. o) Reproduced with permission.[26] Copyright 2016, American Chemical Society.

eletron microscopy (TEM) image of CDs from bituminous coal.[8] By cross-flow ultrafiltration method, CDs with average sizes of 4.5, 16, 41, and 70 nm were fractionated and isolated (Figure 2e).[18] The separated CDs exhibited quantum confinement effects; photoluminescence (PL) emissions show a redshift as the sizes increase[18] (see Figure 2f). High-resolution X-ray photoeletron spectroscopy (XPS) C 1s spectra of PEG-functionalized CDs showed a large increase in C-O bonds and a large decrease in free carboxylic acid due to conversion to amides (Figure 2g),[19] which is important for the follow up applications of CDs.

In terms of applications of coal-based CDs, Figure 2h shows the rate performance curve of CDs/α-Fe_2O_3-2 composite for lithium-ion storage application.[20] The good electrical conductivity of CDs improves the transfer rate and stability of electrons on the composite surface, thus improving the rate performance of the composite. Figure 2i shows the boron and nitrogen co-doped CDs for oxygen reduction reactions (ORR). With B and N doping sites from CDs and high electrical conductivity from graphene, the optimized hybrid nanoplatelets exhibit excellent ORR activity with ≈15 mV more positive onset potential and similar current density when compared to commercial Pt/C.[21] Figure 2j shows the performance of photocatalytic conversion of CO_2 to hydrocarbons using aminated coal-based CDs as the catalysts.[22] CDs possess enhanced visible light response and generate more electrons for the photocatalytic CO_2 reduction. The CH_3OH yield in the third cycle was 89.4% of the yield in the first cycle, suggesting the CDs can be used as stable and effective catalysts. Besides CO_2 reductions, CDs also display good photodegradation performance and are used as absorbents for pollutant removal. For example, the degradation rate of rhodamine B was improved by 21.4 times when 2wt% lignite-derived CDs were incorporated into TiO_2, as shown in Figure 2k.[23] Due to their rich functional groups and surface charges, CDs are also used as fluorescent probes for the detection of metal ions in water. Figure 2l shows the fluorescent emission spectra of coal-derived CDs at different Cu^{2+} concentrations ranging from 0–110 µM. CDs exhibited a specific fluorescence response to the concentration of Cu^{2+}. The fluorescence intensity decreased with the increase in copper ion concentration, and the detection limit was calculated to be 0.29 µM.[24] Figure 2m gives an example of the application of PEG-CDs as efficient antioxidants for in vitro cellular protection.[19] PEG-modified CDs impart improved solubility and biological stability, quenching both superoxide and hydroxyl radicals in vitro and in vivo. Figure 2n illustrates the incorporation of CDs in poly(vinyl alcohol) (PVA) to make fluorescent composite films, which makes its anticounterfeiting application in solid media possible.[25] Because of their low toxicity and high photostability, CDs are also used in bioimaging as shown in Figure 2o.[26] No significant in vitro toxicity was observed when the CDs were used up to 40 µg mL^{-1}.

The technology of coal-based CDs prepared by strong acid oxidation was licensed in 2014 by Dotz Nano Ltd., a company dedicated to commercialize CDs. So far, Dotz Nano has achieved a few successful implementations by using CDs for anti-counterfeiting, oil-field tracers, and COVID-19 test kits, all through their proprietary modified syntheses.[27] While there are still technical challenges in order to expand the market share of CDs in the quantum dots industry, Dotz Nano is paving the way for high-value applications.

Coal-based CDs with quantum yields (QY) of ≈10% were obtained through the original research. Thus, their initial luminescent properties were uncompetitive when compared with semiconductor quantum dots, restricting some applications. However, their electrochemical, electrocatalytic, and mechanical properties are promising for lithium-ion batteries, supercapacitors, and composite additives.[28] CDs have the characteristics of fast electron transfer and high specific surface area; the presence of functional groups of heteroatoms (oxygen, nitrogen, sulfur, phosphorus, boron, etc.) provides more active sites for improving electrochemical performance.[21] In addition, due to their unique electronic structure, CDs can act as good electron acceptors and donors. After photoexcitation, the formation of electron-hole pairs can be well inhibited due to the inherent surface defects of coal-based CDs. Therefore, coal-based CDs can be used as photocatalysts for many chemical reactions with much higher catalytic activity.[29] Besides, the rich and tunable functional groups on the surface and their larger specific surface area give coal-based CDs good water solubility, controlled chemical properties, and many adsorption sites, favorably to be used as a probe for ion detection and biological analysis.[30] The TRL for the above applications is 1–3. The synthesis conditions and methods have to be optimized to yield coal-based CDs with larger sp^2-carbon domains and precisely controlled edges for better conductivity, preferred catalytic and absorbent activity, and increased mechanical enhancements in composites.

Medium QY (10-70%) is feasible through post functionalization of coal-based CDs. The surface of CDs is usually distributed with functional groups such as hydroxyl, amide, carboxyl, and carbonyl groups, and their QY may be improved by heteroatom doping, alkylation, esterification, imidization, passivation, and introduction of fluorescent ligands.[17] CDs are blended into polymer matrices or liquid media as effective anticounterfeiting markers; the validation process of the item is assessed through CD fluorescence using an ultraviolet (UV) lamp or by UV spectroscopy. The technology has been successfully implemented in different scenarios by Dotz Nano which brings its TRL to 7–8. Unique optical characteristics of CDs have to be further studied in order to gain more market share. For example, the combination of fluorescence and phosphorescence may help it stand out from other anticounterfeiting formulations. Oil-field tracer application is another successful example of using CDs with TRL at 6 performed by Dotz Nano.[27] Pilot scale production and 600 L of CDs went through a field test on US land, and identical fluorescence signals were detected from the produced water even 40 days after injection. The advantages of CD tracers are that they are stable, easily detectable, non-toxic, and environmentally friendly. More importantly, they can provide immediate on-site results, whereas commonly used fluorobenzoic acid tracers require lab analysis using liquid chromatography–mass spectrometry that takes hours or even days. The time delay between sampling and results could lead to poor decision-making in oil fields. Expanded use of CDs in the oilfield markets for tracing water or even pipeline oil could markedly increase CD applications. This could be realized by optimizing the CDs yield from coal, or by boosting their QY to lower the detection limit (part per billion to parts per trillion level). Oil-soluble CD tracers and partitioning CD tracers could be investigated as well in order to expand their service window to compete with other oil-field tracers.

Coal-based CDs with high QY (>70%) have not been reported yet. Most CDs with high QY are produced through a bottom-up approach by using precursors like phloroglucinol or *o*-phenylenediamine.[31] CDs with high QY are highly desired to replace semiconductor quantum dots (CdSe, InP) for displays, illumination and bioimaging areas, because of their low toxicity and high stability. Although CDs from coal have made progress in low and medium QY, high QY would be extremely difficult due to the nature of the top-down approach. A possible way might be the bottom-up approach to synthesize coal-based CDs by first converting coal into carbon species. One alternative approach may be laser- or electron-beam-induced CDs by post functionalization with an electron-donating group. The extremely high temperature from a laser or electron beam can generate C_2 dimers from coal,[32] and these dimers could become the carbon source for CDs reassembling under appropriate conditions. Besides QY, the full width at half maximum (FWHM) of the optical spectra absorbance of CDs from coal (>80 nm) is another important parameter to consider. This is true especially for display applications. In fact, the FWHM of semiconductor quantum dots is less than 30 nm, which gives purer color to generate a higher color gamut for displays.[33] Broad emissions of CDs are attributed to the following factors. First, CDs do not easily undergo a size sieving process, resulting in the existence of multiple size distributions with different emissions, thus forming broader FWHM. Second, it is possible that the basal plane of CDs is a sp^2- and sp^3-hybrid structure, and different sp^2- domains act as fluorescence centers with different emissions. In addition, multiple functional groups like $-OH$, $-NH_2$, $-COOH$ can contribute to the broad emission.[17] Therefore, CDs with uniform size, monocrystalline and single electron donating functional groups would be effective ways to reduce the FWHM. This work rightly needs further research.

In terms of synthesis methods, coal-based CDs were also made by a supercritical fluid method, a hydroxyl radicals (OH*) method, a solvothermal method in *N,N*-dimethylformamide (DMF), and a pulsed laser ablation method in liquid.[34] Those methods all show promising results without using acids, which is more environmentally friendly. However, more research has to be performed to further validate their feasibility and scalability toward commercialization.

Obstacles to the development of coal-based CDs exist due to a lack of clear product standards. The use of different synthesis methods and coals can result in the co-existence of two crystalline structures (GQDs and CQDs) and one non-crystalline structure (CNDs) in coal-based CDs. The three forms of products are identical in size and functionality, making it challenging to be separated and purified. The constantly evolving naming system for coal-based CDs adds to the confusion. A standard definition of coal-based CDs requires further research, potentially by measuring the crystallinity, number of layers, sizes, functionalities, and compositions. More study is necessary before coal-based CDs can establish standards and progress toward commercialization.

3. Coal-Based Flash Graphene

Graphene is a material with unique properties and interesting challenges. Graphene was rediscovered in 2004 by Novoselov and Geim through micromechanical cleavage of graphite using adhesive tape. Graphene consists of a honeycomb sheet of sp^2-hybridized carbon atoms, which grants the material outstanding thermal, electrical, and mechanical properties. As such, graphene has found applications in a variety of areas, such as in energy generation and storage, and composite materials.[35] However, the widespread use of graphene in industrial applications has not been fully realized, due to the lack of cost-effective, bulk-scale fabrication techniques.

Graphene production techniques are normally categorized into bottom-up and top-down methods.[36] Generally speaking, the former techniques produce high-quality graphene sheets on small scales, whereas the latter techniques can produce bulk-scale graphene flakes, but with relatively low quality. Because of the difficulty of production, the cost of graphene ranges from between \$30 000–1 000 000 per ton, depending on its quality.[37] Such techniques include mechanical or chemical exfoliation, chemical oxidation or reduction, shear exfoliation, and other techniques.[9] Bottom-up techniques that produce graphene sheets with low defect concentrations are generally time-, energy-, or chemically intensive, limiting the scalability of these processes. Electrochemical exfoliation has been demonstrated to produce high-quality graphene on the kilogram-scale, but ton-scale production has not yet been achieved. Top-down methods such as direct exfoliation of graphite produce ton-scale materials but have poor performance in comparison to graphene made from bottom-up methods. No commercialized technique has yet been able to provide bulk-scale production of high-quality graphene.

Flash Joule heating (FJH) has recently been demonstrated as a viable technique for converting any carbon-containing feedstock into high-quality, turbostratic graphene.[38] The feedstock is compressed between copper or graphite electrodes and a current is passed through the material (**Figure 3**a).[9] Joule heating causes the temperature of the feedstock to rise above 3000 K in a matter of milliseconds, causing the carbon-carbon bonds within the material to break and re-assemble into the more energetically favorable form of graphene, as determined by high-resolution transmission electron microscopy (HR-TEM) (Figure 3b–d).[9] At these temperatures, even impurities such as aluminum and silicon sublime out in the process, rendering the method as self-purifying. This results in graphene with very low defect concentrations, as shown by Raman spectroscopy.[9] The intensities of the D and G bands in the Raman spectrum correspond to scattering from defects and in-plane vibrations of graphene, respectively. The ratio of these two bands can be used as a measure of graphene quality, where an I_D/I_G intensity ratio of <0.2 indicates high-quality graphene.[38] The I_D/I_G ratio of graphene made through FJH is much lower than 0.2, indicating that FJH produces high-quality material. The process does not require the use of solvents or any chemical post-treatments. Since the inception of the technology, batch sizes have grown from 50 mg per batch to 10 g per batch in university laboratories.[9]

Various types of coal have been found to be suitable feedstocks for FJH conversion into FG, including anthracite, charcoal, calcined coke, and petroleum coke.[9] Metallurgical coke, a coal-based material used in the production of aluminum, has also been found to be effective as a feedstock and as a conductive additive to other less-conductive carbons, such as waste plastic, in order to FJH those less soluble materials into FG.[39] The yield and processability of these feedstocks are highly dependent on their carbon content. For example, due to its high purity and carbon content, metallurgical coke has higher process yield, FG yield, and conductivity. The process yield, calculated as the mass of the product divided by the mass of the feedstock, can be between 80–95%, depending on the initial carbon content of the coal feedstock, with metallurgical coke affording >95% mass yield of FG. The FG yield of coal-derived FG, meaning the amount of the flashed sample containing graphene, as determined by Raman spectroscopy, regularly reaches >95% (Figure 3e).[9] FG yield is calculated by finding the percentage of spectra that meet the following criteria (1) minimum I_{2D}/I_G ratio of ≥0.3, (2) signal-to-noise ratio of >5 in the 2D band region, and (3) 2D band with a

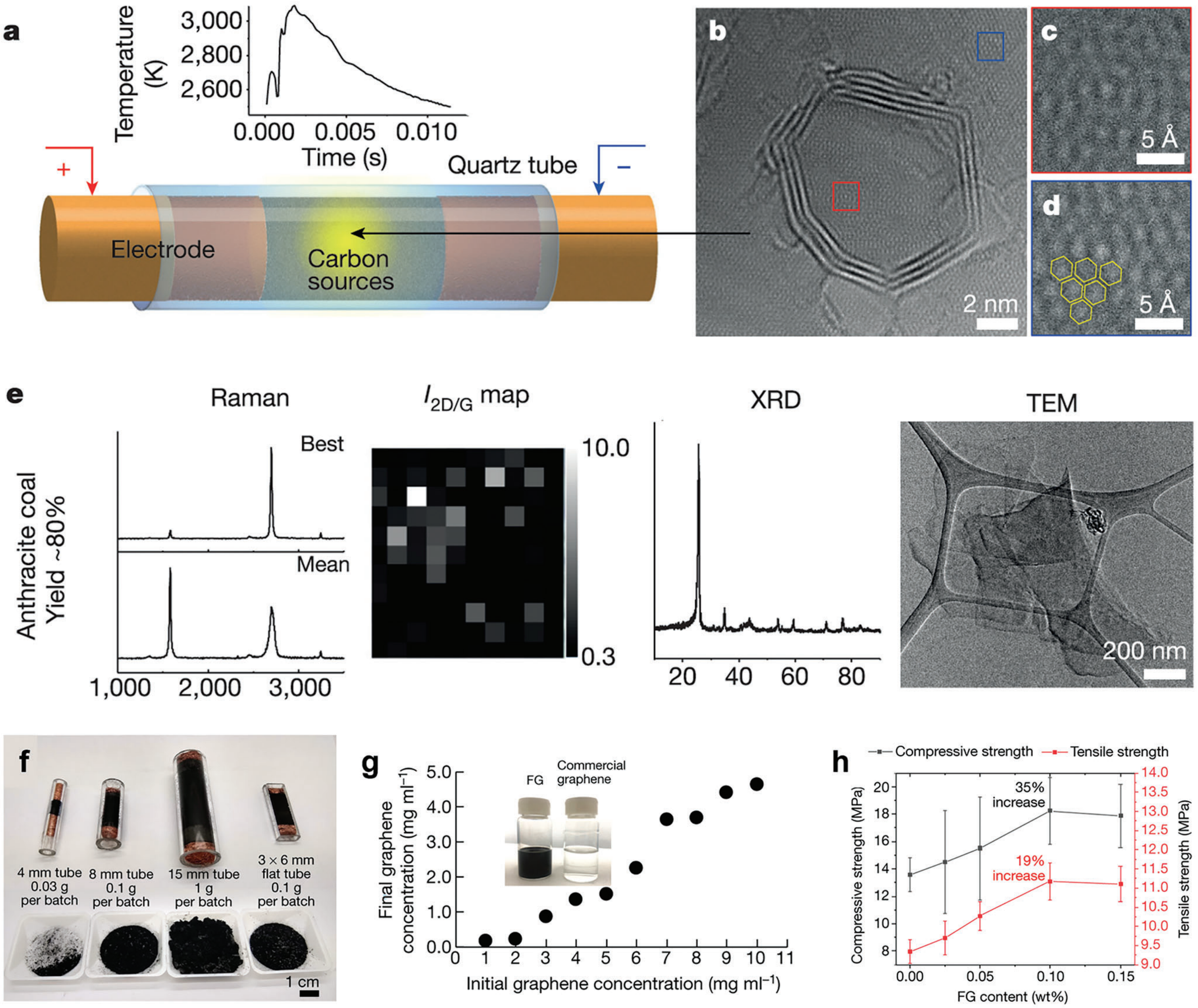

Figure 3. a) Schematic of the FJH process and plot of the temperature rise versus time during flashing (inset). b–d) HR-TEM image of carbon black-derived FG on top of a single layer of coffee-derived FG. e) Characterization results, including Raman spectra (showing the best and the mean obtained spectra), XRD spectra and TEM images for FG derived from anthracite coal. f) FJH quartz tubes of different sizes and shapes used to synthesize FG. Two separate synthesis processes were conducted with each tube, providing the samples in the tube and those in the plastic dishes. g) FG dispersion in a water–Pluronic (F-127) solution (1 wt%). h) Mechanical performance of cement compounded with FG. a–h) Reproduced with permission.[9] Copyright 2020, Springer Nature.

FWHM of <100 cm^{-1}. While there is not yet a standard specification to classify graphene, the I_{2D}/I_G ratio measured through Raman spectroscopy is commonly used as an indicator of graphene character, where a greater I_{2D}/I_G ratio indicates more 2D-material behavior. As such, graphene sellers have used a range of I_{2D}/I_G ratio thresholds to market their materials, generally with a minimum I_{2D}/I_G ratio of ≥0.3. Below this ratio, the material tends to behave more like a 3D material with less of the desired graphene characteristics. Conductivity is also important for a feedstock, as too high of resistance makes the feedstock difficult to flash Joule heat. As such, some lower purity coals, such as bituminous coal or lignite require the addition of conductive additives, like carbon black or metallurgical coke, to effectively flash Joule heat. Due to the low cost of the FJH process, FG can be made from ≈$150/tonne metallurgical coke and only $30/tonne in electrical energy costs.[9]

Due to the rapid nature of the FJH process, the resultant FG is also turbostratic, meaning that the sheets of graphene are rotated about the axis normal to the graphene sheets. This rotational mismatch results in an increase in interlayer spacing as overlapping electron-rich areas drive the layers apart. This is most easily demonstrated through X-ray diffraction (XRD). Conventionally produced, AB-stacked graphene has a (002) peak that normally appears at 26.4°.[9] The (002) peak in turbostratic graphene shifts to a lower diffraction angle and increases its FWHM (Figure 3e).[9] This process can be carried out in a variety of batch sizes, ranging from 0.03 to 1 g per batch (Figure 3f),[9] with recent developments in the technology enabling batch sizes of 10 g. As a result, turbostratic FG is easier to exfoliate and disperse than conventionally produced, AB-stacked graphene (Figure 3g),[9] even in oils, lubricants, and water.[40] This increased spacing also enables FG to retain the desired 2D properties of monolayer graphene, even with an increased number of layers, due to a reduction in electron mobility between layers.

Concrete is a particularly important application for FG as each year, over 30 billion tons of concrete are produced, outpacing the per capita production of any other material. It is the most consumed material in the world, other than water.[41] Production of cement accounts for 2–3% of total global energy use, 9% of global annual industrial water withdrawals, and 8–9% of anthropogenic generated CO_2 emissions.[42] FG derived from various feedstocks has been used as a reinforcing additive in cement. The addition of carbon-black derived FG to cement pastes increased their compressive strengths by 35% at 0.1 wt% loadings and their tensile strengths by 19% at the same loading (Figure 3h).[9] FG derived from post-consumer high-density polyethylene (HDPE) waste increased the compressive strength of Portland cement by 30% at 0.035 wt% loading.[43] During FJH of the HDPE, significant off-gassing was observed. This volatile stream can be captured, preventing the emission of pollutants and enabling the re-use of the captured oligomers in petroleum hydrocarbon streams or as additives in detergent composites. Furthermore, because FJH does not require solvents or post-processing and requires relatively little energy, bulk-scale production of graphene can be achieved with much less greenhouse gas emission than conventional production techniques.[44] Due to the scale of concrete use globally, it has been difficult to use conventionally produced graphene even with low loadings of the material. However, FJH may provide the key to enabling industrial-scale use of FG in concrete.

In addition to applications in concrete, FG can also be used as an additive in lubricants and epoxy composites. As a lubricant additive, FG significantly reduces the friction of coefficient and wear scar diameter of surfaces treated with graphene-modified lubricants. FG flakes deposit on the worn surface and form a protective film that smooths the contact surface and reduces the surface roughness of the contact pairs.[44] In epoxy composites, graphene operates as a reinforcing additive, improving toughness through crack bridging and consuming fracture energy by stopping crack formation.[45] Lubricants and epoxies are commonly used materials that benefit greatly from addition of even small amounts of graphene. The low cost of the FJH process, high quality of the product, and the ready availability of carbon-containing feedstocks, such as coal, make FG an ideal additive for these lubricant and epoxy roles.

Currently, there is little government regulation regarding the production and use of graphene.[46] However, as graphene usage continues to grow, regulation will likely be needed to guarantee the reliability, quality, and safety of graphene. The safety of graphene and graphene-based materials is determined by several characteristics, such as the number of layers, average lateral dimensions, and carbon-to-oxygen ratio.[47] The functionalization of graphene-based materials can also alter their properties and biological behavior. As such, regulation of graphene production will likely be necessary to facilitate its use. The TRL of FJH technology for the manufacture of graphene is 7–8 and Universal Matter Inc. has obtained relevant patent rights from Rice University for the development of FG applications in concrete, asphalt, rubber, medical technology, polyurethanes, and other fields.[48] The Universal Matter production rate of FG is slated to be 1-ton per day by mid-2023. Additionally, due to its geological stability, graphene can require hundreds of years to be microbially decomposed, which slows the re-entry of carbon into the carbon cycle. As such, FJH enables FG to be used as a near-terminal natural sink for carbon. Moving forward, the structure and performance of FG made with different coals will need to be studied and optimized to meet different applications, but further study will enable the use of any coal as a feedstock for high-value, high-quality carbon sequestration, and utilization.

The FJH process also permits the formation of nanodiamonds or carbon onions from carbons.[49] This is done merely by controlling the Joule heating time through a 1 s evolution process. At ≈5 ms, nanodiamonds form, at ≈100 ms FG forms, and at ≈1 s carbon onions form. Hence, there is broad versatility in the FJH process to provide high-value materials from coal.

4. Other Coal-Based Nanomaterials

Other coal-based nanomaterials such as fullerenes,[10] NDs,[11] CNTs[12] have also been carefully investigated in recent years, as shown in **Figure 4**a–c. Unlike coal-based CDs and FG, these nanomaterials are still in the early stage with TRLs less than 4. Their syntheses and properties have already been properly reviewed elsewhere.[28,34] In this section, we will briefly describe the progress of these coal-based nanomaterials, summarize the common issues, and propose possible solutions to bridge their performance gaps with their commercial counterparts.

Owing to its high purity and crystallinity, graphite is commonly used as the carbon source for the commercial production of fullerenes, NDs, and CNTs. Meanwhile, various approaches have been taken to produce these three materials from coals, unfortunately, the properties of the end products are still far from satisfactory. Currently, much of the research on these coal-based nanomaterials is focused on understanding their formation mechanisms, and no product or standard has yet been established. Low purity, yield, and performance are the major drawbacks that impede their further applications. For example, fullerene can act as an effective electron buffer for catalytic reactions,[50] coal-derived fullerenes either provided few convincing characterizations, or their quality and purity are too low to be commercially implemented. A similar scenario occurs with NDs, coal-derived NDs are produced using liquid laser ablation, ultrasonic methods, strong acid oxidation methods, and electron beam irradiation,[34] but none of them provided mechanical, electrical, and thermal evaluations necessary to reveal their efficacy for downstream applications. CNTs are widely used as reinforcement fillers for composite materials and batteries.[12] Catalytic pyrolysis techniques, arc discharge and DC arc techniques have been reported for coal-based single and multiwall CNT syntheses.[28] However, the yield and performance of coal-based CNTs are inferior to those made from graphite by arcing methods.[51]

To tackle these challenges, continuous optimization of the coal processing methods could be one viable direction, however the root cause is likely due to the composition of coal itself. Coal is a complex mixture, and even anthracite, which has the highest

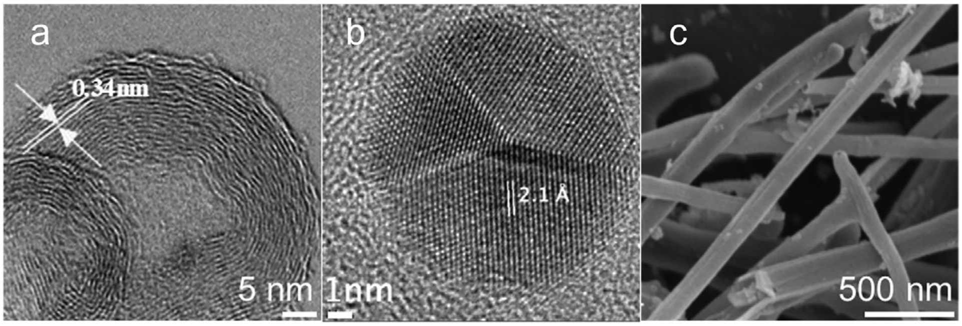

Figure 4. a) TEM image of coal-based fullerenes. Reproduced with permission.[10] Copyright 2007, Elsevier. b) TEM image of coal-based nanodiamonds. Reproduced with permission.[11] Copyright 2014, American Chemical Society. c) SEM image of coal-based carbon nanotubes. Reproduced with permission.[12] Copyright 2022, Elsevier.

coalification level (CL) and carbon content, still contains some impurities, e.g. ash, volatile matter, and minerals etc. These impurities play a detrimental role in the yield and purity of coal-based nanomaterials, so high CL coals such as anthracite are preferred precursors compared to low CL coals like lignite and bituminous coal. Therefore, an alternative approach we propose is to first convert high CL coals into an intermedia graphitic material with higher purity and crystallinity, and this process can be realized by pre-washing and/or post heat-treatment of coal under appropriate conditions.[28] This can be further implemented through FJH if desired, thereby minimizing the energy input. With improved quality of feedstocks, superior coal-based fullerenes, NDs and CNTs might be expected under certain processing techniques. In order to fulfill the commercialization hope, economic factors must be considered in order to find a balance between the extra cost of coal purification and the end product profit margin.

In terms of low CL coals, the weak bonds in their macromolecular structure requires less energy to convert them into CH_4, H_2 and CO via a mature technology called gasification.[52] The three gases, mixed in certain ratios, can act as precursors to synthesize high quality fullerene, NDs, and CNTs by widely used chemcial vapor deposition (CVD) methods.[53] With better control of the growth parameters, the proposed solution could also be expanded into the synthesis of single-crystalline diamond or high-quality graphene,[53] which could trigger coal-based nanomaterials used in even broader areas like electronics, semiconductors, and energy conversions.

Figure 5 summarizes the two proposed strategies to convert coal into carbon nanomaterials with performance approaching or meeting commercial product demands. Coal is classified and utilized by different routes according to its CL. One route is to use high CL coal as an abundant and cost-effective source to produce graphitic carbon through a graphitization process, as shown in Figure 5a, so high quality fullerenes, NDs, CNTs, and FG could be produced by known routes like plasma arc,[54] high temperature and high pressure (HTHP),[55] electric arc[56] and FJH,[57] respectively. Another approach is to convert low CL coal into syngas (H_2 + CO) and methane through a gasification process, as shown in Figure 5b; impurities of coal turn into slag that can be

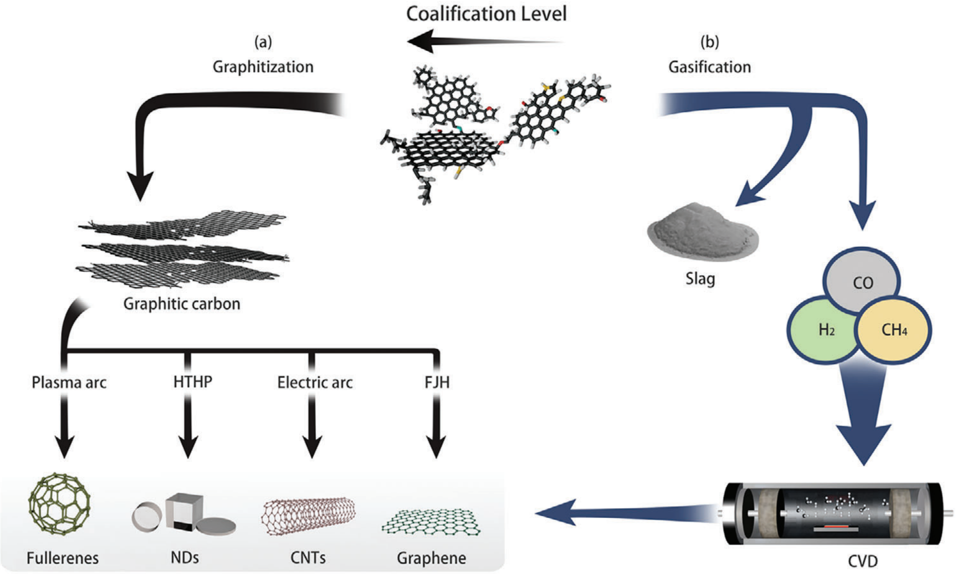

Figure 5. Strategies of clean coal conversion into carbon nanomaterials: a) graphitization route; b) gasification route.

further processed and used as construction materials. The gases can be further grown into high quality fullerenes, CNTs, NDs, and graphene by CVD methods. Since CO_2 is generated in this process, the method for its capture and storage, conversion or utilization must be considered.

5. Conclusions and Outlook

Coal-based nanomaterials are an exciting area that has yet to be well developed. More effort has to be taken in order to realize coal's contribution to the overall clean coal conversion concept. Although coal is an abundant and cost-effective carbon feedstock, its end products might not competitive when compared with their counterparts. This will depend on the process efficiency for each material. The ability to prepare high-quality coal-based nanomaterials is a prerequisite for advances in many commercial applications. However, research on each new coal-based material need not depend on price. If the material is highly desired, prices will drop as methods are refined.

Market is another key factor to be considered. Although successful cases like CDs and FG have been demonstrated to readily enter the early phase of commercialization, none of them have the ability to make even a small dent in the coal industry because the markets are too small at the moment. Broad markets have to be initiated for the thriving of coal-based nanomaterials. For example, 1 wt% addition of FG to asphalt roads will triple the life of the road.[48] But in the end, our desire is to fully replace asphalt and concrete with low-CO_2-yield coal-based materials. Can we just use a material that is very high in graphene content, like 50–90% graphene, and the remainder being an organic binder? Concrete is 2500 years old. Can it be replaced? Only when we have avenues like this, might coal-based nanomaterials be utilized in sufficiently large volumes to replace the superabundance of coal that is presently consumed for energy through combustion.

Government policies also play a key role in the development of such industries. A variety of policies, such as financial incentives, research and development funding, procurement mandate, regulatory support, emission standard, carbon tax, international agreement etc., can be implemented to promote the deployment of coal-based nanotechnology. For example, the government may offer subsidies, tax credits, or other financial incentives to companies running business in this area. Government funding for research and development in coal-based nanotechnology can also drive innovation and commercialization. Government may require companies to purchase a certain number of coal-based nanomaterials, providing a market for this area.

Finally, the control of pollutants or CO_2 emissions generated during the production or use of coal-based nanomaterials should not be overlooked. Although often neglected in lab-scale research, proper treatment of these emissions is crucial when transitioning to industrial applications. For instance, CO_2 can be captured and utilized as a feedstock to produce hydrocarbons or enhance plant growth through CO_2 fertilization. Achieving net zero CO_2 emissions ultimately depends on the effective management of each step in the clean coal conversion process.

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Conflict of Interest

Rice University owns intellectual property on the coal-based graphene quantum dots process. Dotz Nano Ltd. produces graphene quantum dots. Rice University owns intellectual property on the FG process. Universal Matter Inc. and Universal Matter Ltd. produce FG. J.M.T. is a stockholder in all of these companies, but he is not an employee, officer, or director in them. Conflicts of interest are managed by regular disclosure to the Rice University Office of Sponsored Programs and Research Compliance. The authors declare no other potential conflicts.

Keywords

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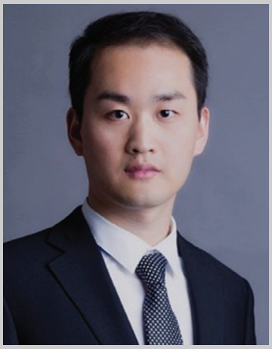

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