

Perspective

## Story of carbon nanotube in energy—Booms and lapses?

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**Abstract:** In light of eras of scientific endeavors on carbon nanotubes and related nanomaterials, we notice extending applications of carbon nanotubes from high-tech energy/electronic devices to defense, engineering, and medical fields. Carbon nanotubes, being one of the initial nanocarbon technology breakthroughs, emerged as a frontline competitor for designing advanced energy devices/systems. As per literature so far, carbon nanotubes render valuably high specific surface area/properties, design adaptabilities, structural synergies, low expenses/density/toxicity, interfacial/percolation effects, and desirable energy storage (charge/electron flow, capacity/capacitance, capacity retention, reversible discharge, cyclic span, etc.) and energy conversion (power conversion efficiencies, energy/power density, photovoltaic effects, durability, etc.) parameters for devices. Looking at the up-to-date demand for carbon nanotubes in high-end energy storage and conversion systems (batteries, capacitors, photovoltaics), this perspective manuscript is planned to unveil the actual state-of-the-art and advancements in this field. Despite the success to date, real-world employment of carbon nanotube-derived energy systems seems to rely upon overcoming challenges for integrating these nanomaterials in next-generation energy assemblies. To meet current technological necessities, green-sourced carbon nanotube nanomaterials must be practiced for modern and future sustainable energy industries.

**Keywords:** carbon nanotube; nanocomposite; energy storage; energy conversion; supercapacitors; batteries; solar cells

## 1. Introduction

Among promising energy harvesting/storing systems, batteries, capacitors, and photovoltaics accomplished immense curiosities of the current scientific and nanotechnological era [1]. To enhance design specifications and energy device parameters, efficiencies, and performance, wide-ranging pristine as well as hybrid nanomaterials have been explored by the field researchers [2]. With advancements in the arenas of nanocarbon nanostructures, the worth of carbon nanotubes (one-dimensional miraculous nanoentities) has been analyzed in countless technical zones, like engineering, energy, and electronics, to mention a few. Specifically, in energy systems, wonders and victories of carbon nanotubes and derived nanomaterials have been observed for efficient charge/energy storage and solar to electrical energy/power conversions [3]. Herein, we note abundant scientific reports on the implementation of carbon nanotubes and derivative nanomaterials in energy maneuvers. Owing to structure-property uniqueness, carbon nanotubes and related nanostructures subsidized state-of-the-art design/architectures of lithium and other storage batteries, asymmetrical supercapacitors, and solar cells, revealing radically superior device parameters and efficiencies.

As compared to presently marketable inorganic energy-storing/harvesting systems, integrating carbon nanotubes in these devices depicted merits of low

expenses, low density, transparency, flexibility, facile processing, charge/electron passaging, and photo/thermal/chemical stability, leading to high-end energy device performance [4]. Nevertheless, using carbon nanotubes and related nanostructures in energy devices suffers from a number of challenging factors, including limited lifespans, efficiencies, environment-dependent performance variations, lack of understanding of working/degradation mechanisms, and others, as discussed in other sections of this manuscript. Unfortunately, such factors seem to be causing major sprints hindering effective disposition of carbon nanotubes in industrial-level batteries and photovoltaics. To resolve these technical glitches, we suggest focused future research and ecological/sustainable design innovations to unfold the commercial significance of carbon nanotubes and allied nanomaterials in energy applications.

This perspective manuscript expansively showcases structural/physical properties/performance aspects of carbon nanotube nanomaterials in today's most necessitating energy storage/conversion systems. Presently, there are lots of competing nanocarbon contenders (graphene, fullerene) for energy systems, so we planned this perspective review as a handy guideline for struggling scientists/researchers seeking future opportunities of carbon nanomaterials in this field. By judging the present state of carbon nanotube-related energy technologies, we can say that more thorough surveys must be accomplished for designing proficient, functional, and green/sustainable carbon nanotube nanocomposites for future energy industries.

## 2. Carbon nanotube—A nanotechnology initiator



**Figure 1.** Aspects of carbon nanotube.

Since discovery (1991), carbon nanotubes have emerged as one of the most widely studied carbon nano-allotropes [5]. It is a one-dimensional hollow cylindrical nanocarbon made up of hexagonally arranged  $sp^2$  hybridized carbon atoms. Depending upon the number of overlapping cylinders, carbon nanotubes have been

named as single-walled, double-walled, or multi-walled nanostructures in the literature. Single-walled carbon nanotubes have a diameter of ~1–2 nm and a length of ~100 nm to a few  $\mu\text{m}$ . These unique one-dimensional nanoentities have been prepared via numerous efficient top-down/bottom-up methods such as chemical vapor deposition, laser ablation, arc discharge, catalytic, and chemical methods (**Figure 1**).

Various state-of-the-art technologies have been considered for the synthesis, purification, and characterization of carbon nanotubes. Hollow nanotubes with high surface area have been frequently prepared using three important techniques, including chemical vapor deposition (CVD), arc discharge method, and laser ablation methods [6]. The arc discharge method demands high temperature and vacuum conditions for condensing carbon vapors in the presence of an arc discharge and inert atmosphere; however, it showed a disadvantage of impurities in the final carbon nanotube product. The laser ablation technique (laser source for carbon evaporation) allows controlled synthesis parameters for synthesizing precisely controlled carbon nanotube dimensions; nevertheless, cost and impurities remain as major concerns. In addition, these methods face challenges of amorphous carbon and metal catalyst impurities. Herein, traditionally used large-scale synthesis techniques have been noticed as CVD (carbonizing hydrocarbon gas at very high temperature, 1000 °C) and related methods, such as plasma-enhanced CVD and inductively coupled plasma CVD approaches. Furthermore, regarding carbon nanotube purification, nonecological chemical methods have been used on a lab scale; nonetheless, annealing methods have been preferred for efficient and scalable purification. To analyze specific atomic structure and physical and chemical characteristics of carbon nanotubes, a number of experimental as well as theoretical techniques have been practiced. Notably, infrared spectroscopy, Raman spectroscopy, X-ray diffraction, neutron diffraction, and microscopic techniques have been used to validate these nanostructures. Notably, microscopic techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been widely used to analyze various characteristics of carbon nanotubes [7]. In this regard, carbon nanotube shape, length, diameter, crystallinity, packing, bundling, defects, composition, etc., have been analyzed using SEM and TEM techniques.

Generally, carbon nanotubes have notable features of high surface area, aspect ratio, unique microstructure, chirality, optical/electronic/magnetic properties, electron/charge transport, thermal conduction, mechanical/thermal constancy, and other physical characteristics [8]. Reliant upon structure-property inimitability and efficacy of synthesis technique used, we noted applications of carbon nanotubes in the fields of energy devices, electronics, aerospace/automotive/defense, membranes/coatings, civil, textile, sports, and biomedical, to name a few.

Remarkable advancements in the field of carbon nanotubes revealed its use in the form of scientifically important nanomaterials/nanocomposites [9]. In this concern, abundant researchers have been observed in varying nanotechnological disciplines for a myriad of valuable morphological, mechanical, thermal, electrical, dielectric, tribological, rheological, non-flammability, anticorrosion, and allied beneficial features of high-performance polymer/carbon nanotube nanocomposite designs. In nanocomposites, carbon nanotube concentration, surface functionalities, interaction

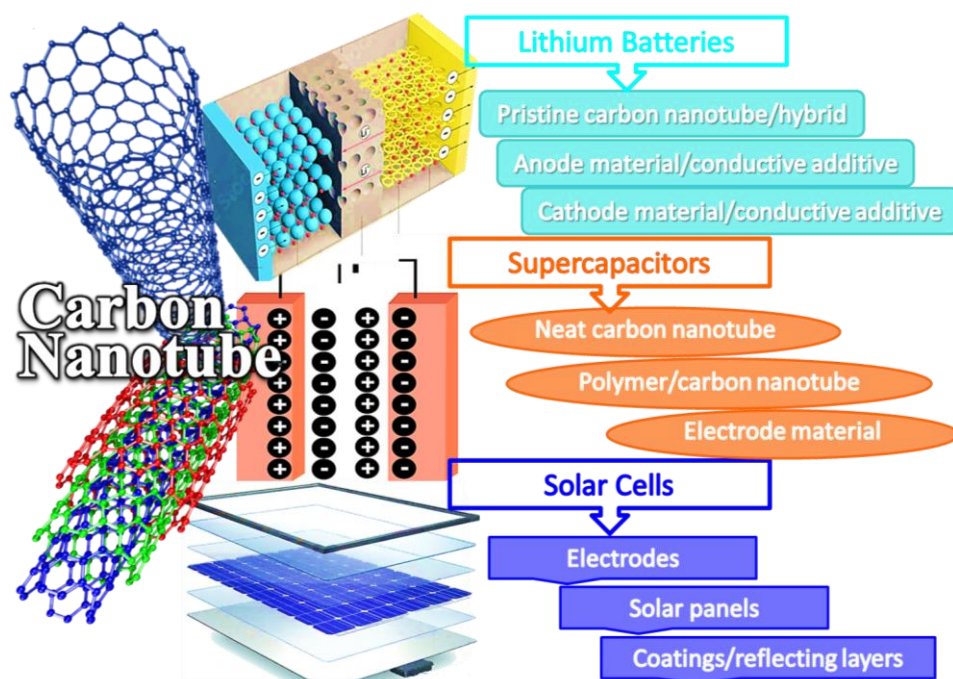
with matrices, and appropriate processing routes affect the final material properties and applications.

In this concern, we found countless applications of polymer/carbon nanotube nanocomposites in almost every known nanotechnology discipline, ranging from space/automotive to sophisticated devices and biological sectors. An important use of carbon nanotubes can be seen as electrocatalysts for water splitting and hydrogen evolution reactions desirable for advanced sustainable clean energy technologies [10,11]. Other notable applications of carbon nanotubes can be seen as pollutant (dyes, ions, drugs, organic toxins) adsorption and removal, as well as photodegradation, under varying pH, temperature, and environmental conditions [12].

Especially when we talk about applications like energy storage and conversion systems, electronic devices, electrostatic coatings, etc., polymer/carbon nanotube nanocomposites have been found practicable owing to distinct electronic, optoelectronic, electrical, and dielectric features [13]. It seems that dispersion/alignment of nanotubes in polymeric phases may develop continuous electron/charge-conducting networks, electron tunneling, and percolation effects useful for energy device applications. In the following sections of this novel article, indispensable aspects of carbon nanotubes and derived materials in energy sectors have been debated.

### **3. Victory of carbon nanotube in energy storage/conversion scenarios**

After decades of scientific endeavors on the fundamentals and uses of carbon nanotubes, a multitude of nanocomposites/hybrids have been found competent for energy systems (**Figure 2**). In this regard, we note considerable literature reports on advanced energy storage/conversion devices using carbon nanotube-derived nanomaterials [13]. Among energy storage batteries, carbon nanotubes have been successfully applied to form components (mostly electrodes) of lithium-ion batteries, lithium-sodium batteries, lithium-sulfur batteries, zinc-carbon batteries, and so on. Among previous attempts, Chen et al. [14], for example, synthesized carbon nanotubes by in situ chemical vapor deposition for lithium battery anodes. They reported high surface area ( $> 1800 \text{ m}^2 \text{ g}^{-1}$ ), pore volume ( $> 1 \text{ m}^3 \text{ g}^{-1}$ ), and reversible capacity ( $> 1100 \text{ mAh g}^{-1}$ ) over repeated cyclic performance. With polymers, like polypyrrole, carbon nanotubes depicted a capacity of  $> 600 \text{ mAh g}^{-1}$  when used as lithium battery cathodes [15]. In a very recent report by Liu et al. [16], rice husk-derived green carbon nanotube nanocomposites were designed for lead carbon battery electrodes. They reported a sustainable capacity (10 times higher than the non-carbon nanotube battery) in  $\sim 5000$  cycles, due to the high specific surface area and hierarchically nanoporous architecture of carbon nanotube. Similarly, abundant research articles and reviews have been seen so far on the use of carbon nanotube and polymer/carbon nanotube as modern flexible battery electrodes [17].



**Figure 2.** Carbon nanotube nanotechnology for energy—Batteries, supercapacitors, solar cells.

Similarly, a bulk of old and new literature reports have been perceived for carbon nanotube hybrid-derived supercapacitor components [18]. A worth mentioning recent report by Liu et al. [19] documented carbon nanotube/graphene quantum dot hybrid-based supercapacitor electrodes. They found outstandingly high electrochemical performance of ensuing supercapacitor devices in the form of specific capacitance ( $> 2000 \text{ F g}^{-1}$ ), energy density ( $> 94 \text{ Wh kg}^{-1}$ ), and power density ( $> 800 \text{ W kg}^{-1}$ ) characters. As per our analysis, synergistic interfacial effects and the structure-property relationship of carbon nanotubes towards hybrid components (nanocarbons, metal ions, or polymers) play a crucial role in enhancing capacitance and energy/power density of supercapacitors.

In today's most demanding renewable energy conversion systems, like solar cells, carbon nanotubes as well as carbon nanotube hybrids have been employed as advantageous nanomaterials to enhance device efficiencies [20]. Notably, utilization of these nanomaterials has been investigated for silicone solar cells, perovskite solar cells, dye-sensitized solar cells, bulk heterojunction solar cells, organic solar cells, etc. As per literature so far, chemical/physical deposition, solution, spin coating, etc., type techniques have been frequently used to form high-performance solar cell electrodes and coating materials, showing considerably high photovoltaic efficiencies, even beyond 20% [21]. A latest study by Wang et al. [22], for instance, stated a markedly high power conversion efficiency of  $\sim 17\%$  via bis(3-aminopyrid-2-yl) sulfide/carbon nanotube-based perovskite solar cell. In addition,  $\sim 89\%$  solar cell efficiency was retainable even after a prolonged working life of  $\sim 700 \text{ h}$ , probably due to the stability and interface passivation effects of the carbon nanotube-based nanostructure. In the field of solar cells, carbon nanotubes seem to offer economical ways to future energy industries via stable solar cell designs having malformed absorption of solar radiation. Furthermore, carbon nanotubes offer high specific surface area, electrical

conductivity, donor-acceptor interfaces, charge carrier transportation networking, optical transmittance, physicochemical features, low sheet resistance, and other valuable properties for high-tech solar cell components. On the basis of all these characteristics, we can suggest carbon nanotubes as next-level nanomaterials to replace expensive and environmentally toxic electrode materials (e.g., ITO) in traditional solar cell devices. Even so, the present and future success of carbon nanotube-based solar cell technologies relies on the deployment of environmentally friendly fabrication methods as well as ecological base materials for the development of green devices.

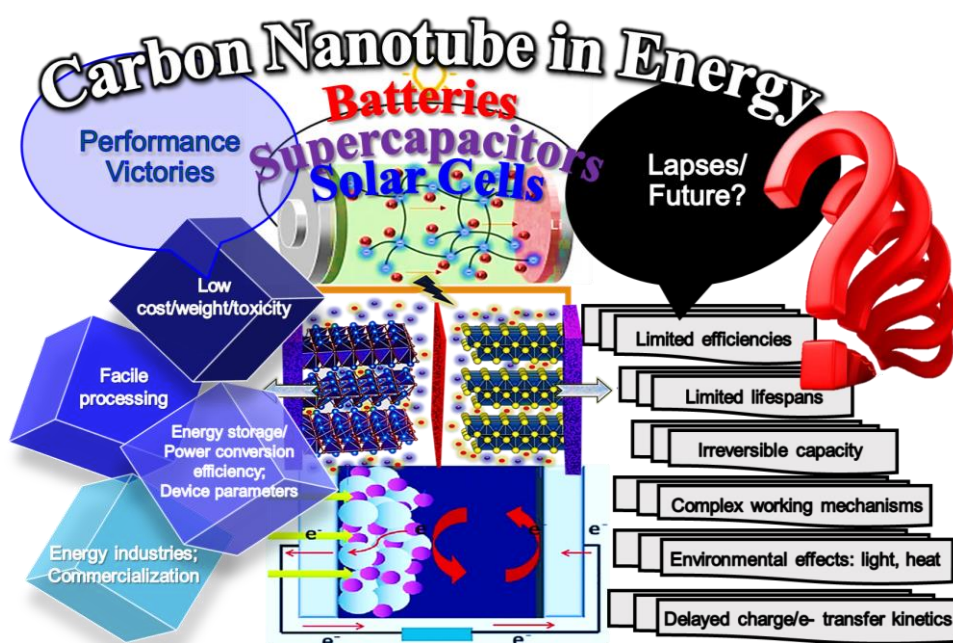
In topical years, scientific efforts seem to be turning towards low-priced ecological source materials and techniques for the formation of green carbon nanotube nanomaterials derivative device components to advantageously substitute traditional commercial non-ecological energy systems. Comparatively, literature revealed poor performance of supercapacitor and battery electrodes/electrolytes based on inorganic nanomaterials such as MXene, MoS<sub>2</sub>, etc. It seems that two-dimensional MXene and MoS<sub>2</sub> face a major nanosheet restacking issue, thereby limiting specific capacitance, capacity, and cyclic performance [23]. To address these issues, carbon nanomaterials such as carbon nanotubes and graphene have been considered advantageous. Herein, two-dimensional graphene also faces stacking problems owing to strong van der Waals forces, so preventing ion, electron, or charge movements through the nanosheets [24]. In this way, actual surface area and specific capacity have been observed to be lower than carbon nanotube. Therefore, as compared to graphene, several advanced carbon nanotube-based energy storage device components own superior charge storage, flexibility, durability, and prolonged cyclic stability. Henceforth, we can state that real modern world industrial scale potential/commercialization of carbon nanotube-based energy storage/conversion maneuvers demands pollution-free power generation via sustainable ways. Nevertheless, it seems challenging to replace all existing commercial energy devices with green carbon nanotube designs due to several underlying challenges/limitations. For example, there is a lack of adequately focused research on predefined large-scale carbon nanotube modules, lifetime/cyclic limitations, temperature/weather sensitivity of ecologically designed nanomaterials, and intricate working/degradation mechanisms to be applied in real-life energy systems.

#### **4. Carbon nanotube lapses in energy and way forward?**

After looking into the above-declared miracles in the field of energy-storing/converting devices, it seems that carbon nanotubes may be the most trending and promising future nanomaterials in these sectors. However, unfortunately, it is not a true picture when we carefully observe the real-world industrial state of carbon nanotube hybrids (**Figure 3**) [25]. As an instance, although carbon nanotube-based anodes may capably enhance lithium storage capacity, cyclability, and the lifetime of lithium batteries, these nanoentities have the disadvantage of irreversible capacity, limiting their use in substituting commercial graphite/inorganic-type battery materials. The same challenges/limitations are true for hindering industrial-level substitution of supercapacitor components with carbon nanotube and related hybrids. Compared with



traditional high-performance solar cells based on crystalline silicon or inorganic materials, carbon nanotube-based systems yet need to be commercialized. Here, probable challenging factors of energy losses, charge carrier recombination, delayed charge transfer kinetics, and limited efficiency and lifetime have been observed.



**Figure 3.** Carbon nanotube in energy sector—Performance victories and lapses.

Particularly, using varying synthesis techniques, both single-walled and multi-walled carbon nanotubes have been obtained. Both types of carbon nanotubes have distinct relative advantages and disadvantages regarding their substantial properties and technical applications. In general, multi-walled carbon nanotubes have limitations of less rigid nanostructure and weak interlayer bonds than single-walled carbon nanotubes. Even though single-walled carbon nanotubes had a smaller diameter and high crystallinity and purity, they still showed disadvantages for supercapacitor or battery electrodes. Mainly, the problem of electrolyte decomposition on single-walled carbon nanotube surfaces has been observed, thereby causing large irreversible capacity and reducing electrode performance. Therefore, it has been found valuable to work with multi-walled carbon nanotubes (having overlapping cylinders) in energy devices owing to lower electrolyte encapsulation, lower irreversible capacity loss, and higher physical durability, relative to single-walled carbon nanotubes.

Broadly speaking, superior features of single/multi-walled carbon nanotubes (relative to other nanocarbons) can be seen as ultra-fast electron/charge transfer to attain efficient energy storage/conversion. For energy storage devices (capacitors/batteries), carbon nanotubes can be integrated in a conjugated way, therefore allowing to achieve femtosecond charge transference properties. Consequently, finely integrated carbon nanotubes can enhance the reversible charge storage efficiencies of supercapacitor and battery electrodes. Similarly, fine alignment of high surface area and pure carbon nanotube may enhance electricity generation of solar cell devices.

As per literature, the performance of carbon nanotubes and derived nanocomposites in energy devices can be improved by heteroatom doping and doping-based surface modifications [26]. The doping process not only promotes electrical conductivity and charge transfer through nanotubes but also enhances transport hydrodynamics and reduces undesirable degradation issues. In other words, appropriate doping of carbon nanotubes has been found beneficial to tune specific capacitance, capacity, rate capability, and prolonged cyclic performance of electrochemical energy storage systems like supercapacitors and batteries. Moreover, appropriately doped carbon nanotubes have been used to enhance electrocatalytic performance for hydrogen evolution reactions in advanced fuel cells and other energy conversion systems [27,28].

For example, lithium-sulfur battery electrodes and electrolytes have been designed using a range of nitrogen or heteroatom-doped carbon nanotubes (specific discharge capacity  $> 1000 \text{ mAh g}^{-1}$ ) [29,30]. In addition, self-templated and self-assembled hierarchies of carbon nanotube (specific discharge capacity  $> 900 \text{ mAh g}^{-1}$ ) [31–33] as well as inorganic compound-modified nanotubes like  $\text{Ni}_3\text{V}_2\text{O}_8$ -carbon nanotube (specific discharge capacity  $> 1150 \text{ mAh g}^{-1}$ , columbic efficiency 100%, heat stability) [34] have been applied for batteries and supercapacitor electrodes. It has been observed that all types of carbon nanotube modifications, like applying doping, self-assembling, and nanoparticle functionalization, have revealed considerable enhancements in specific discharge capacity, cyclic sustainability, heat stability, and structural durability of carbon nanotubes for battery and supercapacitor electrode applications.

From here, we must peer forward to practical solutions for the industrial implementation of carbon nanotubes in energy devices. To minimize challenges of carbon nanotubes in battery/supercapacitor components, the most promising resolutions can be the use of doped nanotubes or carbon nanotube/metal or inorganic hybrids (e.g., carbon nanotube/silicone) and ecological manufacturing techniques (e.g., ball-milling, coating). In this way, performance advantages of carbon nanotube-based energy storage devices can be attained (via recurrent future research) in terms of durability, specific capacity/capacitance, charge-discharge, energy density, prolonged long cyclic life, etc. For replacing indium tin oxide (ITO), fluorine-doped tin oxide (FTO), or transparent conductive oxide (TCO) type expensive and non-green commercial solar cell components, carbon nanotube nanomaterial-based thin conducting film electrodes may offer the best technical resolution [20]. However, the future outlook of carbon nanotubes as promising candidates for flexible/wearable optoelectronics depends upon continuous scientific research towards next-generation low-price, chemically/mechanically stable, transparent, and high-power efficiency designs. Through controlled and green manufacturing of carbon nanotubes and related nanocomposites, the above-pointed-out challenges and critical parameters limiting solar cell efficiencies can be efficiently controlled.

As per literature reports to date on carbon nanotube-based energy storage and conversion devices, we suggest opting for new progressive approaches for materials fabrication, testing, and optimization, green technologies, and focused efforts to bridge gaps between lab-scale research and industries. Incidentally, by rational efforts of the field researchers, academia, and industry searches on carbon



nanotubes can be combined to resolve key issues for market commercialization in the form of green energy devices. In the bargain, owing to the remarkable potential of carbon nanotubes in the energy sector, further integration of these photovoltaics for modern semiconducting devices, light-emitting displays, and flexible electronics can be suggested.

To meet future energy-related nanotechnological concerns, environmentally friendly or green approaches must be used for carbon nanotube designs and deployment in real life and commercially necessitated supercapacitors, batteries, and photovoltaics [35]. In this regard, field scientists must consider the use of green carbon nanotube nanomaterials, reagents, and chemicals along with green synthesis techniques for upcoming high-end energy devices. Nevertheless, it still seems challenging to attain industrial-level energy devices by using all green carbon nanotube nanostructures and approaches due to a lack of comprehensive research efforts in these directions [36]. Future progress on carbon nanotube-based nanocomposites must also be expanded towards competent energy devices, such as light-emitting diodes, fuel cells, supercapacitors equipped with LEDs, etc.

## 5. Summation

Unconditionally, this perspective manuscript presents an outlook on the evolution of carbon nanotube technologies in diverse energy applications. As per reported articles, growing scientific interests can be seen for the employment of carbon nanotubes and derived hybrids in industrial/commercial batteries, supercapacitors, and solar cell marketplaces. These advancements of carbon nanotubes in the energy sector can be attributed to low price, high surface-to-volume ratio, design feasibility, flexibility, stability, structural/physical properties, charge/electron transfer, superior capacity/capacitance, capacity retention, cyclic life, power conversion efficiencies, and the like. We analyzed the current state, existing challenges, and possibilities for substituting traditional energy devices/systems with carbon nanotube-based maneuvers. Despite the scientific progress to date on carbon nanotube nanomaterials-based energy storage and conversion devices, we suggest indispensable future research activities to solve underlying structure/property/performance challenges in order to develop promising next-generation energy storage and conversion devices/systems on an industrial scale.

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