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The Trio of Carbon Nanomaterials: Fullerene, CNT, and Graphene—A Review of Their Discovery and Development in the Last Decade

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ABSTRACT

Carbon, due to its versatile allotropes with exceptional structure and properties, continuously contributes to the application of nanotechnology in different sectors of electronics, energy and environment, biomedical and agricultural fields. After the discovery of 0D fullerene, 1D carbon nanotube, and 2D graphene, these carbon nanomaterials are the most fascinating and wonder materials for fundamental and applied research, as a large number of publications and patents have been reported investigating their structure, synthesis, properties, and potential applications. The timeline and discovery of these carbon nanomaterials and various synthesis techniques have been summarized in this review. It is forecasted that the world's energy demand will double by 2050, and this calls for efficient and clean energy sources to meet the energy challenges in the future. Carbon nanomaterials, with their unique properties including superior electrical and thermal conductivities, mechanical strength, and catalytic properties, can be leveraged for various energy applications. In this context, advancements in the application of carbon nanomaterials in one of the major renewable energy technologies, i.e., fuel cells, during the last decade are presented. Various synthesis techniques for carbon nanomaterials, challenges for mass production, and the transformative potential of artificial intelligence in carbon nanomaterials science are also briefly discussed.

Keywords: Carbon nanomaterials, Fullerene, Carbon nanotubes, Graphene, Fuel cells

Introduction

In his Nobel prize talk "Discovering the Fullerenes," Richard Smalley mentioned, "what nature has in store for us with carbon, is still ongoing,"[1] This came true as 1D carbon nanotubes (CNTs) and 2D graphene followed the discovery of 0D fullerene. Until the discovery of the hollow carbon cage fullerenes, only two known structured allotropes of carbon were graphite and diamond.

Curl, Kroto, and Smalley—along with graduate students J R Heath and S C O'Brien—collaborated on experiments on laser vaporization of carbon and interestingly found a mass spectrum dominated by 720 peaks, corresponding to 60 carbon atoms.[2] Curl, Kroto, and Smalley came up with the idea of a spheroidal cage structure with 60 carbons arranged in a few pentagons. Inspired by the geodesic dome concept, they named it fullerene after the geodesic dome discoverer, Buckminster Fuller.

The discovery of the fullerene (1985) happened at the epitome of the knowledge and progress made over several years starting from Archimedes' conception of a truncated icosahedron, Osawa's prediction about the stability of aromatic carbon chains (1970, 1993), David Jones imaginative complex curvature of closed spheroidal cages with pentagonal defects (1966, 1982), and Boch var and Gal'pern's calculations about C60 as a closed-shell molecule with a huge HOMO-LUMO gap (1973).[1] However, the Nobel Prize in Chemistry in 1996 was awarded for the discovery of the novel concept of "carbon's genius for spontaneously assembling into fullerenes." Nobel Prize press release also stated that an entirely new branch of chemistry with consequences in diverse areas such as astrochemistry, superconductivity, and materials chemistry/physics has been developed.[3]

The discovery of CNTs (1991) also shares some backstories. The first mention of the probability of carbon filament formation from the thermal decomposition of a gaseous hydrocarbon was reported nearly two centuries ago.[4] This was in a patent that claimed the use of filaments in the light bulbs proposed by Edison at the Paris Universal Exposition the same year (1889). TEM images of nano-sized carbon filaments appeared in the Journal of Physical Chemistry of Russia in 1952 and showed the tubular nature.[5] Following this, the history of carbon science witnessed great contributions from many other scientists in the field. However, these early discoveries did not receive the attention of the broad scientific community. The main reasons include poor TEM resolution at the time and failure to portray the arrangement of graphenes in the nanotube walls. The materials scientists who studied the carbon filaments and nanotubes were mainly focused on understanding the growth mechanisms to prevent their formation for practical purposes, not on the fundamental physics. Moreover, these scientists missed the materials and chemistry-related aspects of these materials published at the time in those specific journals.[6]

The paper titled "Helical microtubules of graphitic carbon" by Sumio Iijima in 1991[7] got a big foot in carbon science owing to the right combination of favorable factors, such as a high-quality paper published in a top-ranked journal such as *Nature* with diverse scientific readers, the inspiration and attention of worldwide researchers from the Nobel prize-winning fullerene discovery, thus preparing a fully mature scientific audience ready for a nanotechnology revolution. The same arc-discharge method that invented fullerenes enabled Iijima to mass-produce the new type of needle-like tubes, for which he proposed a new growth model, of individual tubes with spiral growth steps at the tube ends.

Thirteen years later, in October 2004, a paper in *Science*[8] reported the electric field effect in atomically thin carbon films, aka graphene, for which the authors Novoselov and Geim got the Nobel Prize in Physics in October 2010. Both ordinary men and the scientific community may not disagree with joining hands with the Nobel committee in their saying, “Carbon, the basis of all known life on earth, has surprised us once again,” which they attributed to its exceptional properties originating from the remarkable world of quantum physics.[9]

The invention of these novel species of carbon allotropes has shown a significant impact in diverse scientific fields. The trio’s exotic electronic, thermal, and mechanical properties and potential applications are a hot research topic worldwide.

The present review investigates the synthesis techniques, developments, and applications of different carbon nanomaterials in a single platform. The progress made in carbon nanomaterials-based fuel cells in the last decade has also been investigated.

Timeline of Discoveries and the Scientific Impact

Figure 1 shows the timeline of the discovery of all three carbon nanomaterials. It is interesting to see one discovery after the other, every decade.

Synthesis Techniques

Fullerenes

Fullerenes are represented by the formula Cn, with n being the number of carbon atoms in the cage. Two classifications of fullerenes exist: classical and non-classical fullerenes. A closed carbon cage of 12 pentagons and any number of hexagons is termed classical, whereas if it includes heptagons, octagons, and a further number of pentagons or squares, it becomes non-classical.

Krätschmer et al. developed a method to produce large quantities of fullerenes in 1990.[10] They characterized the material by mass spectroscopy, infrared spectroscopy, X-ray diffraction, and electron diffraction. Using the flash vacuum pyrolysis (FVP) technique, Scott et al. synthesized C60 with no by-products during the production process.[11] The same FVP method was also employed for the synthesis of larger fullerenes such as C78. Since the discovery of C60, various higher fullerenes have been investigated including C70, C76, C78, C82, C84, C90, and C96.[12] Figures 2a, b shows the time-of-flight negative ion mass spectra and optical absorption spectra of different fullerene compounds. However, there are experimental difficulties in isolating large quantities of fullerenes beyond C84 in pure form. Experimental and theoretical studies of buckybowls (fullerene fragments) have also attracted considerable interest from researchers. Formation mechanisms of fullerenes and metallofullerenes were proposed in the 1990s as the “bottom-up” and the “top-down” formation theories (Figure 2c).[13] According to the bottom-up hypothesis, graphite is first completely vaporized into atoms or C2 units during the synthesis process, and then the constant reactions of carbon fragments and C2 units will lead to the formation of fullerenes. The bottom-up hypothesis has two major sub-theories: the pentagon road model and the fullerene road model.

The “top-down” hypothesis relates to the likely condition of the outer space formation of fullerenes, as it states that fullerenes can be formed from large carbonaceous structures, such as graphene and polyaromatic hydrocarbons. The dangling bonds on graphene and high temperature can result in warping and eventually rolling up, forming large fullerenes. This then can decay into energetically favorable smaller fullerenes via C2 or small chain ejections until stable molecules are reached.[14]

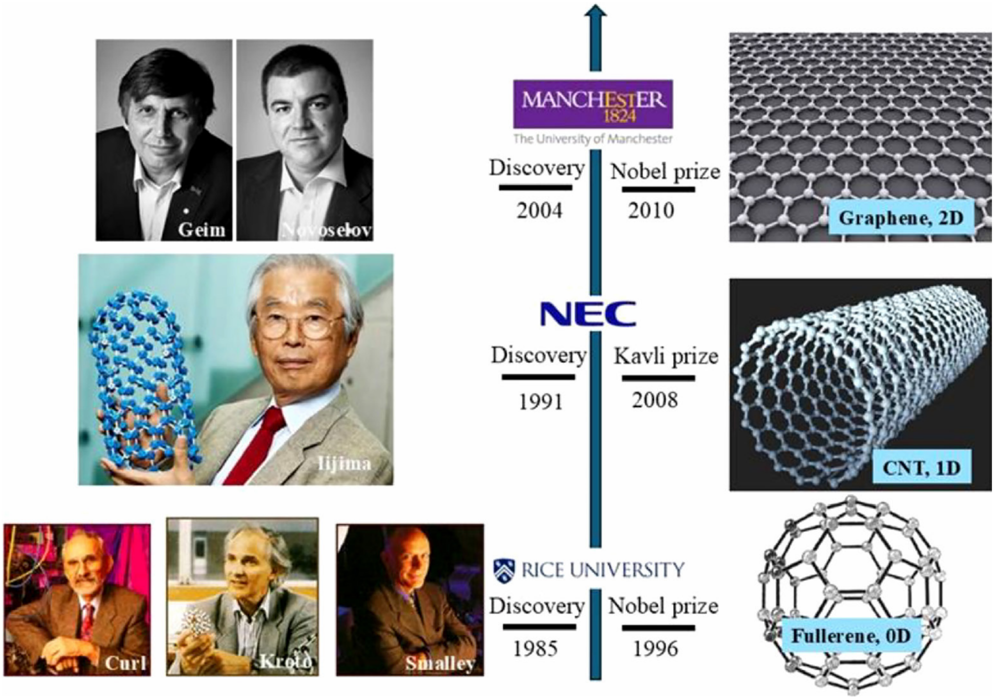

Fig 1 | The timeline of carbon nanomaterials discovery

It is important to understand the size dependence of the fullerenes to tailor these systems for nanotechnology applications. Closed carbon cages smaller than C60 consisting of adjacent pentagons are projected to have unusual electronic, magnetic, and mechanical properties owing to the high curvature of their molecular surface.

CNTs

The fourth allotrope of carbon, CNTs (after graphite, diamond, and fullerene), are of two types: those composed of multi-tubular structures nesting concentrically,[7,15] namely multi-walled carbon nanotubes (diameter ranging from 2 to 100 nm) and those with a single-wall CNT (SWCNT) (diameter ranging from 0.7 to 2 nm).[16] Tubular carbon structures have not been found naturally occurring, so CNTs are synthetically created types of carbon solid. Both nanotubes possess remarkable mechanical and electrical properties. In addition, the smaller size and unique structure of SWCNT endow them with fascinating quantum phenomena.[17,18]

The practical application of CNTs demands their economic, large-scale production. There are different synthesis techniques reported, such as arc discharge,[19] laser ablation,[20] and chemical vapor deposition (CVD).[21] Iijima's first report on MWNTs was about using the arc-discharge evaporation of carbon in an argon-filled chamber, resulting in 4–30 nm diameter MWNTs.[7] Figure 3a shows the electron micrographs of CNTs with various graphitic sheets. Following this, researchers widely employed the arc-discharge method to synthesize high-quality MWNT and SWNTs.[22–24] The laser ablation method also attracted interest, as seen from numerous reports with varying lasers, and experimental conditions such as metal catalysts, buffer gases, oven temperature, flow conditions, etc.[20,25] Chen et al. reported large-scale synthesis of CNTs using pulsed laser ablation of a graphite target in metal nano-sol under ambient conditions.[26]

Of the three methods, the CVD technique yields CNTs at much lower temperatures and ambient pressure and, hence, is simpler and more economical.[27] Shaijumon et al. reported large-scale production of MWNTs by pyrolysis of acetylene over misch metal-based catalysts.[21] Purification of CNTs is generally needed to get rid of amorphous carbon impurities and metal catalyst particles after the CVD process. They have employed air oxidation and acid treatment for this purpose. The author has prepared MWNTs using this method for various applications and utilized spectroscopic and microscopic characterization to confirm the formation and purification of these nanotubes (Figures 3b and d).[28] Raman spectrum is another powerful tool that characterizes the purity of carbon nanomaterials. Figure 3c shows Raman spectra of as-synthesized and functionalized (acid-treated) MWNTs.[28] It can be seen that the purified and functionalized CNTs show a shift in their peak positions, which is an indication of the intercalation of acid molecules in the interstitial channels of CNTs. The doping of CNTs with elements such as nitrogen has been carried out to improve the catalytic activity, as well as conductivity by raising the fermi level toward the conduction band.[29] Figures 3e and f show the AFM image of nitrogen-containing CNTs prepared by this template synthesis method.

Graphene

Two main routes exist for the synthesis of graphene: top-down and bottom-up methods. In the top-down method, breaking down bulk materials like graphite or graphite oxide creates graphene. Examples include the mechanical cleavage of graphite that Geim and Novoselov employed in their discovery, liquid phase

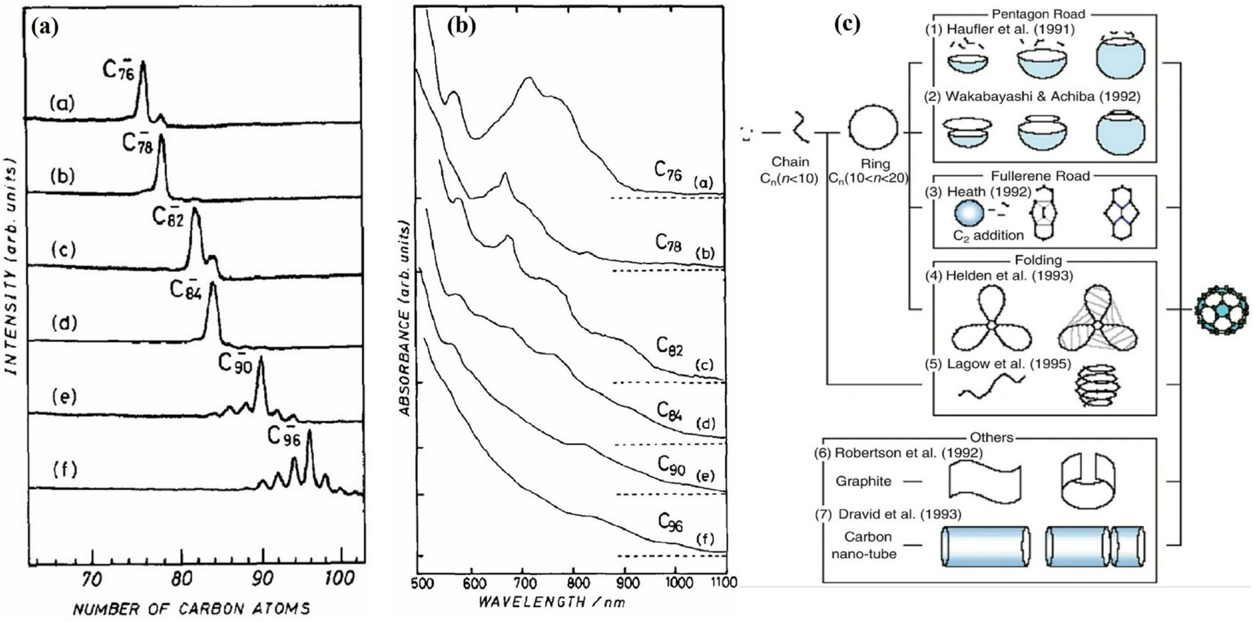

Fig 2 | Time-of-flight negative ion mass spectra of isolated fullerenes (b) Optical absorption spectra of fullerenes in benzene solution at room temperature (Reprinted from [12] Copyright (1992), with permission from Elsevier) and (c) The hypothetical fullerene formations model. Reprinted from [13] copyright (1998) with permission from Begell House, Inc

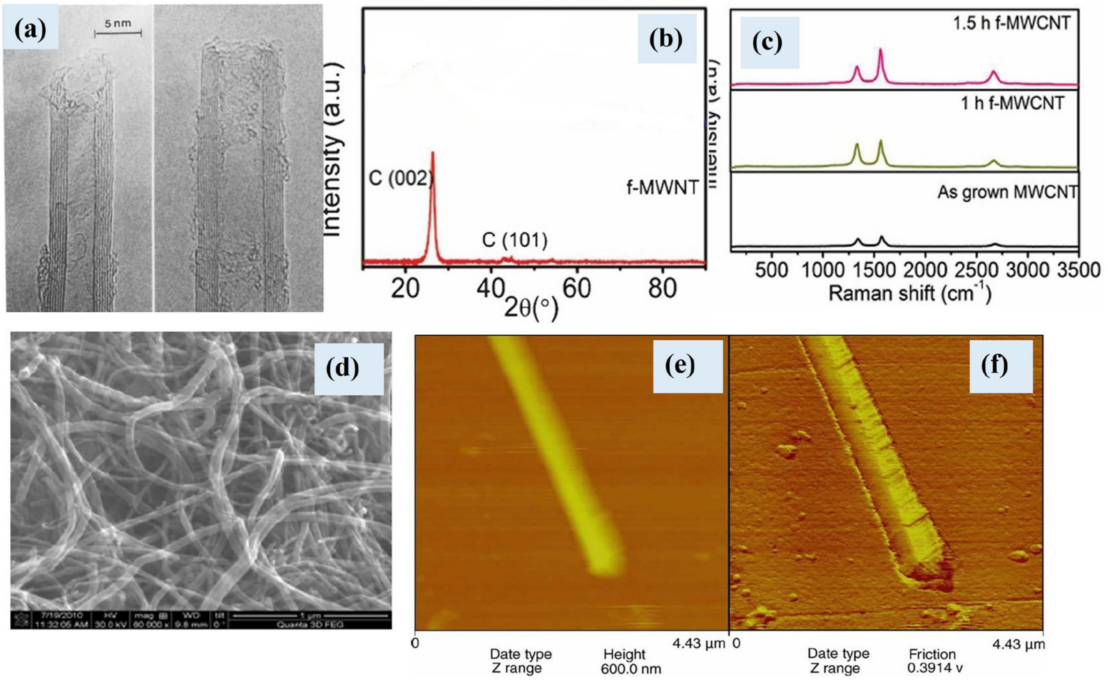

Fig 3 | (a)TEM images showing open ends of MWNTs (Reprinted from [15] Copyright (1993), with permission from Elsevier) (b) Powder XRD of functionalized MWNT (Reproduced from [30]) (c) Raman spectra of MWNT with different functionalization timings (Reprinted (adapted) with permission from [28]. Copyright (2011) American Chemical Society) (d) FESEM image of purified MWNT (Reprinted from [31] Copyright (2011), with permission from Elsevier (e, f) AFM imagesof nitrogen-doped CNTs (Reprinted from [28], Copyright (2005), with permission from Elsevier)

exfoliation,[32] laser ablation,[33] plasma etching,[34] electrochemical exfoliation,[35] chemical reduction,[36] and photothermal reduction[37] techniques. Cai et al. reported the liquid phase exfoliation of graphite into graphene nanoplatelets by the high-power tip sonication method.[32] Achee et al. reported the electrochemical exfoliation of compressed graphite, and their method could produce graphene with high yield and large lateral size.[38] Graphene nanosheets produced in the form of stable aqueous dispersions by chemical reduction of graphene oxide and deposited onto graphite substrates were reported by Paredes et al.[39] The author has contributed to developing a two-step solar reduction technique to prepare graphene from graphite.[37] Figure 4 (a-e) shows the solar exfoliation technique and structural and morphological characterization of the prepared graphene material. Figure 4f shows the AFM image of single layer graphene prepared by Novoselov et al., by mechanical exfoliation.[8]

In the bottom-up method of production of graphene, the decomposition of carbon-containing precursors (gas/liquid) results in the formation of the hexagonal structure of graphene layers. The main techniques in this route are CVD, epitaxial growth,[40] and thermal pyrolysis.[41] Schematic diagram of the chemical vapor deposition of graphene from simulated coal pyrolysis gas is shown in Figure 4g.

There were also efforts to reduce graphene costs so that graphene could be commercialized for practi-cal purposes. For instance, researchers have reported cheaper materials, such as bio-waste,[42] food, insects, etc., for synthesizing graphene (Figure 4(h)).[43]

Properties of Carbon Nanomaterials: A Comparison

Table 1 provides a comparison of the electrical, thermal, and mechanical properties of all three carbon nanomaterials. The market price range of these materials and large-scale synthesis techniques from the literature are also outlined. Prices vary depending on the quality, and there still needs to be industry consistency considering all aspects of pricing for all these products. This may take some more time, as these are comparatively new materials with still expanding markets, and hidden costs like future legislation can be another factor.[45]

Developments in the Last Decade

Since their discovery, the trio of carbon materials attracted broad interest from researchers worldwide. The third candidate, graphene, after its discovery in 2004,[8] became one of the most researched, contemplated, and promising nanomaterials in the past decade. A patent search in the World Intellectual Property Organization's (WIPO) database with the keyword graphene at the end of November 2024 returned 229015 results between 2015 and 2024, much higher than the number of world patents in CNT (37034) or fullerene (8002) during the same period (Figure 5).

Figure 6 compares the global share of patents in carbon nanomaterials, and the significant contribution comes from China in all three categories of patents for materials. Perhaps this is the most substantial number of patent contributions from any one element of the periodic table. Now, this stems from the exclusive combination of unique properties of CNT and graphene, which are not achievable with standard materials,

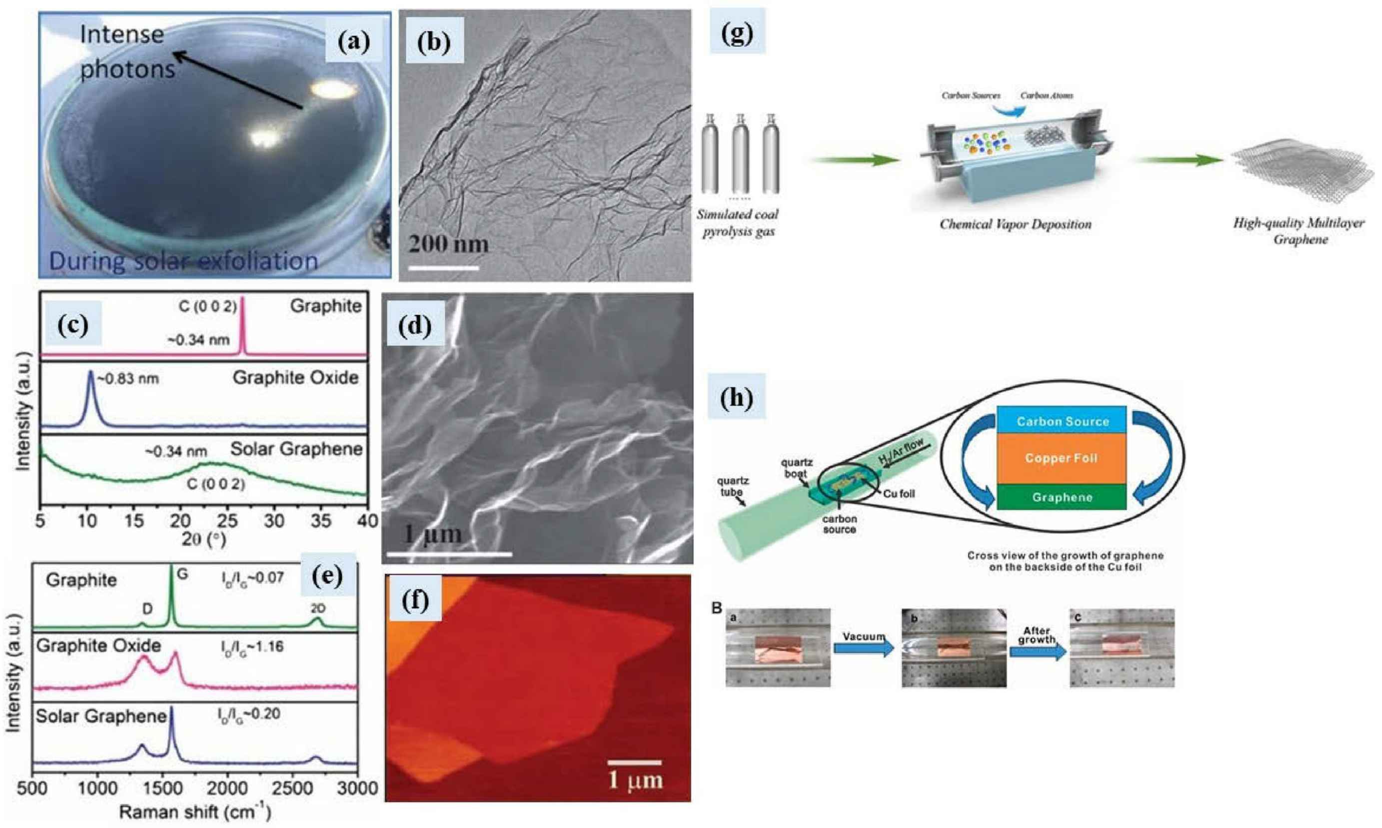

Fig 4 | (a) Photograph showing solar exfoliation of graphite oxide into graphene. The path of intense photons coming through the convex lens can be seen. (b) TEM image of solar exfoliated graphene (c) XRD and (e) Raman spectra of the precursors: graphite, graphite oxide and solar exfoliated graphene (d) FESEM image of solar graphene (Reprinted with permission from [37] (f) AFM image of single layer graphene (From [8]. Reprinted with permission from AAAS) (g) Schematic diagram of the chemical vapor deposition of graphene from simulated coal pyrolysis gas (Reprinted from [44] Copyright (2011), with permission from Elsevier) (h) Diagram of the experimental apparatus for the growth of graphene from food, insects, or waste in a tube furnace (Reprinted (adapted) with permission from [43] Copyright (2011) American Chemical Society)

Table 1 | Properties comparison of carbon nanomaterials

Material	Electrical Conductivity	Thermal Conductivity	Tensile Strength	Cost	Scalable Techniques
Fullerene	2×10^{-5} S/cm[46]	0.4 W/mK[47]	50 GPa[48]	35–250/g[49,50]	Combustion[51]
SWNT	283–1369 S/cm[52]	3500 W/mk[53]	25–66 GPa[54]	75–300/g[55]	CVD,[56] Floating catalyst CVD[57]
Graphene	$(1.46 \pm 0.82) \times 10^4$ S/cm[58]	$(4.84 \pm 0.44) \times 10^3$ to $(5.30 \pm 0.48) \times 10^3$ W/mK[59]	130 GPa[60]	20–2000/kg[61]	Liquid phase exfoliation,[62] CVD[63]

and this paved the route for the exploitation of carbon nanomaterials in a wide variety of applications.

Figure 7 outlines some of the major properties and applications of all three carbon nanomaterials. The developments in energy applications, mainly fuel cells, during the last decade, will be examined further in this review.

Contributions to the Energy Sector

The biggest challenge in the twenty-first century for humankind is to find an efficient alternative to fossil fuels to achieve a sustainable society devoid of environmental pollution. Carbon nanomaterials such as CNT and graphene play a vital role in advanced energy storage systems, with their charge storage capacity and good electrical properties. Research reports on carbon nanostructures as electrodes for fuel cells, solar cells, lithium-ion batteries, and supercapacitors indicate promise toward establishing a renewable energy economy based on such materials.

Figure 8 displays the patent statistics with the search terms “graphene and specific application” in WIPO over the last decade, where the applications are fuel cells, solar cells, supercapacitors, and Li-ion batteries. The consistent application of graphene in all four energy sectors shows its potential as a future material. Also, graphene’s exploration in the field of solar cells is much more prominent than that of other sectors. Graphene’s excellent electrical conductivity, transparency, and flexibility make it a promising catalyst-supporting material in solar cells.[64] A similar search with CNTs shows an interesting trend in different fields. CNT’s contribution to Li-ion batteries and supercapacitors has shown steady progress over the decade, as opposed to solar cells in the case of graphene. Overall, the number of patents published in graphene-based applications far exceeds CNT’s. A similar search with fullerene returned 39, 26, and 8 results for batteries, solar cells, and fuel cells, respectively (Figure 9).

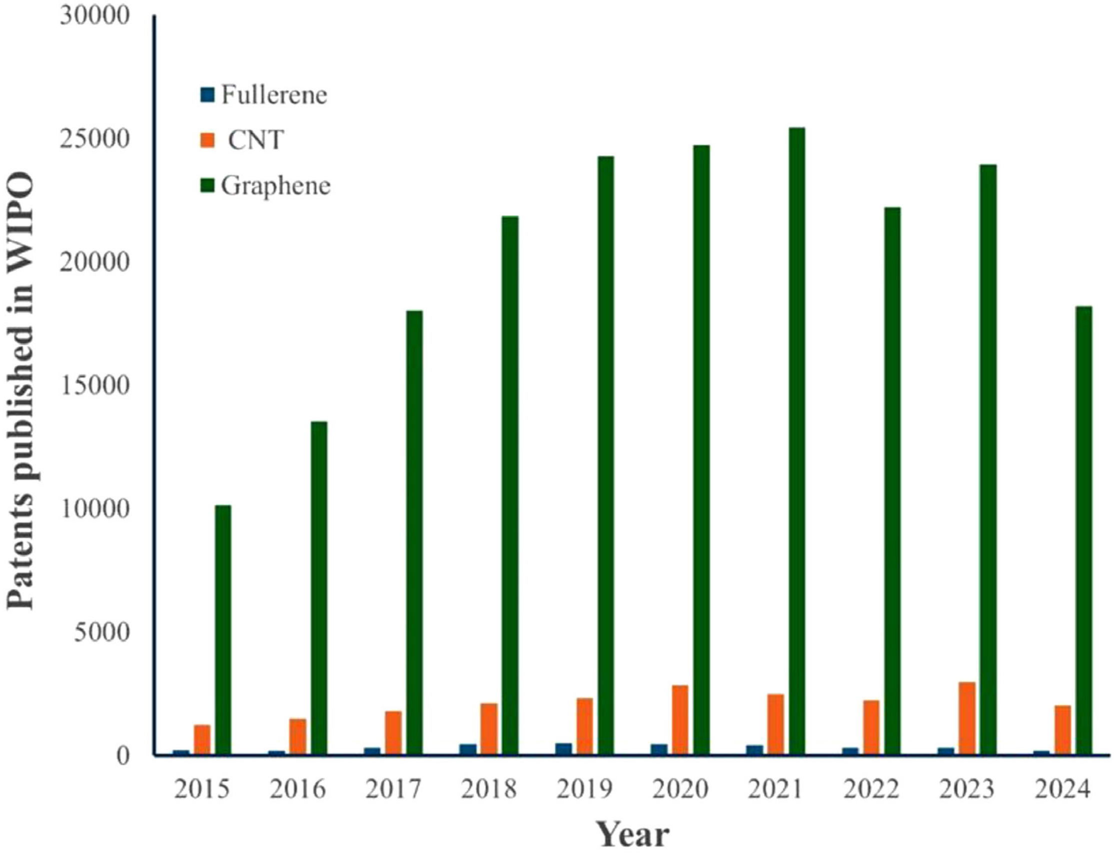

Fig 5 | A comparison of the number of world patents published in WIPO in the last decade in graphene, CNT, and fullerene research fields

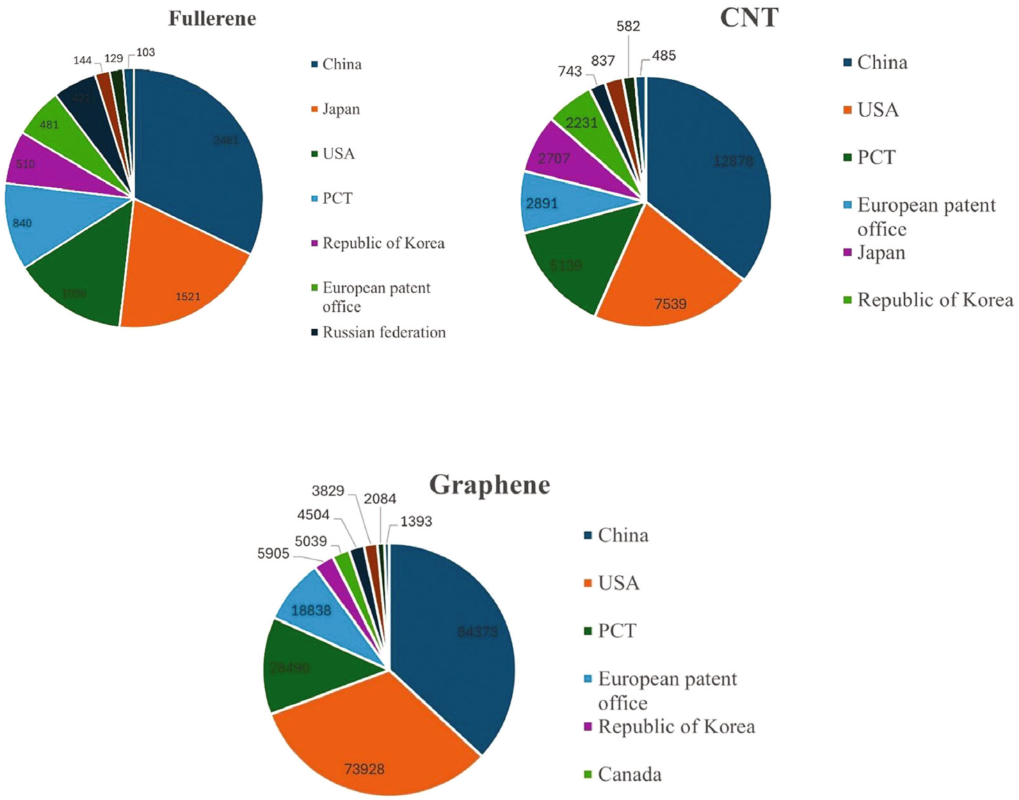

Fig 6 | Global patent share in the trio of carbon **nanomaterials**

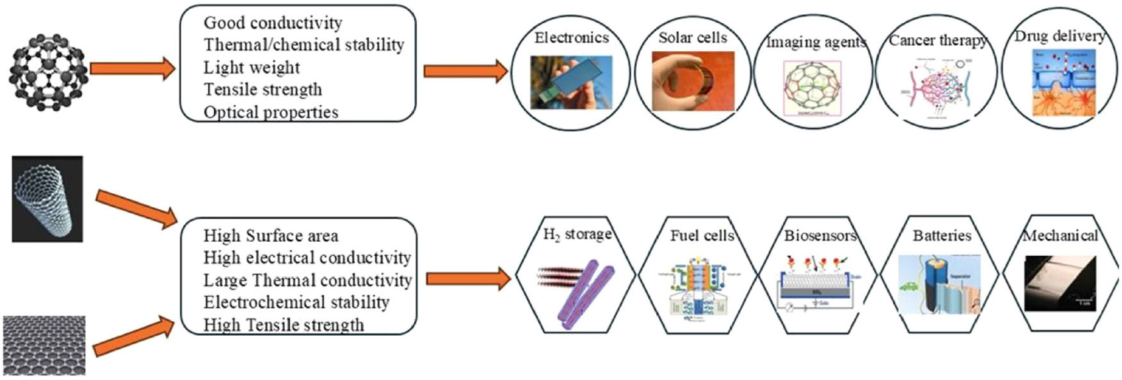

Fig 7 | Real-world applications of carbon nanomaterials

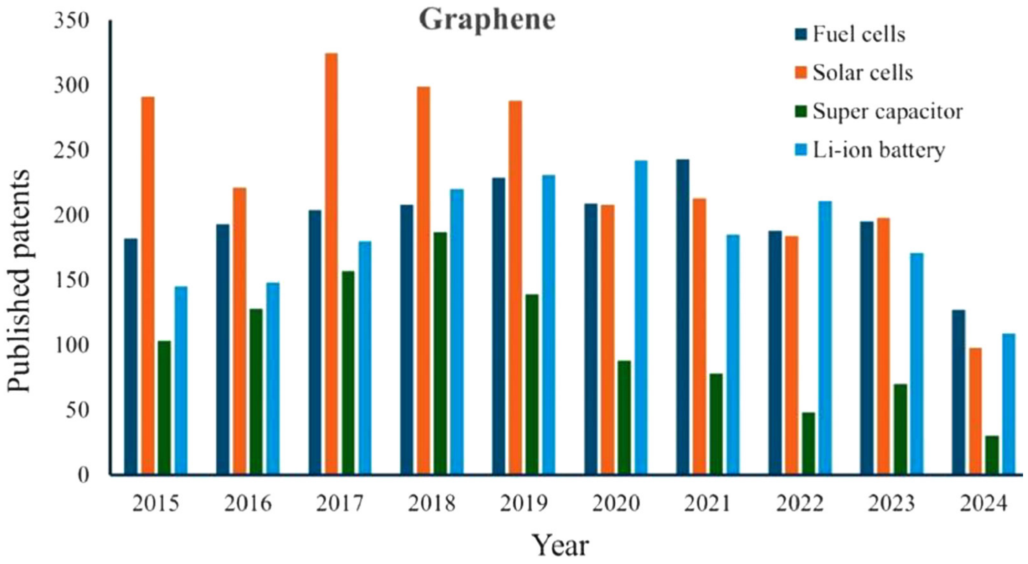

Fig 8 | World patent applications of graphene in different energy sectors in the last decade

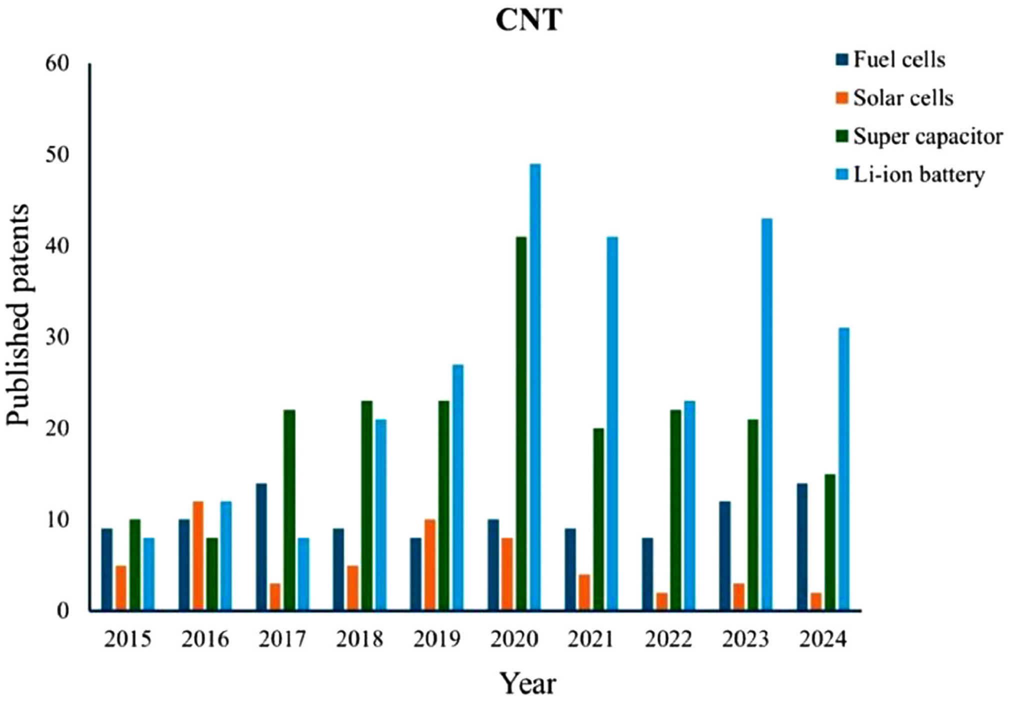

Fig 9 | World patent applications of CNT in different energy sectors in the last decade

CNTs in Fuel Cells

CNTs as catalyst supports are of better durability and catalytic activity compared to conventional support materials such as carbon black. Pt-dispersed CNTs with good electrocatalytic properties and better electronic transmission have been considered potential electrocatalysts for various types of fuel cells. Figure 10(a) shows the photographs of catalyst-coated carbon cloths, Nafion membrane electrolyte, the pressed membrane electrode assembly (MEA), gas diffusion plates, and the assembled single cell prepared by the author. A recent study by Youn et al. reported the fabrication of flexible polymer electrolyte membrane (PEM) fuel cells in which they incorporated raw and purified CNT sheets. Their study showed that purified CNTs improved contact resistance, leading to better performance than other flexible PEMFCs (Figure 10b). Figure 10c shows the images of the purified CNTs-based flexible PEMFCs under different curvatures.[65] It has been reported that nitrogen doping on CNTs is an effective strategy to improve the oxygen reduction reaction while employing CNTs in fuel cells, due to enhanced active sites.[66] Nair et al. employed a simple thermal pyrolysis technique to synthesize N-doped CNTs using melamine as a carbon and nitrogen source.[67] Further, they have synthesized the electrocatalyst (Pt/N-CNT) using the microwave-assisted polyol method to decorate Pt nanoparticles. Figure 10d shows the CVD experimental setup, and the histogram in Figure 10f portrays the change in ECSA before and after a 5000-cycle stability test in 0.5 M H_2SO_4 and % ECSA loss. The reduction of ECSA mainly comes from the dissolution and Pt particle agglomeration. The authors have attributed the enhanced ECSA in the case of N-doped material to the better anchoring sites offered by N-doping to the Pt particle dispersion and the resultant durability improvement and loss reduction. N-doped CNTs are attractive candidates for other kinds of fuel cells as well. A study by Forootan Fard et al., using PtRu/N-CNT for direct methanol fuel cells, reported that the addition of N to the structure of CNTs considerably enhances the physical and electrochemical characteristics of the catalyst.[68] The power density curves comparing three different MEAs clearly show a large difference in current density and power output in the case of the fuel cell with N-doped material (Figure 10d).

Hanif et al. reported the synthesis and alkaline fuel cell performance of NiCo-N-doped CNTs as cathode catalysts with a power density of 65 mW/cm^2.[69] FESEM image of NiCo/NCNTs can be seen in Figure 10(e) and a comparison in Tafel plots in Figure 10(f) clearly shows a smaller Tafel slope for the NiCo/NCNTs, implying its better ORR activity compared to Pt/C. The authors attributed the improved electrochemical performance and stability to the synergetic effect of the nitrogen-doped CNTs and the Ni/Co-active sites. Another interesting application of CNTs in fuel cells reports the development of sulfonated polysulfone-based composite PEMs filled with polydopamine-modified CNTs. As such, prepared PEMs have been employed in direct methanol fuel cells, resulting in a 75% decrease in methanol permeability compared to the Nafion® 117 membrane.[67] Recently, Ganguly et al. reported the preparation of Pt-decorated N-doped etched CNTs and compared their properties and electrocatalytic activities against commercial Pt/C, Pt/CNT, Pt/N-doped CNT, and Pt/etched CNT.[68] The superior fuel cell performance of the Pt/NECNT catalyst has been ascribed to the N-doping and surface modification of CNT support.

Graphene in Fuel Cells

Graphene is investigated as an electrocatalyst support in fuel cells, owing to its ability to improve the number of active sites and accelerate the transport of

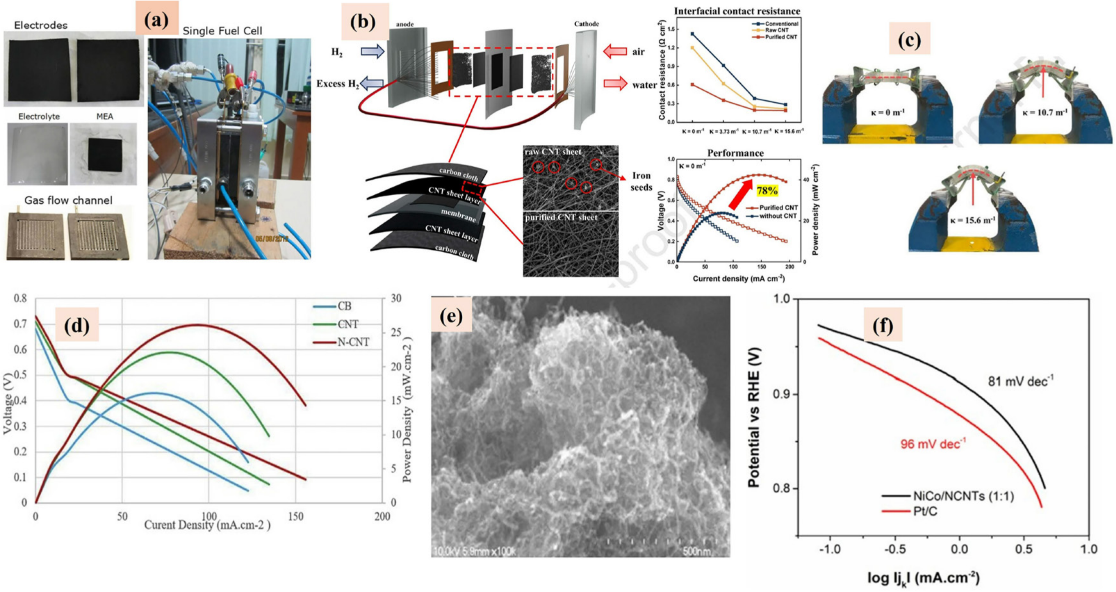

Fig 10 | (a) Photographs showing the components of the PEM fuel cell and single cell assembly (b) schematic of flexible PEMFC withvarious components and a performance comparison showing improved performance (Reprinted from [65], Copyright (2025), with permission from Elsevier) (c) Flexible PEMFCs under different curvatures (Reprinted from [65], Copyright (2025), with permission from Elsevier) (d) polarization study of PtRu/N-CNT based direct methanol fuel cell illustrating the enhanced performance with N-doping (Reprinted from[68] Copyright (2020), with permission from Elsevier) (e) FESEM image of NiCo/NCNTs (f) Tafel plots of Pt/C andNiCo/NCNTs (Reprinted from [67] Copyright (2020) with permission from Elsevier)

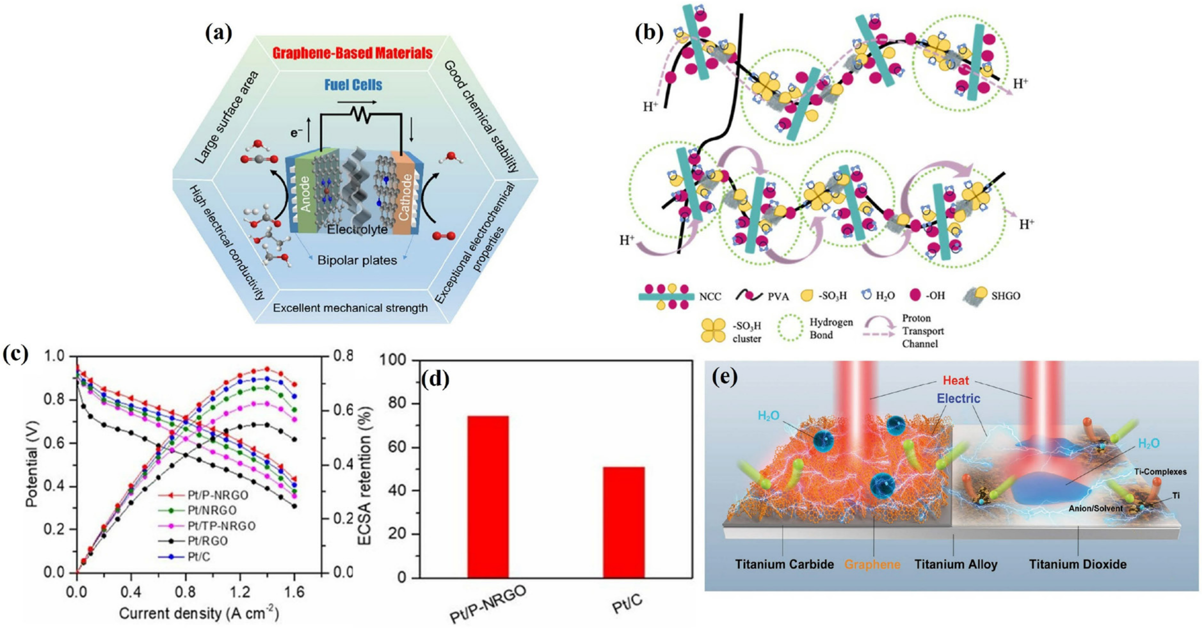

Fig 11 | (a) Schematic showing graphene-based materials in each component of the fuel cell (Reprinted with permission from [74]) (b) Suggested proton transfer mechanism of nanocrystalline cellulose/PVA-sulfonated holey graphene oxidenanocomposite membrane (Reprinted from[80], Copyright (2023), with permission from Elsevier) (c) Fuel cell performance comparison showingthe superiority of porous nitrogen doped reduced GO based electrocatalyst (d) Accelerated durability test of the porous nitrogen doped reduced GO based fuel cell vs commercial Pt/C based fuel cell (Reprinted with permission from [78]) (e) Schematic of vertical graphene-Ti alloy with enhanced conductivities, corrosion resistance and hydrophobicity (Reprinted with permission from [79])

electrons for both half-cell reactions. The possibility of exploiting graphene in other fuel cell components has also been investigated to improve the overall efficiency, durability, and electrochemical performance of the fuel cells. For instance, graphene-based materials are incorporated in polymer membranes to improve ionic conductivity and minimize the crossover of fuels.[72] Another application of graphene-based materials in fuel cells is in the current collectors, wherein they help to improve the current collection, stability of bipolar plates, and fuel/air distribution.[73]

Figure 11a shows the schematic of a fuel cell with graphene-based materials in each component.[74] Graphene Oxide (GO) is also explored as an electrolyte for PEMFC in place of the expensive Nafion, due to its excellent physical and chemical properties arising from oxygenated functional groups. A mixture of GO paper and Nafion[75] and sulfonic acid functionalized GO were employed as electrolytes for fuel cell applications.[76] Tateishiet al. reported the performance of a simple H_2/O_2 fuel cell with a 100% GO paper as electrolyte and the proton conductivities at low relative humidity and 23–25°C.[77] Muhmed et al., introduced sulfonic acid group in graphene oxide (GO). The resultant sulfonated graphene oxide (SGO) and the hole effect on the graphitic plane of GO for SHGO on nanocrystalline cellulose/PVA shows improved proton conductivity of membranes by creating more interconnected proton transfer channels and promoting proton transfer across the membrane. Figure 11(b) shows the suggested proton transfer mechanism of nanocrystalline cellulose/PVA-sulfonated holey graphene oxide nanocomposite membrane.[80]

The polarization curves of Pt supported on different carbon materials in H_2-air PEMFCs are displayed in Figure 11c. Pt-dispersed on porous nitrogen-doped reduced GO (P-NRGO) exhibited the highest peak power density compared to the other three Pt/graphene catalysts. Possible reasons include a much better utilization of active sites for the catalyst in H_2-air PEMFCs than for the other three Pt/graphene catalysts, owing to the porous structure and high nitrogen content of P-NRGO.[78] Further, an accelerated durability test to check the durability of the MEA performance for evaluating the stability of catalysts for practical H_2-air PEMFCs shows that the MEA based on Pt/P-NRGO shows better performance (70% of initial ECSA after 30000 cycles of square-wave accelerated degradation test [ADT]) than that of commercial Pt/C (50%, Figure 11d). The authors concluded from this result that the Pt/P-NRGO has better stability and, hence, is a more suitable material in H_2-air PEMFCs than the commercial Pt/C catalyst.

Yu et al. reported another interesting application of graphene in fuel cells.[79] Metallic bipolar plates, a crucial component in PEMFCs, suffer from interfacial contact resistance between bipolar plates and gas diffusion layer as well as corrosion in acid operating conditions. However, surface reinforcement of titanium alloy by vertical graphene coating using plasma CVD reduces corrosion by 1–2 orders of magnitude and decreases interfacial contact resistance by ≈100 times in the simulated PEMFC operating environments. Figure 11e shows the schematic of vertical graphene-Ti alloy with enhanced electrical and thermal conductivities, corrosion resistance, and hydrophobicity.

Muhmed et al. reported the preparation of an organic-inorganic nanocomposite membrane with green material by incorporating sulfonated holey GO (SHGO) into the nanocrystalline cellulose/polyvinyl alcohol matrix as a PEM via the solution casting method.[80] The study concluded that sulfonation and the holey graphitic plane structure observed in SHGO could construct additional pathways for proton transport, resulting in better fuel cell performance. A Pt alloy integrated into a cobalt-nitrogen-nanocarbon matrix by a multiscale design principle for efficient oxygen reduction reaction in hydrogen-air fuel cells was reported by Huang et al.[81] This platinum-carbon integrated catalyst demonstrates 11.7 times higher mass activity than commercial Pt/C, remarkable durability, and a power density of 980 mW/cm^2. Recently, Chowdury et al, reported that Pt-free, GO-based fuel cells, and their best-performing catalyst N-rGO-AA@180, exhibited a maximum power density of 17.57 mW/cm^2 with a load current density of 87.50 mA/cm^2, better than the rGO-based fuel cells.[82]

CNT-G-Based Fuel Cells

Though CNTs offer better electrochemical durability than commercial carbon black, the functionalization process, often carried out to achieve better dispersion of Pt nanoparticles, can hamper their electrical conductivity. Graphene, on the other hand, can offer edge plane anchor sites for the Pt nanoparticles, and it has been suggested that the heterogeneity of carbon support with edge planes can better stabilize and enhance the catalytic activity of the Pt catalyst. However, the 2D graphene sheets tend to re-stack, and this can impede the transport of reactants inside the fuel cells. Several studies were reported to address this challenge. The growth of a hierarchical carbon nanostructure in which CNTs are grown directly onto Toray carbon paper and graphene is directly and densely grown onto the CNTs is reported by Pham et al.[83] The authors reported that the composite material possesses an ultra-high density of exposed graphene edges while retaining the porous structure of CNTs on carbon paper. An ultra-low loading of Pt onto the G-CNT hybrids is achieved by magnetron sputtering, and their hybrid electro-catalyst-based fuel cell demonstrated an enhanced polarization performance compared to a commercial carbon black-supported Pt catalyst. In another study, the same group reported the durability studies of these materials.[84] Figure 12A shows the polarization performance of the Pt/CNT, Pt/G-CNT, and Pt/ VXC72 electrode catalysts. The hybrid catalyst-based electrodes showed superior electrocatalytic performance over both commercial Pt/VXC72 and Pt/CNT cathodes throughout the current density range. Figure 12B

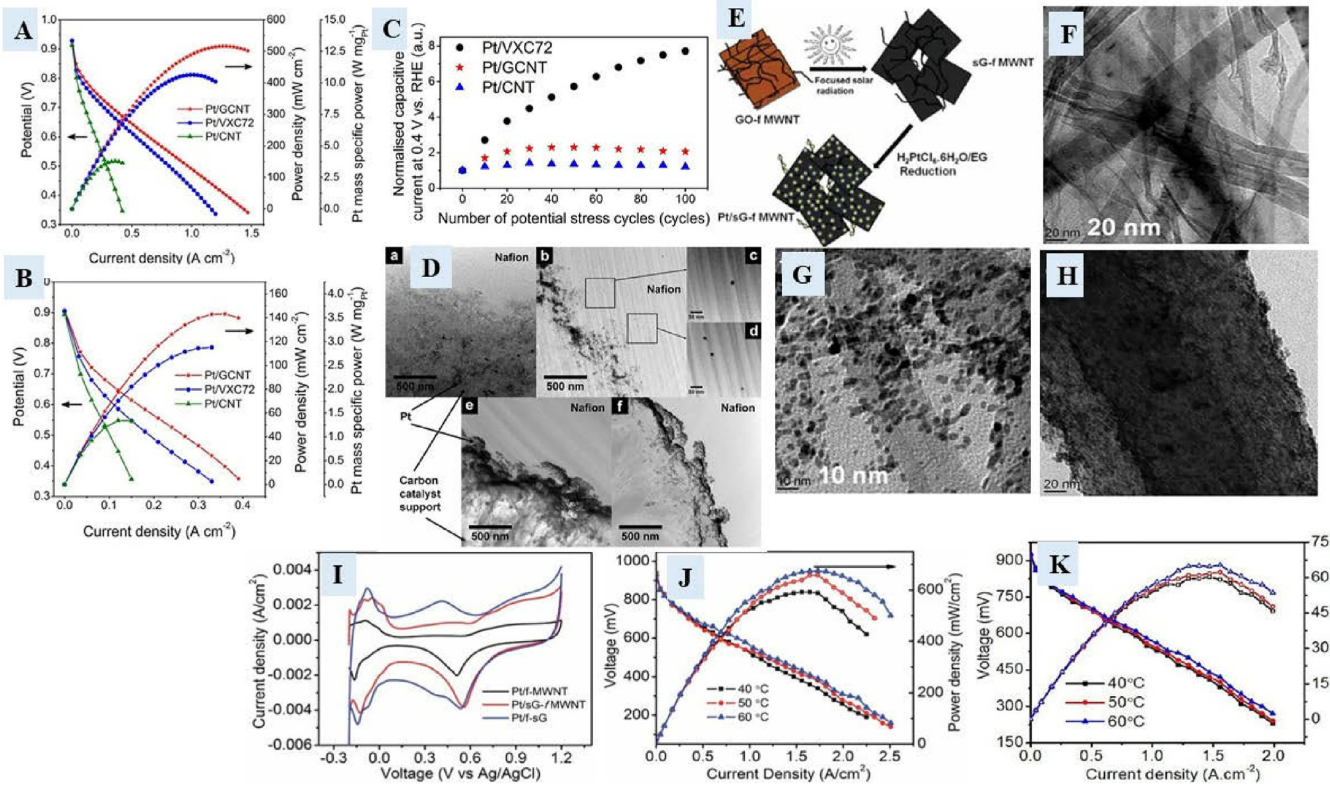

Fig 12 | Polarization curves of the Pt/G-CNT, Pt/VXC72 and Pt/CNT cathodes before (A) and (B) after the accelerated degradation test (C) carbon corrosion of the Pt/G-CNT, Pt/VXC72 and Pt/CNT cathodes during ADT, expressed in terms of relative changes in double layer capacitance (D) Electrode structural study using transmission electron microscopy. TEM micrographs of the Pt/VXC72cathode (a) before and (b) after ADT, with (c) and (d) magnified views of the re-deposited Pt nanoparticles inside Nafion membrane. TEM micrographs of the Pt/G-CNT cathode (e) before and (f) after ADT(Reprinted with permission from [84]) (E) Schematic showing the various steps in the synthesis of Pt dispersed solar graphene-MWNT composite material (F) TEM image confirming the formation of the hybrid composite material (G) TEM image of the Pt/sG-MWNT electrocatalyst depicting the uniform dispersion of the Pt particles (H) TEM image of Pt/CNT-G composite prepared by one step CVD technique (I) cyclic voltammograms of pure and hybrid composites based fuel cells (J) Polarization graph of Pt/sG-f MWNT (cathode catalyst) and Pt/f-MWNT (anode catalyst) and (Reprinted with permission from [85]) (K) Polarization graphs of fuel cells with Pt dispersed 1D graphene wrapped MWNT composite fuel cell (Reprinted with permission from [86]) compares the polarization performance after ADT of all three electrodes in order to examine the electrochemical stability of the Pt/GCNT. The CNT-graphene hybrid demonstrates a superior power output to the Pt/VXC72 and Pt/CNT cathodes in the entire range of the polarization curve.

The durability of the G-CNT-supported Pt catalyst, commercial carbon black-supported, and a CNT-supported Pt catalyst through an ADT is shown in Figure 12C. These studies and transmission electron microscopy imaging (Figure 12D) suggested superior electrochemical stability for highly crystalline graphitic nanomaterials, such as G-CNT and CNT supports, as compared to the commercial Pt/carbon black catalyst. Though their Pt/CNT electrocatalyst showed a lower catalytic activity than the commercial Pt/C catalyst, the Pt/G-CNT hybrid catalyst possesses an enhanced intrinsic catalytic activity. The study suggested the possibility of replacing the Pt/VXC72 commercial catalyst with a Pt/G-CNT hybrid catalyst owing to its higher catalytic activity (due to the high density of graphitic edges present in the hybrids) and superior electrochemical stability (arising from high crystallinity of the G-CNT support). Good stability, as expressed by a lower loss in polarization performance, a smaller increase in charge transfer resistance, a lower loss in the platinum electrochemical surface area, a lower rate of carbon corrosion, and a more stable catalyst microstructure, is an important aspect of sought-after catalyst material in fuel cells.

The author has reported a CNT-graphene hybrid composite preparation by a two-step CVD-solar reduction process in an attempt to use CNTs as spacers to avoid the restacking of graphene layers.[85] The combination of one-dimensional CNT and two-dimensional graphene has thus been investigated as a catalyst support material in fuel cells. Figure 12E shows the schematic for the preparation of Pt-dispersed graphene-CNT fuel cell catalyst material. The TEM images (Figures 12F and G) of the carbon hybrid and electrocatalyst are shown. The cyclic voltammogram (Figure 12I) of the hybrid composite material-based electrocatalyst is different from that of the pure catalyst supports, possibly due to the various crystalline (hkl) planes or differences in the shape of the nanoparticles in the CNT-G composite implying a possible governing of the morphology of Pt nanoparticles by the hybrid carbon nanomaterial. The polarization curve in Figure 12J of the fuel cell based on the Pt/graphene-CNT electrocatalyst resulted in maximum power densities of 592, 657, and 675 mW cm^2 at 40, 50, and 60°C, respectively. The study reported better performance with the hybrid composite-based fuel cell compared to the pure carbon nanomaterial-based fuel cell electrocatalysts. The ECSA measurement was also superior to the hybrid electrocatalyst. The enhancement in electrochemical performance with the hybrid nano composite-based MEA can be attributed to the synergistic effect of 1D MWNT and 2D graphene.

Another study from the same group developed a graphene-wrapped CNT composite using the CVD technique, and an electrocatalyst based on this composite material also showed promising results while employed in PEMFC.[86] Figure 12H shows the TEM image of the Pt/CNT-G 1D composite, and Figure 12K shows the power density curve of the material-based fuel cell. With this composite as well, the power density was higher compared to the pure catalyst-support-based fuel cells, and the authors attributed this to enhanced electrochemical reactivity and good surface area of the nanocomposites.

In summary, fuel cells are a promising alternative energy source with high electrical efficiency and zero emission, so the application of CNT, graphene, and CNT-graphene-based hybrid composites as catalyst support materials in various fuel cells has been discussed. However, future research efforts are required to employ carbon nanomaterials-based fuel cells for practical purposes. Optimization in material processing techniques and cost reduction are two significant areas to be considered. On a positive note, increased environmental awareness and developed governmental approaches have helped in promoting hydrogen FC applications in the decarbonization of stationary and mobile power and heat generation sectors. Such supports can, in turn, result in better cost and performance of hydrogen fuel cells similar to those of solar PV and batteries and thereby constitute an adaptable low-carbon option across the energy system.[87] Hence, there is considerable interest in integrating fuel cell technologies with the existing energy sources to smoothly transition to low-carbon energy supplies. According to the “Road Map to a U.S. Hydrogen Economy” report, the fuel cell and hydrogen sector is expected to generate 700000 jobs and USD 140 billion in revenue by 2030, which again is a positive sign for fuel cell technology.[88]

Challenges Toward Commercialization and Potential Solutions

Scalable and cost-effective manufacturing of carbon nanomaterials, especially SWNTs, is critical to achieving many of their real-time applications. Another important factor is the dependency of properties on the synthesis conditions, as different nanomaterial preparation conditions offer nanotubes with varying physical properties. Since specific applications require CNTs with certain physical properties, reproducible and scalable techniques are of utmost importance. Global CNT production over the past several years has focused mainly on low-cost MWNTs. SWNTs in randomly organized, powdered form are also mass-produced using CVD techniques, and these are adequate for certain applications like reinforced composites, Li-ion batteries, and electromagnetic shielding. However, applications of nanotubes in semiconductor electronics, filtration membranes, and advanced composites demand their controlled growth with tailored properties such as length, diameter, and helicity/orientation in order to meet the requirements of that specific application.[89] Control over the structure of SWNT is still a challenge due to limitations in catalytic conditions during CVD growth. Recent computational studies targeting SWNT growth mechanisms offer several insights into structure-controlled growth,[90,91] and advanced experimental techniques based on these simulation results can aid the manufacturing of such tailored nanotubes.

Like any other nanomaterial, the commercial application of graphene depends on the manufacturing of graphene powder and films of suitable morphology and quality by safe methods and in industrial capacity. Commercialization also depends on the economic takeover of other materials in current products by graphene.[92] Large-scale synthesis is often achieved by techniques such as CVD, two-step oxidation-reduction method, liquid exfoliation, and wet chemical synthesis.[63] Though CVD produces 2D films of sufficient quality under atmospheric pressure, the high-temperature reactions (above 500°C) resulting in high energy consumption and cost could be a drawback for industrialization.

On the other hand, liquid exfoliation can produce a large quantity of graphene under atmospheric pressure and at room temperature. However, graphene from this method suffers from apparently unavoidable damage and non-uniform nanosheet thickness. Mass production techniques of graphene nanoflakes must also be reproducible. Raw graphite materials from different sources will have different morphologies and may have diverse contaminants, leading to a range of quality and intrinsic properties of the exfoliated graphene flakes. Hence, the present commercial applications of small graphene nanoflakes are limited in areas such as additives in composites, wherein repeatability and consistency of performance are not serious concerns.[92]

Wet chemical synthesis provides controllability of crystallite size and surface morphology of 2D materials and allows direct synthesis of materials on desired substrates, though with long synthesis times. These syntheses, unfortunately, involve the use of corrosive chemicals most of the time. Furthermore, the surfactants and solvents used in graphene synthesis, as well as graphene products themselves, would cause pollution, and some active oxidizing species are known to be susceptible to detonation.[92] Hence, it is very important to employ green and safe processes/techniques for the production, storage, transport, and application of graphene nanoflakes at the industrial scale. The author has reported a solar-induced green reduction route to prepare large-scale quantities of powder graphene.[37] The advantage of this technique was that the reduction process was devoid of any chemicals and also that the reaction happened at a low temperature. For an elaborate reading on this topic, Yu et al. recently reported a review on green synthesis techniques for graphene.[93]

The development of artificial intelligence has stimulated remarkable transformations in materials science, through its capability to discern patterns and formulate predictions from data.[94] AI models can reveal connections between material properties and their underlying crystal structures by analyzing experimental data and computational simulations.[95] Inverse design methodologies, combined with machine learning models, have also been employed for predicting material properties, which can considerably shorten material development cycles.[96] AI-assisted approaches can also be employed in high-quality graphene preparation strategies and the production of application-tailored materials. Research exploring the frontier of autonomous material synthesis via an artificial neural network, specifically focusing on the streamlined production of graphene, is a promising study in this direction.[97]

Conclusions and Future Perspectives

During the last several years, the paramount interest in carbon nanomaterials, especially CNTs and graphene, could be justified by the multitude of publications and patents describing their distinguishing characteristics, which could be exploited for diverse applications. The uniqueness of carbon nanomaterials also comes from the awarding of two Nobel prizes over a short span of 15 years for discovering fullerene and graphene and the Kavli prize for contributions to the nanoscience and discovery of CNTs. Hence, the present review outlines the story behind the discovery of these unique carbon nanomaterials and primary synthesis techniques that have been reported in the literature during the last couple of years. These novel materials have promising applications in renewable energy production and storage, bio-nanotechnology, photo/electrocatalysis, mechanical/structural composites, and other fields. However, the economical, safe, and scalable production of carbon nanomaterials is still a developing field. With the advent of artificial intelligence, materials science is witnessing a new era of innovative synthesis approaches. Combined with machine learning models, inverse design methodologies can be vital in predicting material properties, considerably shortening the material development cycles.

Fuel cell technologies and applications can play a significant role in strengthening energy security and promoting the decarbonization of all energy sectors. Over the last couple of years, fuel cells have influenced various industry sectors, producing clean and dependable power for networks of various characteristics, establishments, and vehicles, and hydrogen fuel cells are one of the most sought-after technologies coming to the market. In this context, the review was focused on some of the major developments in fuel cell technology using unique carbon nanomaterials. However, large-scale commercial applications of carbon nanomaterials-based fuel cells may require more research and development efforts, as high costs and issues with scalable processing techniques limit their wide-range applications. Even then, increased environmental awareness and eco-friendly governmental policies in light of global warming are promising factors that can accelerate the decarbonization of stationary and mobile power and heat generation sectors.

The carbon nanomaterials market is a rapidly evolving sector driven by the unique properties and applications of CNTs, graphene, and fullerenes. In 2024, the carbon nanomaterials market size was USD 3.2 billion and is forecast to achieve USD 8.5 billion by 2033, with an 11.5% CAGR from 2026 to 2033.[98] Advancements in nanotechnology, increased industry demands, and an ever-expanding need for sustainable materials with reduced environmental impact and better performance can all contribute to the carbon nanomaterial market growth. Each carbon nanomaterial can play its role in the energy landscape. For instance, in the case of PEM fuel cells, graphene can offer better durability and conductivity, while CNTs come with good mechanical strength and electron transport properties when used as catalyst supports. Hybrid approaches have been proven to circumvent the intrinsic challenges associated with individual materials, and graphene-CNT hybrid composites can be a better option for high-performance fuel cells and energy storage applications.

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