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Review

Technical Competence of Nanodiamond Nanocomposites in Energy Sector (Solar Cells, Fuel Cells, Batteries, Supercapacitors)-State-of-the-Art

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Abstract: This state-of-the-art overview is designed to present indispensable features of nanodiamond nanocomposites and their utilization of advanced energy devices/systems including solar cells, fuel cells, batteries, and supercapacitors. For these systems, nanodiamond nanocomposites have been used in electrodes, electrolytes, membrane-electrode assembly, separators, and other components. Nanodiamond and related nanocomposites have high surface area and unique structural, microstructural, electrochemical, and physical properties to be utilized in efficient devices. Nanodiamond nanocomposites have been designed using sonication/solution preparation, layer-by-layer deposition, chemical vapor deposition, ink deposition, high temperature annealing, doping, solution casting, and in situ polymerization. In this context, various polymeric matrices have been reinforced with nanodiamond to attain the desired design/performance. Accordingly, polypyrrole/nanodiamond and graphene/nanodiamond nanomaterials have been documented for solar cells with photovoltage of ~ 99 mV. Direct methanol fuel cells with platinum/nanodiamond nanocomposites exhibited high electrochemical catalytic activity, high surface area of 80-90 $m^2 \cdot g^{-1}$ and power density of 55 $mW \cdot cm^{-2}$. Silica/nanodiamond and polypyrrole/nanodiamond nanocomposite-based battery designs revealed high capacity of 600-650 mAh/g (1,000 cycles). For supercapacitor electrodes, polyaniline/nanodiamond systems depicted specific capacitance > 640 $F \cdot g^{-1}$ and capacitance retention > 80%. Future progress in designing efficient nanodiamond nanomaterials may overcome microstructural, conductivity, compatibility, and long-time functioning challenges toward high-performance energy devices.

***Keywords*:** nanodiamond, nanocomposite, electrical conductivity, electrochemical, fuel cell, batteries, solar cells

1. Introduction

To meet the modern technological demands, carbon-based nanomaterials having superior electron and charge transportation properties have been applied to design energy devices and systems [1]. Specifically, energy production and storage systems have been used in transportation, electronics, engineering, and biomedical fields. Carbon nanoparticles have thermal stability, robustness, and other structural and physical characteristics. One of such efficient carbon nanomaterial is nanodiamond having zero-dimensional structure, high specific surface area, lightweight, optical properties, electrical/heat conductivity, robustness, nontoxicity, biocompatibility, and other physical features [2-4]. Nanodiamond nanoparticles have been applied in wide ranging fields of electronic devices (like sensors,

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microelectronics, actuators, etc.) [5], aerospace/automobile engineering structures [6], and biomedical systems [7, 8]. Correspondingly, nanodiamond nanoparticles have also been applied in energy production or storage systems [9]. For optoelectronic applications, traditionally metal oxide/inorganic nanoparticles like copper oxide, manganese-zirconium dioxide, strontium-titanium oxide, etc. have been used [10-13]. However, to achieve superior performance, hybrid systems based on nanodiamond nanomaterials have been preferred in advanced optical devices. Accordingly, nanodiamond and related nanomaterials have been applied in solar cells owing to their high surface area and optical/electronic characters. The surface functionalization, doping, or nanocomposite formation of nanodiamond seemed to further enhance the potential of these nanomaterials for solar cells. Utilization of nanodiamond nanocomposites in lithium ion battery electrodes [14], electrolytes [15], or separators [16] has been observed due to superior electrochemical, electronic, capacity, charge-discharge, energy/charge density, and cyclic performance [17]. Moreover, research has pointed towards the utilization of nanodiamond nanocomposites in supercapacitors [18]. The nanocarbon based components have been known to exhibit superior specific capacitance, power/energy density, and capacitance retention parameters of supercapacitors [19]. For fuel cells, nanodiamond based nanomaterials have been applied in the electrodes, electrolytes, catalysts, etc., due to their fine electrical conductivity, catalytic, electrocatalytic, and ion/proton transference potential [20]. However, in order to desirably enhance the electron/charge transportation and devices related specific properties of nanodiamond, advanced surface functionalization methods must be focused on the formation of their nanocomposites [21, 22]. In this regard, the properties of hybrid nanomaterials have been enhanced using design variations and advanced fabrication techniques for the formation of efficient fuel cells, batteries, and supercapacitors.

Though nanodiamond belong to the class of nanocarbon and allied zero dimensional nanomaterials like fullerene have been reported, nanodiamond own several functional benefits to be employed in nanocomposite forms [23, 24]. Particularly, nanodiamond have the advantages of low cost synthesis, inexpensive large scale production, countless surface modification preferences, facile processing towards nanocomposite designs, and environmental friendliness [25]. Therefore, literature concerns have increasingly turned towards opting the nanodiamond as effective nanofillers relative to the expensive zero dimensional nanocarbons like fullerenes [26, 27]. For that reason, we aim to review the impact of nanodiamond nanocomposites on energy devices specifically exploring the exclusive designs aiming at fuel cells, solar cells, supercapacitors, and batteries. To the best of my knowledge, this is a novel and pioneering overview of nanodiamond based energy production/storage systems in terms of its outline, recent literature included, systematic design-property descriptions, and performance discussions, focusing on the underlying challenges. Although, earlier literature reports were observed on nanodiamond nanocomposites for energy systems, no comprehensive review article has been observed so far revealing the current state, challenges, and predicted future progress in this area. For example, an earlier review by Wang et al. [28] reported the role of nanodiamond in energy fields, however, no systematic division for energy device categories, literature, or related material properties was included. Moreover, the authors focused only on pristine nanodiamond and didn't explain the design and role of nanodiamond nanocomposites in various energy devices. Consequently, this manuscript will be definitely beneficial for the field scientists struggling to develop nanodiamond base energy device components. Besides the progressive scientific researches seen so far on advanced nanodiamond nanocomposites, their large-scale productions, cost-effectiveness, and high-purity remain challenging compared to the competitor nanocarbons, like carbon nanotubes or graphene [29]; therefore, extensive field surveys need to be conducted in this direction. Henceforward, the forthcoming efforts on nanodiamond nanomaterials may overcome the challenges hindering the uses of these nanomaterials in energy devices and energy systems.

2. Nanodiamond

Nanodiamond is a carbon nanoallotrope [30]. The earliest discovery of nanodiamond nanoparticles was reported in the 1960s [31]. Nanodiamond has been prepared using numerous facile synthetic approaches such as detonation technique, laser procedure, ion irradiation, plasma etching, chemical vapor deposition, plasma enhanced chemical vapor deposition, etc. [32-35]. Appropriate synthesis methods have been used to form nanodiamond nanoparticles with sizes in the range of 2-5 nm [36]. Moreover, nanodiamond may form aggregates of up to 100 nm sizes. Ultra-nanocrystalline nanodiamond nano-allotropes [37] may include diamondoids [38], detonation nanodiamond [39], and nanocrystalline nanoparticles [40]. The detonation approach has been commonly applied for the formation

of nanodiamond nanoparticles [41, 42]. In this method, oxygen deficient explosive has been used in an enclosed chamber and nanodiamond nanoparticles of 5 nm have been formed [43]. Explosive oxygen-deficient 2-methyl-1,3,5-trinitrobenzene or TNT was applied to form crystalline cubic nanodiamond nanoparticles [44]. After the explosion, nanodiamond nanoparticles have been isolated from the detonated soot [45, 46]. However, detonated nanodiamond may have impurities. Consequently, acidic treatment of nanodiamond using hydrofluoric/nitric acids has been recommended in the literature in order to remove metallic impurities [47, 48]. Moreover, thermal oxidation treatment of nanodiamond at 420 °C has been used to remove graphite and amorphous carbon impurities [49]. The nanodiamond nanostructure was studied using techniques, such as the X-ray diffraction method [50], Raman spectroscopy [41], X-ray photoelectron spectroscopy [51], etc. The nanodiamond clusters were found to have sp^2 or sp^3 carbon nanostructure [52]. The nanodiamond sizes have been studied using microscopy as well as dynamic light scattering techniques [53]. Ermakova et al. [54] reported on the ferritin coated nanodiamond surface nanoparticles. The resulting nanomaterials were applied as nanosensors due to fluorescence, and magnetic sensitivity. High resolution transmission electron microscopy images of nanodiamond nanoparticles with ferritin were used to study the surface coating. The 5 nm thick ferrtin layer was found adsorbed on the nanodiamond surface. Furthermore, the relaxation time of the pristine nanodiamond and ferritin coated nanodiamond nanoparticles was studied. It has been observed that the relaxation time was reduced for the ferritin coated nanodiamond nanoparticles, relative to neat nanodiamond nanoparticles. The reason seems to be the effect of iron molecules present on the nanodiamond surface causing a mutual effect with nanoparticles on relation time.

3. Nanodiamond nanocomposites in solar cells

The development of protective layers has been focused on efficient solar cell designs to avoid harmful environmental effects, such as temperature fluctuations, Ultraviolet (UV) degradation, moisture, etc., deteriorating the performance and durability of these devices [55-57]. To alleviate these problems, nanodiamond based efficient protective layers or coating materials have been designed and investigated in the literature [58]. Nanodiamond nanocomposites have been reported to form stable nanostructures because of hybridized carbon atoms in nanodiamond capable of developing conjugation with semiconducting materials like conductive polymers [59, 60]. Nanodiamond based nanocomposites form fine protective layers for photovoltaic solar cells due to fine anticorrosion, environmental, wear resistance. Kim et al. [61] investigated a nanodiamond/molybdenum disulfide based nanocomposite nanosystem using solution and centrifugation techniques. Initially, nanodiamond were acylated using thionyl chloride in anhydrous dimethylformamide solvent at 70 °C for 24 h. Later, MoS_2 nanosheets were added to the solution and centrifuged at 14,600 rpm for 10 min (60 °C). Subsequently, the nanocomposite was washed with distilled water and dried at 60 °C (vacuum oven). A mutually conjugated nanostructure has been observed in the case of the nanocomposite. Nanodiamond nanoparticles have been found finely dispersed in the nanocomposite form. The presence of molybdenum disulfide on the nanoparticle surface enhanced the nanodiamond surface area for better electron or ion distributions. The overall properties were found to be dependent upon the nanophase formation, molecular interlayer, and nanodiamond dispersion. The resulting mutual effects of matrix-nanofiller resulted in enhanced electrochemical capacitance properties of the nanomaterials. Figure 1 shows an outline for the formation of nanodiamond/molybdenum disulfide nanocomposites. Amine functional molybdenum nanosheets and acid functional nanodiamond nanoparticles were found to be interacted through interfacial linking via covalent bond formation. Transmission electron microscopy revealed the dispersed nanodiamond of 80-200 nm and also the nanodiamond/molybdenum disulfide nanocomposite nanoparticles. Due to the mutual chemical reaction of the functionalized nanodiamond and molybdenum disulfide nanostructure, well compatible microstructures were observed. Furthermore, the Fourier transform infrared (FTIR) spectroscopy was performed to study the structural comparison of pristine nanodiamond, carboxylic/acyl chloride nanodiamond, and nanodiamond/molybdenum disulfide nanocomposites. Pristine detonation nanodiamond had intrinsic hydroxyl and carbonyl groups in their structure, as detected in FTIR.

However, the carbonyl C=O and C=C peaks of pristine/functional nanodiamond were diminished due to bonding with molybdenum disulfide during nanocomposite formation. Hence, the structures of nanodiamond as well as nanocomposites were confirmed using the FTIR studies. Ultraviolet (UV) absorbance variations were examined for the solar cell application of these nanocomposites. In the nanocomposite form, the optical band gap of molybdenum

disulfide nanosheets was observed higher than the ~ 1.8 eV.

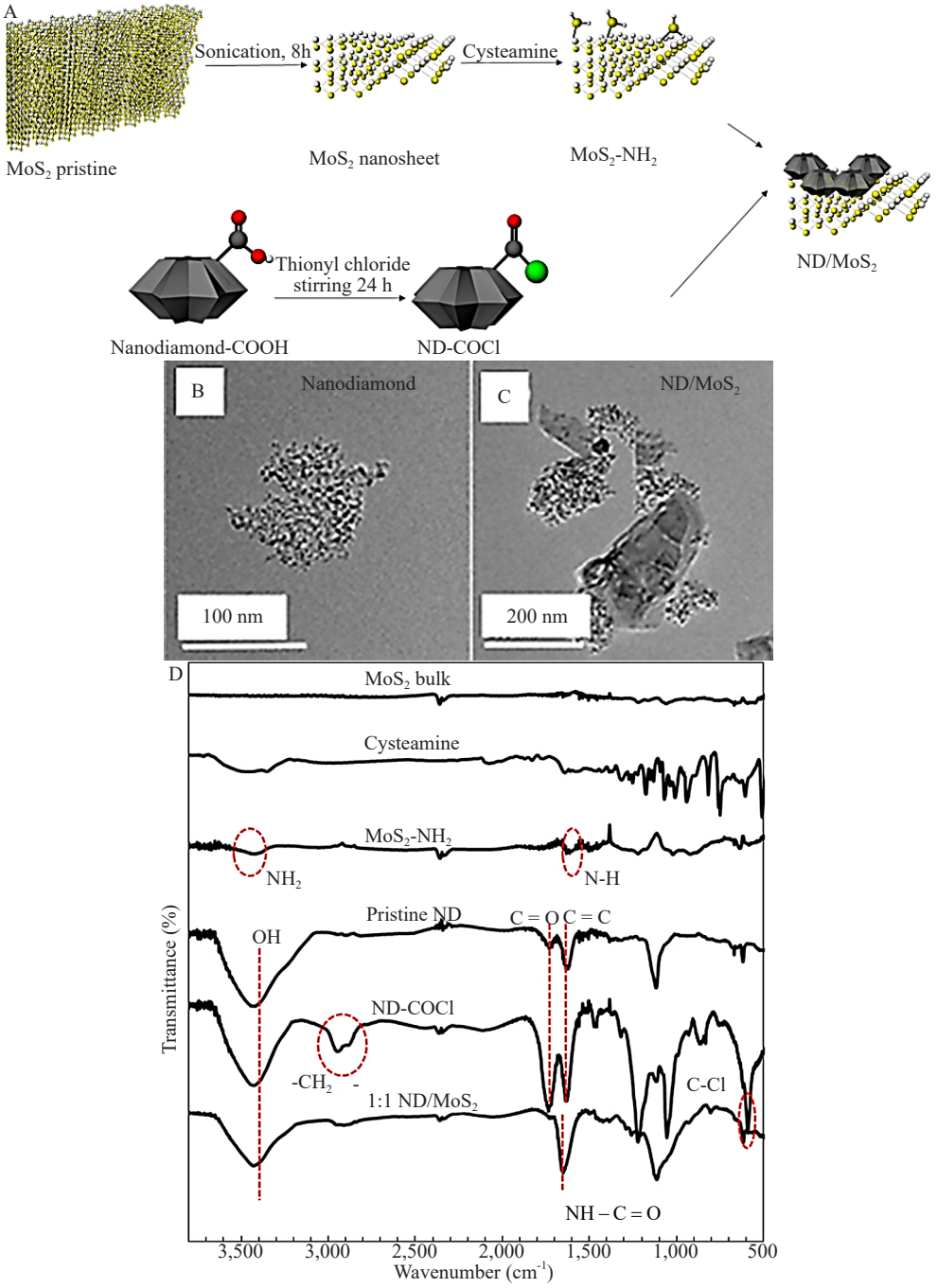

Figure 1. (A) Schematic of nanodiamond/molybdenum disulfide (ND/MoS_2) nanocomposites; (B) Transmission electron micrographs of nanodiamond (ND); (C) ND/MoS_2 nano composites; and (D) Fourier transform infra-red (FTIR) spectra of MoS_2 bulk, cysteamine, amine-functional MoS_2 (MoS_2-NH_2), pristine ND, carboxylated ND, acyl chloride ND, and ND/MoS_2 nanocomposite [61]. Reproduced with permission from MDPI

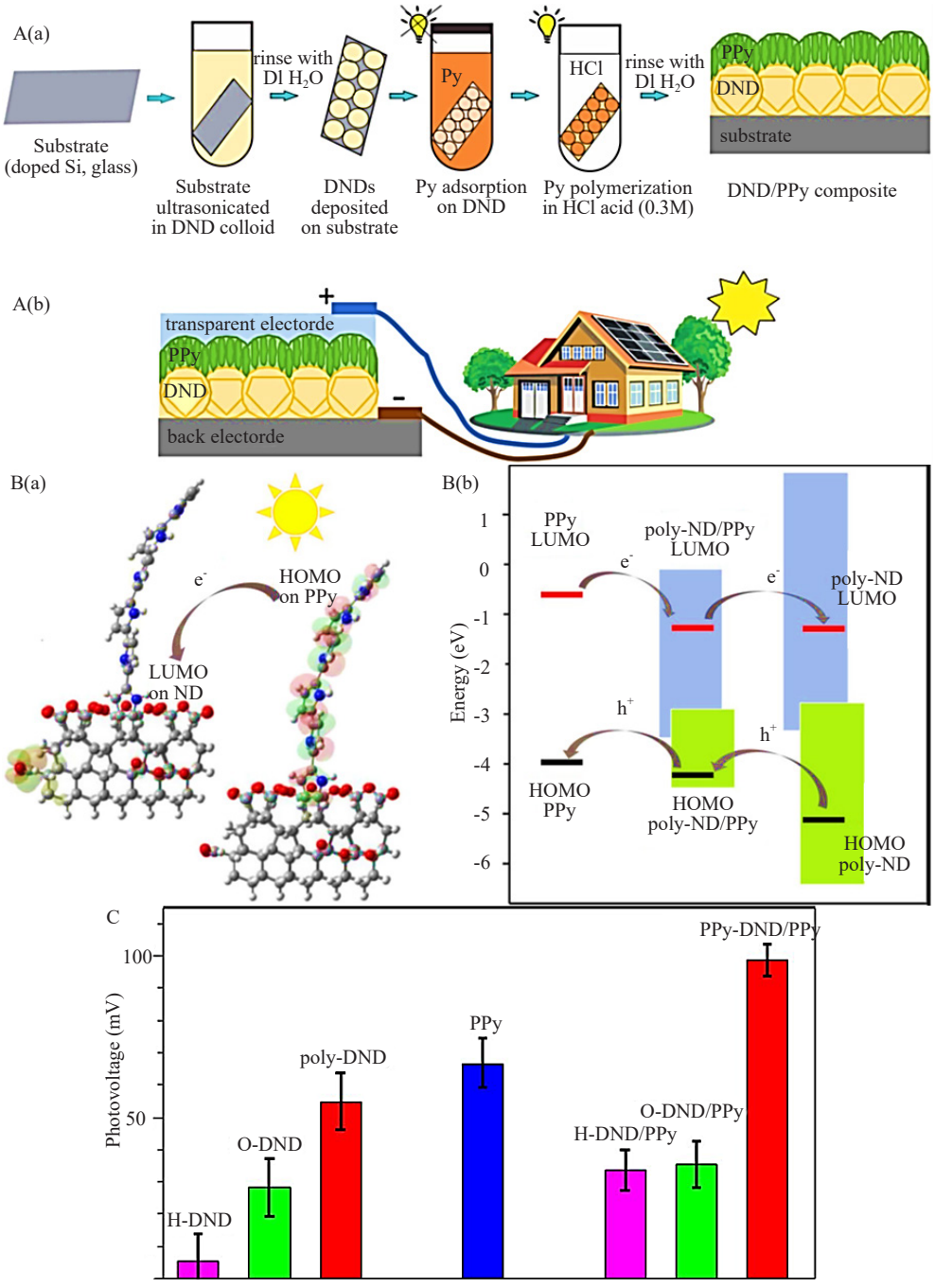

Figure 2. (A) Scheme of: (a) fabrication process of detonation nanodiamond/polypyrrole (DND/PPy) nanocomposite; (b) test solar cell with embedded nanocomposite as an active material; and (B) (a) Example of spatial separation of polypyrrole HOMO and ND LUMO based on DFT calculations; (b) scheme of HOMO and LUMO energetic levels nanocomposite of separate materials and their interface with probable charge transfer due to level alignment; and (C) photovoltages (with error bars) of DND/PPy nanocomposite, DND, and PPy references [63]. DFT = density functional theory; ND = nanodiamond; PPy = polypyrrole; HOMO = highest occupied molecular orbital; LUMO = lowest occupied molecular orbital; H-DND = hydrogenated detonation nanodiamond; O-DND = oxidized detonation nanodiamond; poly-DND = polyfunctional detonation nanodiamond Reproduced with permission from Nature

Simões et al. [62] conducted studies on the nanodiamond film and graphitized nanodiamond film for grain size, film morphology, thickness, and adhesion to the glass substrate. A protective layer of nanodiamond (500 nm) was deposited on a glass substrate using a hot filament chemical vapor deposition technique for photovoltaic cell application. This technique was found effective in depositing nanodiamond films with reduced sizes, good substrate coverage, and

smooth surfaces to regulate their refractive index and transmissivity properties. Scanning electron micrographs of the nanodiamond nanoparticles revealed fine dispersion and smooth morphology of the coated film. In addition, the transmittance percentage of neat glass surface was comparatively with respect to nanodiamond coated glass substrate. The nanodiamond coating with 500 nm thickness was found to reduce the transmittance percentage of the glass surface. Since, the pristine glass surface had a transmittance percentage of 90%, which was decreased to about 60-70% for the nanodiamond coated glass surface. This effect was observed because of the light scattering by nanodiamond nanograins on the glass surface. It was suggested that future studies in this direction may lead to the formation of further smaller nanodiamond grains.

Miliaieva et al. [63] fabricated the polypyrrole/detonation nanodiamond nanocomposite as an inorganic electron acceptor layer for energy generation in solar cell designs. In this context, hydrogenated detonation nanodiamond, oxidized detonation nanodiamond, and polyfunctional detonation nanodiamond nanoparticles have been used. A layer by layer technique was used for the deposition of polypyrrole/detonation nanodiamond solar nanomaterial (Figure 2). According to density functional theory, structure of functional nanodiamond and spatial separation of the highest occupied molecular orbital and lowest occupied molecular orbital are presented. In this study, detonated nanodiamond were annealed in air (450 °C; 30 min) to obtain oxidized detonated nanodiamond with -C-H and -C=O type surface functional groups. The functional nanodiamond were suggested to physically interacted with the polypyrrole chains via hydrogen bonding. The resulting polypyrrole/functional nanodiamond nanocomposite revealed a suitable alignment of energy levels of polymer (HOMO) and nanoparticles (LUMO) and spatial separations. In this way, favorable charge carrier separations were observed between polypyrrole and functional nanodiamond. Consequently, the charge transfer behavior and separation between the levels led to the formation of aligned nanostructures in turn promoting the passage of electrons through the system. Accordingly, energy levels of polypyrrole-nanodiamond have been found effective in transferring electrons between the matrix-nanofiller. The maximum photovoltage of the polypyrrole system was 99 ± 5 mV, as compared to the functional nanodiamond with voltages in the range of 34-55 mV.

Doped nanodiamond based electrodes have been efficiently applied to the dye sensitized solar cells [64]. The designed electrodes had high current density, open circuit voltage, and solar cell efficiency. As per the literature, such dye sensitized solar cell designs performed better than the titania based optical electrodes [65, 66]. However, future studies must be conducted to explore structure-property relationship between the doped nanodiamond nanoparticles and precise hybrid designs for high performance solar cell assemblies.

4. Nanodiamond nanocomposites for fuel cell designs

Fuel cells have been identified as efficient green energy sources to form electricity [67]. This technique involves the use of air or oxygen at the cathode and hydrogen at the anode for the formation of hydrogen gas via photo-electrolysis processes (Figure 3) [68]. The hydrogen produced in this process may cross the gas diffusion layer membrane. The catalyst layer usually consists of platinum for oxidation reactions of fuel cells [69]. During the reaction, hydrogen gas is usually broken down into protons and electrons, where electrons can move through the external circuit and protons may pass through the proton exchange membrane [70]. The resulting standard proton layer has been applied in commercial systems [71]. Due to chemical stability, nanodiamond nanoparticles have been used as a support catalyst layer [72]. In this context, neat nanodiamond as well as doped nanodiamond nanoparticles have been applied [73]. These nanomaterials have been further coated with metal nanoparticles like platinum and ruthenium to enhance the final material performance. Later, nanodiamond nanoparticles were tested for the catalyst support layer functioning.

Riveros et al. [75] formed pristine nanodiamond and boron doped nanodiamond based electrodes to explore the electrochemical features for direct methanol fuel cells. The undoped and boron doped nanodiamond nanoparticles were then coated with the Platinum and Ruthenium nanoparticles using dodecyl benzene sulfonate (surfactant) and sodium borohydride (reducing agent). In this fuel cell, membrane electrode assembly was manufactured using an ink paste technique. According to the transmission electron micrographs, Platinum-Ruthenium nanoparticles of 4-5 nm were deposited on the nanodiamond surfaces (Figure 4).

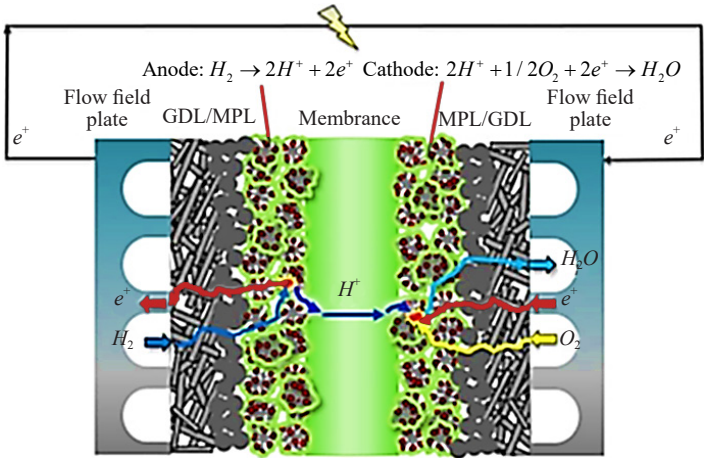

Figure 3. Schematic of fuel cell with flow fields and membrane electrode assembly (MEA) components: gas diffusion layer (GDL) with microporous layers (MPL), anode electrode, cathode electrode, and membrane [74]
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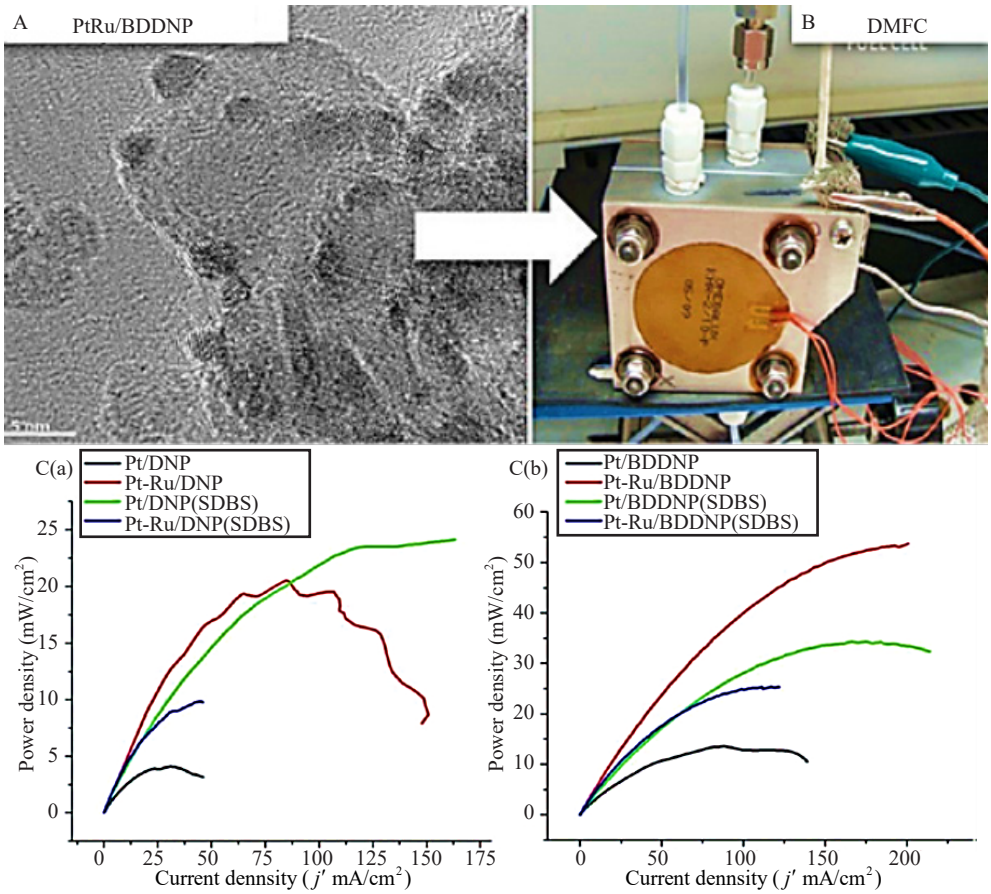

Figure 4. (A) Transmission electron micrographs of Platinum-Ruthenium/boron dopped diamond nanoparticles (PtRu/BDDNPs); (B) Direct methanol fuel cell (DMFC) design; (C) Power density via current density curve produced by direct methanol fuel cell (DMFC) at 80 °C with anodes prepared with: (a) undoped diamond nanoparticle (DNP) decorated with Pt (black) and Pt-Ru (red) catalysts, and Pt (green) and Pt-Ru (blue) synthesized by SDBS; (b) boron doped diamond nanoparticles (BDDNPs) decorated with Pt (black) and Pt-Ru (red) catalysts synthesized by using excess $NaBH_4$, and Pt (green) and Pt-Ru (blue) synthesized by SDBS [75]. SDBS = sodium dodecyl benzene sulfonate; Pt/DNP = platinum/diamond nanoparticle; Pt-Ru/DNP = Platinum-Ruthenium/diamond nanoparticle; Pt/DNP(SDBS) = platinum/diamond nanoparticle/sodium dodecyl benzene sulfonate; Pt-Ru/DNP(SDBS) = Platinum-Ruthenium/diamond nanoparticle/sodium dodecyl benzene sulfonate
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The figure also shows the fuel cell setup developed in this study. The Platinum and Platinum-Ruthenium coated undoped and doped nanodiamond nanoparticles were studied using the power density vs. current density curves. The power density of the Platinum-Ruthenium coated boron doped nanodiamond nanoparticles was observed high ~ 55 $mW \cdot cm^{-2}$. The nanoparticles coated boron doped nanoparticles revealed higher power density values, as compared to the un-doped nanodiamond systems. According to the results, the nanoparticles coated boron doped nanodiamond formed an effective catalytic system for fuel cell application.

In carbon nanostructures, nitrogen doping has been applied to distance the carbon nanosheets to create interlayer spacing [76]. In this regard, Du et al. [77] reported on the formation of nitrogen doped porous carbon nanosheets. Nitrogen doping was used to increase the interlayer spacing, defect formations, and desired mesoporous nanostructure formation for potassium ion intercalation. The resulting nitrogen doped nanodiamond had large interlayer spacing and abundant defect structures. Generally, the introduction of heteroatoms into nanodiamond or graphene type carbon lattice can modify electronic properties, produce active sites, and enhance ion adsorption properties. However, the effects of nitrogen doping on modifying the interlayer spacing of nanodiamond have been rarely reported in the literature. Nevertheless, scientific reports for density functional theory based explanations of nitrogen doping effects for controlling the interlayer spacing of graphene nanosheets have been observed [78]. Anyhow, in this study, nitrogen doped nanodiamond had the largest interlayer spacing and best ordered structure, which was suggested as valuable for storing/diffusion of potassium ions. Herein, by using Bragg's equation, the average interlayer spacing (002) was calculated as 4.20 Å. The resulting, nitrogen doped porous carbon nanosheets intercalated with potassium ions were applied for the supercapacitor electrode application. Afterwards, adding metal nanoparticles seem to intercalate the spaces between the carbon nanosheets in graphene and nanodiamond nanostructures [79]. Furthermore, the nanodiamond based nanostructures have the advantages of causing stiffness to the nanomaterials.

Dong et al. [80] reported on the nanodiamond coating having superior electrochemical stability. The graphitized nanodiamond was formed at an annealing temperature of 1,300-1,600 °C in a vacuum (3-10 Pa). Moreover, the graphitization of nanodiamond has been analyzed for superior electrochemical and electrical conductivity characteristics [81]. The surface chemistry of nanodiamond strongly relies on the synthesis technique used and the modification treatments. It seems that the graphitization of nanodiamond can produce a core-shell-like nanostructure with a nanodiamond core covered by a graphitic shell to improve the electrical conductivity and electrochemical stability. In fact, the graphitic shell acted as a stable support for platinum electrocatalysts towards rapid oxygen reduction reaction processes. The electrochemical surface area was observed as 87-89 $m^2 \cdot g^{-1}$. After 2,500 cycles, the electrochemical surface area was retained at 65%. Zang et al. [82] fabricated the graphene doped nanodiamond nanoparticles using high temperature annealing technique (1,200-1,500 °C). Few layers of graphene have been found to be deposited on the nanodiamond surface. Such nanodiamond/graphene hybrid nanostructure has been applied as platinum catalyst supports in direct methanol fuel cells. The hybrids have been used to enhance the catalytic activity of the platinum electrodes. Graphene doped nanodiamond had a high surface area of 84.2 $m^2 \cdot g^{-1}$, relative to neat nanodiamond (81.6 $m^2 \cdot g^{-1}$). Consequently, electro-oxidation of methanol was seemed to be enhanced by using these nanohybrids.

Titanium carbide and nanodiamond nanomaterial have also been deposited on the platinum electrodes [83]. Consequently, the surface area and electrocatalytic activity of the nanodiamond modified electrodes have been found to increase. Such modified electrodes have been applied in the hydrogen fuel cell catalyst layer. Zhao et al. [84] fabricated the platinum/titanium carbide/nanodiamond system via one pot method for application as a fuel cell electrodes. Including nanodiamond increased the electrochemical surface area of the designed electrode. The electrochemical surface area retention of the nanocomposite electrode was 70-80%, whereas neat platinum/carbon electrode had a lower value of 30%. Lu et al. [85] fabricated the zirconium dioxide doped nanodiamond by a one-step isothermal hydrolysis method for a direct methanol fuel cell. The electrode material had advantageous electrocatalytic activity, relative to the titanium carbide nanomaterial. The zirconium dioxide doped nanodiamond based electrode showed a higher peak current of 5.00×10^{-4} A, than nanodiamond based electrode (3×10^{-4} A) within 500 cycles. Consequently, zirconium dioxide doped nanodiamond system has better stability in fuel cell functioning to decrease the carbon monoxide poisoning effects. The poisoning effects of carbon monoxide were found toxic for active oxidation/reduction reactions in fuel cell application. Liu et al. [86] formed a fuel cell catalyst based on the nitrogen and boron doped nanodiamond. This system was also effective in functioning without causing carbon monoxide toxicity effects to deteriorate the catalytic

reactions.

Primachenko et al. [87] developed perfluorinated Aquivion® and detonation nanodiamond based proton exchange membranes for direct methanol fuel cells. In these membranes, nanodiamond nanoparticles of 4-5 nm were used. Scanning electron micrographs of neat perfluorinated Aquivion® membrane and the membranes loaded with 0.5 and 5 wt.% nanoparticles were scanned. It was observed that nanocomposite membranes had nanoparticle sizes of 200-300 nm dispersed in the polymer membrane matrix (Figure 5A). According to the electrochemical studies of the Aquivion® nanocomposite based membrane electrode assembly, it was observed that including 2.6 wt.% nanoparticles caused sharp enhancements in an ohmic loss at 120 °C (Figure 5B). This increase in the ohmic loss was credited to efficient proton transfer, low lower proton resistance, and higher current densities of the nanocomposites, compared with the pristine membrane.

Shvidchenko et al. [88] reported on the polytetrafluoroethylene based Aquivion® perfluoro sulfonic acid membranes with the sulfonic acid side functionalities through an aqueous-emulsion technique. The sulfonated nanodiamond nanofillers were filled in the matrix to enhance the proton conductivity properties and strength of the membranes. Sulfonated nanodiamond nanoparticles developed proton conduction channels throughout the membrane for high performance hydrogen fuel cell application. Lebedev et al. [89] designed the perfluorinated Aquivion® and detonation nanodiamond membranes. The nanodiamond was processed through detonation and annealing and resulting membranes with 0.5-5.0 wt.% nanodiamond contents were prepared by solution method. The addition of nanodiamond revealed fine hydrophilicity properties, leading to enhanced proton conductivity of the membranes. There was a ~ 20-30% increase in proton conductivity with a rising temperature of 20-50 °C. However, fewer studies have been reported up till now exploring the proton conduction mechanisms of the protonated fuel cell membranes or the use of functional nanodiamond to enhance the proton conductivity of the fuel cell membranes. Furthermore, correlation between the nanodiamond functionalities and formation of proton conduction channels need to be studied in detail in literature.

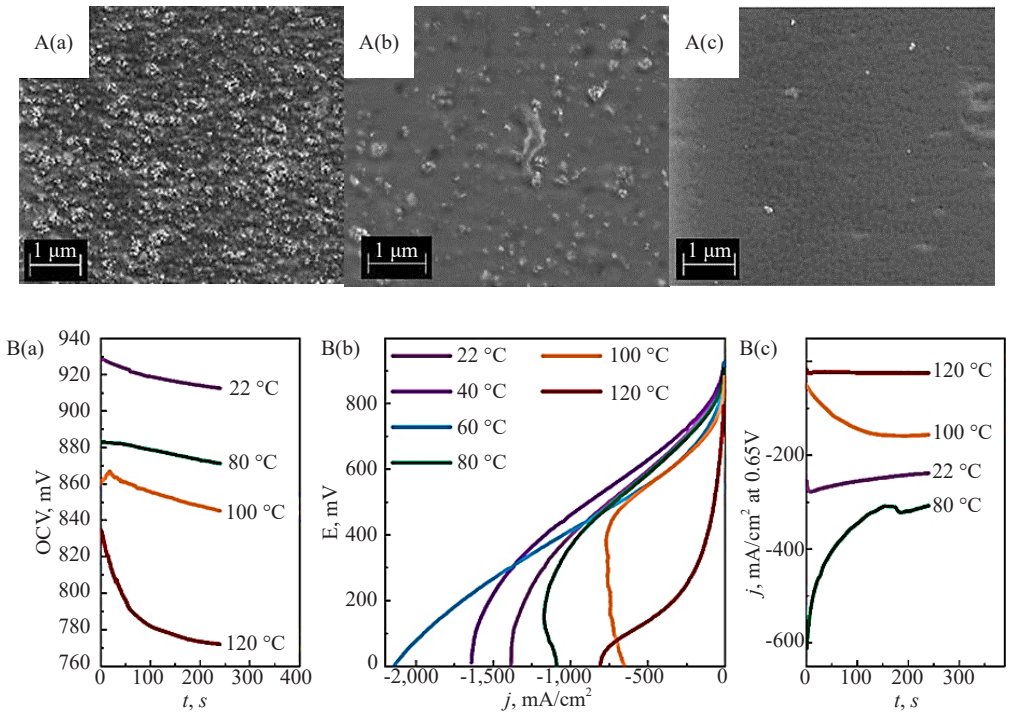

Figure 5. (A) Scanning electron microscopy images of Aquivion®-type membranes (EW = 890 g-eq/mol) with DND Z+: (a) 0% DND (without nanodiamond); (b) 0.5 wt.% DND; and (c) 5 wt.% DND ; and (B) Electrochemical characteristics of the MEA with the Aquivion®-type membrane (EW = 897 g-eq/mol) with 2.6 wt.% DND Z+ at different temperature: OCV vs. time (a); voltammograms (b); and current density in the potentiostatic mode at a voltage of 0.65 V vs. time (c) [87]. MEA = membrane-electrode-assembly; DND = detonated nanodiamond; OCV = open circuit voltage Reproduced with permission from MDPI

5. Batteries employing nanodiamond nanomaterials

Important components of lithium ion batteries have been reported as electrolyte, electrodes (anode or cathode), separators, etc. [90-92]. The electrodes like anode and cathode have been used to store lithium [93]. On the other hand, positive lithium ions have been carried through the electrolyte [94, 95]. Lithium ion batteries work on the principle of charge-discharge processes. During charging, the cathode releases lithium ions, which are collected by the anode, whereas discharging delivers electrical current and lithium ions towards the cathode [96]. Owing to efficient performance, wide ranging applications of lithium ion batteries have been observed in advanced telecommunication and electronic devices. In lithium ion batteries, essential parameters like capacity, power density, and energy density have been investigated [97]. The overall battery performance was analyzed through the power and energy storage properties. Wang et al. [98] formed battery electrolytes with small quantities of nanodiamond. Adding 0.8 g/L nanodiamond enhanced the initial charge capacity to 480-950 mAh/g. Figure 6 shows the cyclic performances of graphite anodes at a current density of 0.1 A/g. The ionic conductivity of electrolytes was found to enhance due to the presence of moisture. However, greater amounts of moisture have not been found suitable due to defect formation in the battery designs.

Owing to high surface area and functional groups, like carbonyl, hydroxyl, etc., nanodiamond owns high physical adsorption capacity towards lithium ions via electrostatic interactions [99] . In commercial scale lithium ion batteries, the presence of moisture is usually avoided to prevent the degradation of electrolytes or electrodes causing irreversible failure of these devices [100]. In this regard, adding nanodiamond can enhance the performance and stability of batteries having electrolytes with high moisture contents [99]. The moisture based electrolyte in turn plays an important role in the passage of electrons/ions between the electrode-electrolyte interface. According to the research report, adding a small amount of nanodiamond to the electrolyte with 5,000 ppm H_2O had long cyclic stability (over 100-1,000 cycles) with reversible capacities (130-950 $mA{\cdot}h{\cdot}g^{-1}$) [98]. In this way, high stability and final performance of batteries have been observed [101]. Hence, the designs of the electrolytes and electrodes have been found indispensable to enhance the solid-electrolyte interface functioning, overall capacity, and cyclability performance of the batteries [102]. The behavior of lithium ions crossing the electrode-electrolyte interfacial barriers has affected the overall battery performance [103]. Liu et al. [104] reported on the stability of poly(ethylene oxide)/nanodiamond based lithium electrolyte interface for anode material. Figure 7 illustrates the formation of a nanodiamond interface through the microwave plasma chemical deposition technique.

Nanodiamond was used to develop a stable lithium protection layer using microwave plasma chemical deposition technique, without any binder, for superior cycling efficiency. The deposited nanodiamond layer had a thickness of 150 nm in scanning electron micrograph. This nanodiamond layer was spin coated with a thin layer of poly(ethylene oxide) (25 mL of 0.5 wt.% polymer in acetonitrile) at 3,000 revolutions per minute. The spin coated polymer layer was again coated with nanodiamond using the same microwave plasma chemical vapor deposition technique. The layered poly(ethylene

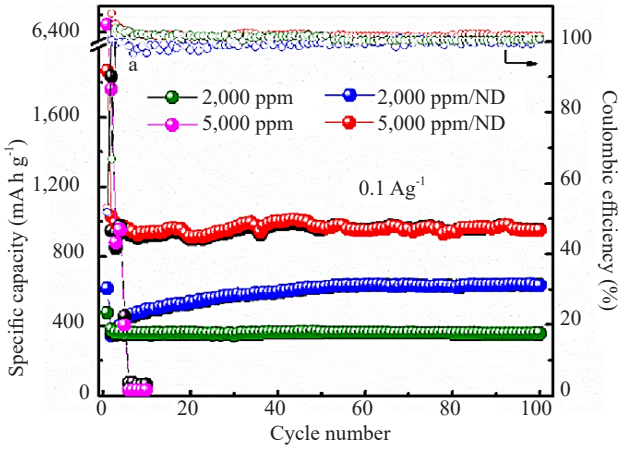

Figure 6. Cyclic performances of graphite anodes with electrolytes having H_2O and 0.8 g/L nanodiamond (ND) at current density of 0.1 A/g [98] Reproduced with permission from Elsevier

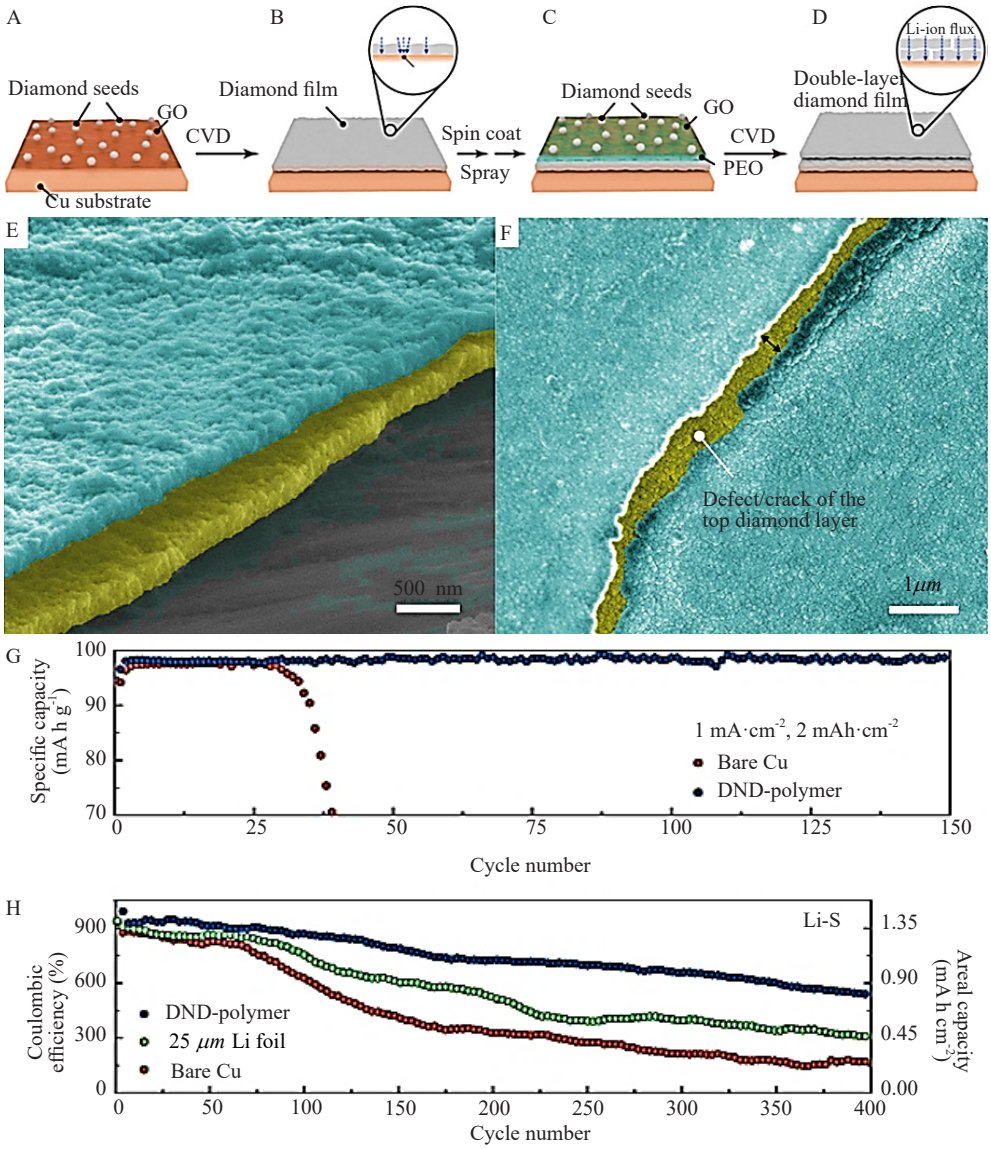

Figure 7. Fabrication and design rationales of nanodiamond interface: (A) colloidal diamond seed was spray coated on Cu substrate pretreated with graphene oxide (GO) release layer; (B) Single-layer nanodiamond film (SND) was grown by microwave plasma chemical deposition (MPCVD); (C) SND covered with poly(ethylene oxide) (PEO) layer; (D) MPCVD to form double layer nanodiamond (DND) film; (E) cross-sectional scanning electron microscopy (SEM) image of DND with false color for double-layer structure; (F) high-magnification top-view SEM image of DND with false color, due to defects in top nanodiamond layer (blue region) can safeguarded by nanodiamond layer (yellow region); (G) long-term cycling CE of bare Cu and DND-polymer electrodes at current density 1 $mAcm^{-2}$ and capacity 2 $mAhcm^{-2}$; and (H) Cycling performance of prototypical Li-S cells at 0.5 C with 25 mm Li foil (~ 5 mAh cm^{-2}), bare Cu with 5 mAh cm^{-2} electrodeposited Li, or DND-polymer with 5 mAh cm^{-2} electrodeposited Li as anode [104]. CVD = chemical vapor deposition
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oxide)/nanodiamond nanocomposite film was used as a lithium battery anode. Lithium ion flux was also studied across the lithium metal interface along with the stable robustness features. The poly(ethylene oxide)/nanodiamond develops a compatible interface and appropriate surface defects to facilitate the uniform Li-ion flux through the nanomaterial. Additionally, mechanically stable nanomaterial was developed due to the integration of nanodiamond with the poly(ethylene oxide) matrix. Furthermore, an interface formation was also found responsible for the stable cyclic performance over long term nanomaterial uses (> 400 cycles). Here, high areal capacity of 2 $mAh \cdot cm^{-2}$ was observed at the current density of 1 $mA \cdot cm^{-2}$ in 150 cycles. The cyclic efficiency was found > 98%. In addition, the battery capacity

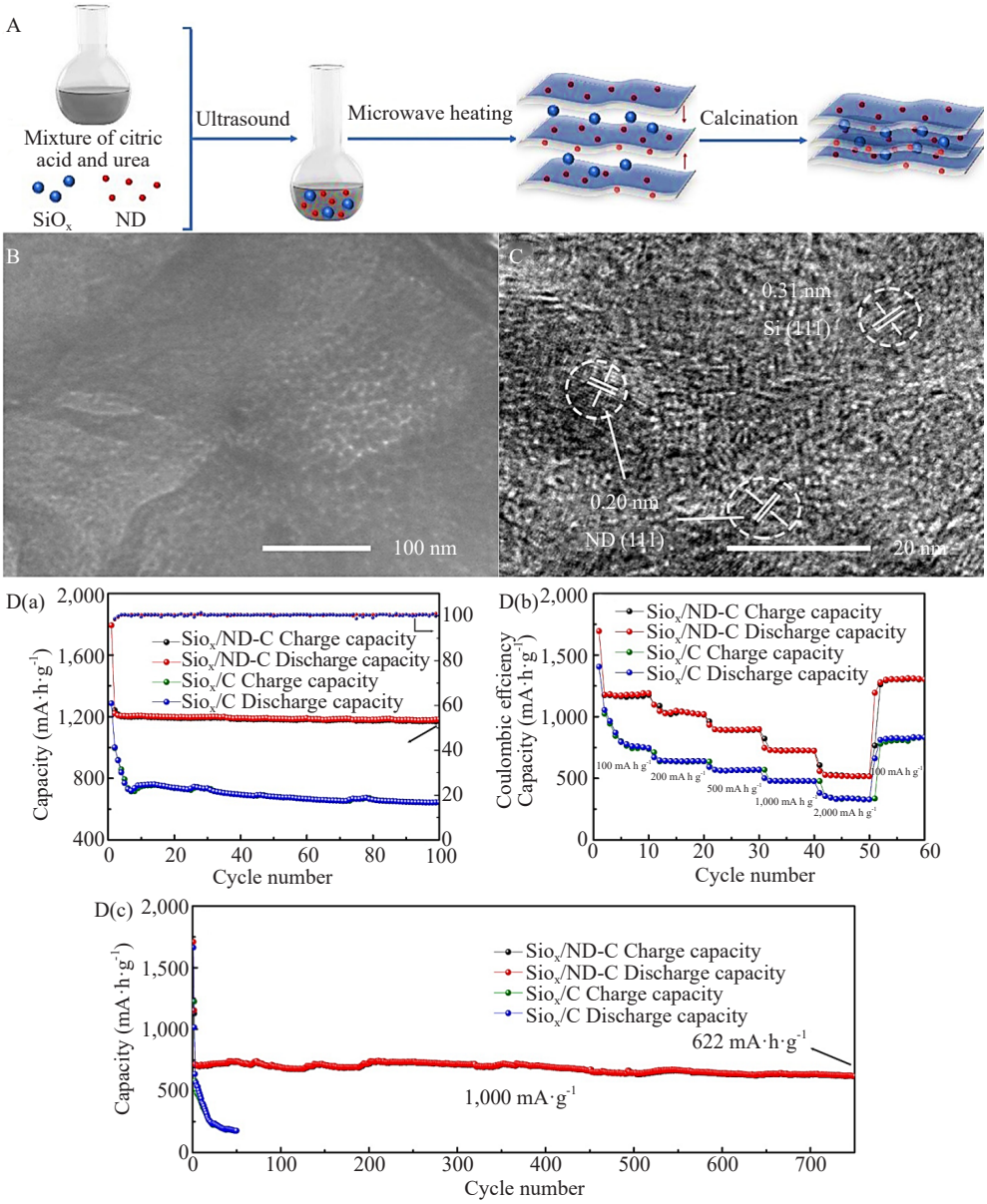

Figure 8. (A) Schematic of synthesis processes of SiO_x/ND-C nanocomposites; (B) TEM image of SiO_x/ND-C; (C) HRTEM images of SiO_x/ND-C. The lattice spacings of 0.31 and 0.20 nm corresponds to (111) of Si and (111) of ND, respectively; and (D) cycle performance at a current density of 100 $mA \cdot g^{-1}$: (a) rate capability at various current densities; (b) long cycle performance at high current density 1,000 $mA \cdot g^{-1}$; (c) of SiO_x/ND-C and SiO_x/C [108]. TEM = transmission electron microscopy; HRTEM = high resolution transmission electron microscopy; SiO_x/ND-C = silica/carbon nanodiamond
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was measured and anode decay was observed after 75-90 cycles. However, capacity retention was found > 90%. It was suggested that formation of multilayered lithium anode material may resolve the problems related to future battery performances and efficiency.

Designs of anode electrodes have been found efficient in enhancing the overall performance of lithium ion batteries [105]. Among carbon nanomaterials, using graphite anode had a high capacity of > 400 mAh/g for lithium ion batteries [106]. Like other nanocarbon nanomaterials, nanodiamond based designs were applied to form battery electrodes [107]. Inorganic nanomaterials like undoped silica (SiO_x) usually have low electrical conductivity of 6-7 × 10^{-4} $S \cdot cm^{-1}$. Consequently,

advanced battery designs based on silica and nanodiamond nanomaterials have been suggested in the literature [109]. Such battery designs had superior charge-discharge and capacity performance. Gao et al. [108] designed an anode based on silica, detonated nanodiamond, and carbon. The scheme for the formation of the nanomaterial is given in Figure 8. Citric acid and urea were used to disperse the nanodiamond and silica nanoparticles and then hydrolysis and microwave heating were performed to form the desired nanocomposite.

Nanodiamond offered fine pathways for the transportation of lithium ions. In fact, the nanodiamond formed a well-aligned and interlinked nanostructure with silica to facilitate the transportation of lithium ions through these nanomaterials. In addition, nanodiamond play an important role in enhancing structural integrity, mechanical stability, and offering a superior surface area for functionalization to facilitate the overall performance of lithium-ion batteries. According to transmission electron and high resolution transmission electron microscopy, the nanodiamond nanoparticles of 5 nm diameter and 0.20-0.31 nm lattice spacing were observed. These nanoparticles beneficially enhanced the interlayer spacing between the carbon nanosheets for lithium ion transference. The cyclic performance of the nanocomposite was studied through Nyquist plots in electrochemical impedance spectroscopy. The studies were performed at a current density of 100 $mA \cdot g^{-1}$ and the corresponding rate performance was studied in the range of 100-2,000 $mA \cdot g^{-1}$. The silica/nanodiamond-carbon-based anode had a specific discharge capacity reducing in the range of 1,709-1,153 $mA \cdot h \cdot g^{-1}$ (first cycle). The charge-discharge performance of the electrode was also studied and a reversible specific capacity of 622 $mA \cdot hg^{-1}$ was perceived (750 cycles).

According to the analysis, the capacity and capacity retention were observed as 1,182 mAh/g and 97%, respectively. The performance of a few silica/nanodiamond-carbon-based battery electrodes is given in Table 1. A study by Gao et al. [108] reported silica/nanodiamond-carbon-based system having high capacity and cyclic performance. Even at the constant current of 1,000 mA/g in 750 cycles, a reasonable capacity of 622 mAh/g was observed for these electrodes. The efficiency was credited to the fine structural design based on nanodiamond and also the facile processing technique used for the formation of these nanomaterials.

Table 1. Electrochemical performance of silica/carbon nanomaterials for anode

Electrode material	Electrochemical performances	Ref
Silica/nanodiamond-carbon	1,182 mA/g (at 100 mA/g after 100 cycles)	[108]
Silica/nanodiamond-carbon	622 mA/g (at 1,000 mA/g after 750 cycles)	[108]
Mesoporous silica/reduced graphene oxide	580 mA/g (at 100 mA/g after 200 cycles)	[110]
Multi-walled carbon nanotube/silicon/silica@carbon	503 mA/g (at 400 mA/g after 500 cycles)	[111]
Polyoly(3,4-ethylenedioxythiophene)/silicon/silica@carbon	~450 mA/g (at 1000 mA/g after 250 cycles)	[112]
Silica@carbon	~408 mA/g (at 200 mA/g after 70 cycles)	[113]
Silica@carbon nanorods	720 mA/g (at 100 mA/g after 350 cycles)	[114]

Detonation nanodiamond possess crystalline nanodiamond aggregates of 4-5 nm having narrow size distribution [115]. This nanodiamond revealed hardness, fine electron/heat conductivity, and heat/chemical stability [116, 117]. A range of efficient nanodiamond nanocomposites have been reported with the polymer matrices such as conjugated polymers, polysiloxanes, polyurethanes, elastomers, rubbers, etc. to fabricate multifunctional nanomaterials [118]. Applications of nanodiamond based nanocomposites have been observed for catalysts, adsorbents, lubricants, engineering, electronics, and biomedical fields [119]. Traditionally, metal oxide cathode and graphite anode were used in batteries [120]. Using advanced porous carbon electrode has the benefits of charge-discharge efficiency and a long life > 500,000 cycles [121]. Due to the low capacity of the porous carbon electrodes, carbon based nanomaterials like nanodiamond have been used to enhance the performance of the resulting electrode materials [122, 123].

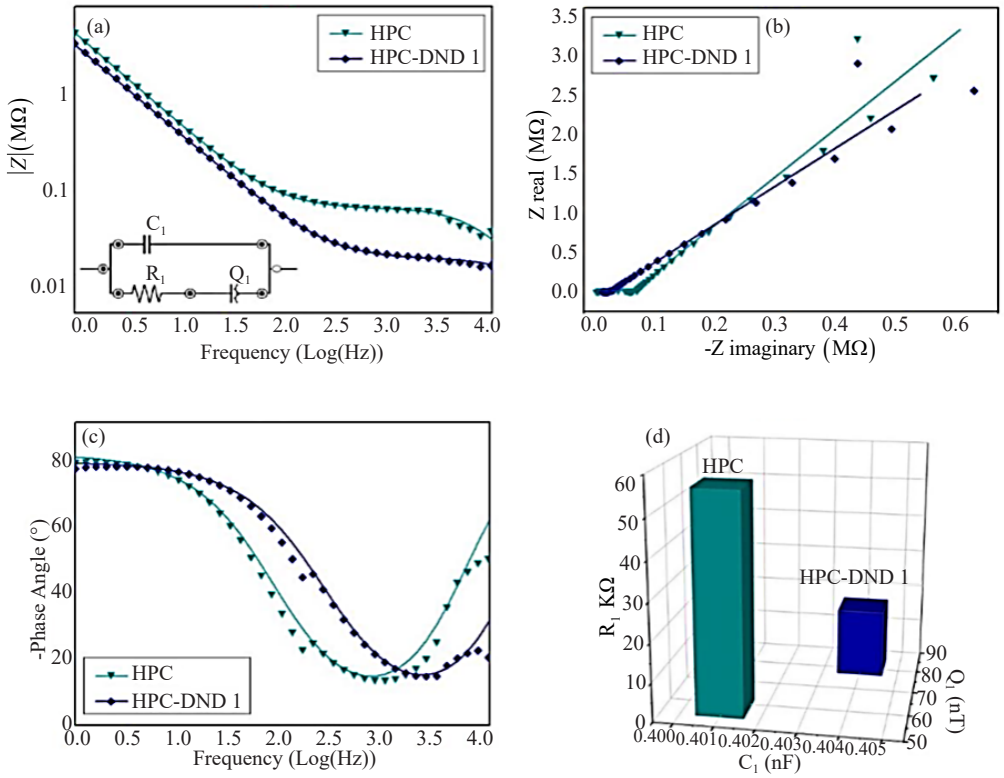

Figure 9. Electrochemical impedance spectroscopy (EIS) experimental data (symbols) and respective fit curves (solid line) for (a) Bode, along with the equivalent circuit in the inset; (b) Nyquist; (c) negative phase angle plots; (d) trend of EIS parameters derived from the fitting procedure for reference HPC and HPC-DND samples [131]. HPC = hydroxypropyl cellulose; HPC-DND = hydroxypropyl cellulose-detonation nanodiamond Reproduced with permission from MDPI

In lithium batteries, separators have also been used in addition to electrode/electrolyte components [124]. Traditionally, polymeric separators based on polyimide or polypropylene have been applied [125]. Sun et al. [126] reported on the polypropylene/nanodiamond separator. Nanodiamond nanoparticles were deposited on the polymer separator using the chemical vapor deposition technique. In this battery system, a capacity of 639 mAh/g was observed during 1,000 cycles. Here, nanodiamond nanoparticles of < 10 nm sizes have offered high lithium ions adsorption capacity. Henceforth, nanodiamond seem to create fine lithium ion transference and diffusion pathways through the system.

According to the reported literature, nanodiamond based materials can improve the stability, reliability, and environmentally friendly performance of the lithium ion batteries [127, 128]. In battery electrodes, nanodiamond nanoparticles have been used as reinforcing agents in anode as well as cathode [129, 130]. In electrolyte form, nanodiamond were suggested to support the movements or precipitation of lithium ions. Palmieri et al. [131] developed the hydroxypropyl cellulose and detonation nanodiamond based nanocomposites by solution method. Including detonation nanodiamond in the matrix enhanced the ionic conduction, charge transportation, and electrochemical properties due to fine nanoparticle dispersion and matrix-nanofiller compatibility. Electrochemical impedance spectroscopy studies of hydroxypropyl cellulose and hydroxypropyl cellulose/detonation nanodiamond are given in Figure 9. Cellulose and detonation nanodiamond derived nanocomposites had inferior total impedance than the pristine nanodiamond in medium/high frequency range of Bode plots. The same behavior was observed by scanning the Nyquist and negative phase angle plots. The ionic conductivity (86 $\mu S \cdot cm^{-1}$) of the cellulose/detonation nanodiamond nanocomposite was found higher than the neat polymer (28 $\mu S \cdot cm^{-1}$). Such behavior was attributed to the dielectric and double layer capacitance occurring at the electrode surface. Since double layer capacitance is directly related to the storage capacity of ions. The high storage capacity of ions suggests that the present system has a large number of free ions leading to high ionic conductivity properties.

Nanodiamond has a high surface area to yield high chemical/heat stability, power density, energy density, and

long cyclic life for charge storage systems [132, 133]. Nanodiamond based electrodes possess high capacity in the form of electrodes [134]. Nitrogen or boron doped nanodiamond nanoparticles have also been used to enhance the charge storage sites for ions due to surface activation [135, 136]. The battery performance was found to be dependent upon the interface between nanodiamond and electrolyte.

6. Nanodiamond nanocomposites in supercapacitors

Among energy storing devices, supercapacitors have also gained prominence [137]. Consequently, several materials have been proposed to attain the desirable supercapacitor performance [138]. For example, the semiconducting polymers have been efficiently explored for the high performance supercapacitor components [139, 140]. Subsequently, polyaniline nanocomposites had a percolation network to support the electron transfer through the system, leading to superior charge storage [141].

Reports on pristine nanodiamond based supercapacitor electrodes have been noticed in the literature so far [142]. Such electrodes usually have low stability and capacitance under a cyclic process. Consequently, conjugated polymers like polyaniline have been reinforced with nanodiamond to enhance the stability, processing, and capacitance properties [143]. Consequently, the polyaniline doped nanodiamond nanocomposites revealed superior specific capacitance of about 640 $F \cdot g^{-1}$ in 10,000 cycles tests (scan rate 1 $mV \cdot s^{-1}$ in the range of -0.6 to 0.6 V) [144]. Palaniappan and researchers [145] fabricated the emulsion polymerized polyaniline/nanodiamond nanocomposites for the supercapacitor electrode designs. The ensuing nanomaterial revealed electrical conductivity and specific capacitance of 2 $S \cdot cm^{-1}$ and 339 $F \cdot g^{-1}$, respectively. Superior electrical conductivity properties seemed to be related to the formation of an interconnecting percolation network for facilitated electron flow through the system. In addition, the supercapacitor electrode had a high power density of 600 $W \cdot Kg^{-1}$ and an energy density of 15.7 $Wh \cdot kg^{-1}$. Hence, the superior stability and cyclic performance of the polyaniline/nanodiamond supercapacitor electrodes were observed. Similarly, further reported systems on polyaniline/nanodiamond nanocomposites have been reported with specific capacitance > 500 Fg^{-1} and capacitance retention > 80 % [146-148]. Nevertheless, limited research reports were noticed on the nanodiamond nanocomposite based supercapacitor electrodes.

7. Prospects of nanodiamond nanocomposites

Energy devices with efficient charge storing and production have been categorized as solar cells, fuel cells, and lithium ion batteries [149-151]. In this concern, efficient electrodes and electrolyte materials have been used in solar cell designs to attain desirably high performance devices [152]. Fuel cell performance has been found dependent on energy/power density, lifetime, and stability [153]. Lithium ion batteries were studied for stability, capacity, charge-discharge, and cyclic behaviors [153]. Using metals or inorganic materials had limitations of high cost and least stability over a long cyclic life. Here, various carbon based nanoparticles have been used to achieve high performance energy storage or production devices and systems. Nanodiamond have been used as one of the exclusive carbon nanoparticles for energy storage/conversion systems depending upon their design efficiencies [154]. The nanodiamond nanocomposites generally have high electron, ion, or charge transfer properties for efficient device performance [155]. Numerous nanocomposite designs with detonated nanodiamond and functional nanodiamond were reported for solar cells, fuel cells, and batteries (Figure 10 and Table 2).

For solar cell designs up till now, acid functional nanodiamond, graphitized nanodiamond, detonation nanodiamond, hydrogenated detonation nanodiamond, and polyfunctional detonation nanodiamond have been applied depicting high optical photovoltage. Along with nanodiamond, inorganic nanomaterials as well as polymers like polypyrrole have been used with nanodiamond in efficient solar cell designs. Limited designs have been observed for nanodiamond nanocomposites for solar cells. The future of nanodiamond based solar cells can be predicted with the formation of improved interfacial designs through doping or nanoparticle modification to affect the solar cell parameters [156].

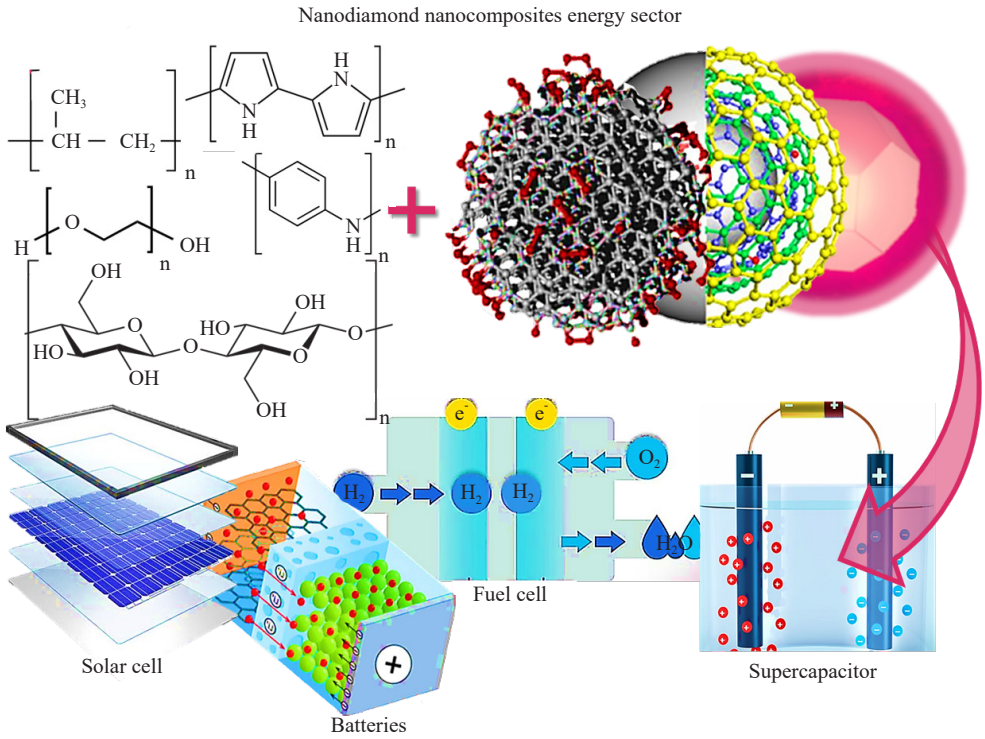

Figure 10. Nanodiamond nanomaterials in energy sector

In addition, developing hybrid nanodiamond nanostructures, that having sustainable, semiconductivity, and synergistic matrix-nanofiller effects, can be beneficial for constructing future high-tech metal free semiconductors or photovoltaics [157].

For fuel cells, successful designs based on detonated nanodiamond filled perfluorinated Aquivion® and polytetrafluoroethylene based Aquivion® perfluorosulfonic acid, having high ionic conductivity and durability properties, were used as proton exchange membranes for hydrogen/direct methanol fuel cells. Such membranes have been known to develop fine proton conduction channels for the passage of ions to ultimately enhance the fuel cell performance with conductivity and high surface area. Again, for fuel cells, limited literature was observed for nanodiamond nanocomposites, and so concentrated research efforts are needed in this direction. Further research in the direction of nanodiamond-graphene or nanodiamond fullerene type nanobifillers in proton exchange membranes can be beneficial for the formation of better proton conduction interfaces. On the other hand, research on nanodiamond based fuel cell catalytic materials needs attention. Here, nitrogen doped nanodiamond nanostructures may show promising catalyst support applications to enhance the catalytic activity and durability [86]. In addition, the formation of doped graphene/nanodiamond hybrids may yield enhanced fuel cell catalytic performance [158].

Besides, the modified nanodiamond and hybrids have been suggested for future thermoelectric energy conversion devices [159]. Here, nanodiamond and BiTeSe based nanocomposite have been suggested for enhanced thermoelectric performance of 0.97 at 473 K, compared with the neat BiTeSe. The thermal conductivity of the nanocomposite was also high in the range of 20-60 $W \cdot m^{-1} \cdot K^{-1}$. In these nanocomposites, the nature of grain sizes/boundaries seems to affect the charge/electron transfer through the system.

For lithium ion batteries, research so far depicted the poly(ethylene oxide) based lithium electrolyte interfaces. Polypropylene and hydroxypropyl cellulose have been found to functional in battery separators or electrolytes with detonation nanodiamond. Such nanodiamond based systems have high durability, specific discharge capacity 1,000-2,000 $mA \cdot h \cdot g^{-1}$, superior cyclic efficiency > 98%, and lifetime. However, some efficient battery electrodes with silica, carbon,

Table 2. Specifications of nanodiamond nanocomposite in energy devices

Design	Nanocarbon	Fabrication	Property/Application	Ref.
Amine functional molybdenum disulfide	Acid functional nanodiamond	Solution; Centrifugation	Solar cell; dispersion nanodiamond 80-200 nm; electrochemical capacitance; optical band gap ~1.8 eV	[61]
Glass substrate	Graphitized nanodiamond	Hot filament chemical vapor deposition	Solar cell; protective layer 500 nm; lower transmittance of nanodiamond coated glass surface than neat glass	[62]
Polypyrrole	Detonation; nanodiamond hydrogenated detonation nanodiamond, oxidized detonation nanodiamond; polyfunctional detonation nanodiamond	Layer by layer technique	Solar cell; separation between highest occupied molecular orbital/ lowest occupied molecular orbital; charge transfer; photovoltage 99 ± 5 mV	[63]
Platinum-Ruthenium nanoparticle	Undoped and boron doped nanodiamond nanoparticles	Chemical deposition; Sonication	Direct methanol fuel cell; electrochemical features; power density 55 mW cm^{-2}; catalytic system	[75]
Platinum	Graphitized nanodiamond	Annealing 1,300-1,600 °C; vacuum 10^{-3} Pa	Electrical conductivity; oxidation reduction reaction catalytic activity; electrochemical surface area 87-89 $m^2 \cdot g^{-1}$; electrochemical surface area retention 65%, after 2,500 cycles	[80]
Few layer graphene	Nanodiamond nanoparticles	High temperature annealing technique (1,200-1,500 °C)	Direct methanol fuel cell; electrocatalytic activity; catalyst layer high surface area of 84.2 $m^2 \cdot g^{-1}$	[82]
Platinum/titanium carbide	Nanodiamond	One pot synthesis	Direct methanol fuel cell; electrochemical surface area retention 70-80%	[84]
Zirconium dioxide	Nanodiamond	One step isothermal hydrolysis	Direct methanol fuel cell; electrocatalytic activity; zirconium dioxide/nanodiamond peak current 5.00×10^{-4} A; nanodiamond peak current 3×10^{-4} A; low carbon monoxide poisoning effect	[85]
Perfluorinated Aquivion® membrane	Detonation nanodiamond	Solution casting	Hydrogen fuel cell, nanoparticles 200-300 nm; proton exchange membrane; sharp enhancements in ohmic loss at 120 °C	[87]
Polytetrafluoroethylene based Aquivion® perfluorosulfonic acid membranes	Nanodiamond	Aqueous-emulsion technique	Direct methanol fuel cell; nanoparticle sizes 100-150 nm; proton conduction channels	[88]
Perfluorinated Aquivion®	Detonation nanodiamond	Detonation; annealing; solution route	Proton conduction mechanism; ~ 20-30% increase in proton conductivity in 20-50 °C; nanodiamond contents 0.5-5.0 wt. %	[89]
Graphite	Nanodiamond	Solvent method; water	Battery electrolyte nanodiamond > 3,000 ppm; 0.8 g/L nanodiamond enhanced initial charge capacity 480-950 mAh/g; current density of 0.1 A/g	[98]
Poly(ethylene oxide)	Nanodiamond	Microwave plasma chemical deposition technique	Lithium electrolyte interface for anode; nanodiamond layer deposited thickness 150 nm; areal capacity 2 mAh cm^{-2}; current density 1 mA cm^{-2} in 150 cycles; cyclic efficiency > 98%	[104]
Silica	Detonated Nanodiamond	Hydrolysis; microwave heating	Lithium ion battery electrode; nanodiamond 5 nm; 0.20-0.31 nm lattice spacing; current density 100 $mA \cdot g^{-1}$; rate performance 100-2,000 $mA \cdot g^{-1}$; specific discharge capacity 1,709-1,153 $mA \cdot h \cdot g^{-1}$; reversible specific capacity 622 $mA \cdot hg^{-1}$ in 750 cycles	[108]
Silica/carbon	Nanodiamond	Hydrolysis; microwave heating	Lithium ion battery electrode; 1,182 mA/g at 100 mA/g after 100 cycles; 622 mA/g at 1,000 mA/g after 750 cycles	[108]
Polypropylene	Nanodiamond	Chemical vapor deposition technique of nanodiamond on polymer surface	Lithium ion battery separator; capacity of 639 mAh/g in 1,000 cycle; lithium ion diffusion pathways	[126]
Hydroxypropyl cellulose	Detonation Nanodiamond	Solution method	Lithium ion battery; electrochemical properties; nanodiamond dispersion; nanocomposite ionic conductivity 86 $\mu S \cdot cm^{-1}$ lower than neat polymer (28 $\mu S \cdot cm^{-1}$); low total impedance of nanocomposite than pristine nanodiamond	[131]
Polyaniline	Nanodiamond	In situ polymerization	Supercapacitor; specific capacitance 640 $F \cdot g^{-1}$ charge-discharge cycles 10,000 cycles	[144]
Polyaniline	Nanodiamond	Emulsion polymerization	Supercapacitor electrode; electrical conduction 2 $S \cdot cm^{-1}$; specific capacitance 339 $F \cdot g^{-1}$; power density 600 $W \cdot Kg^{-1}$; energy density 15.7 $Wh \cdot kg^{-1}$	[145]
Polyaniline	Nanodiamond	Oxidative aniline polymerization	Specific capacitance 150.20 $F \cdot g^{-1}$; cyclic stability 84%; charge-discharge cycles 1,000	[146]
Polyaniline	Nanodiamond	In situ polymerization	Specific capacitance 520 $F \cdot g^{-1}$; energy density 22.3 $Wh \cdot kg^{-1}$; power density 1.4 $kW \cdot kg^{-1}$; capacitance retention 83%	[147]
Polypyrrole	Nanodiamond; gold nanoparticles	Electro-polymerization	Morphology; coating on steel electrode; electron/charge transfer; supercapacitor	[148]

and graphite have also been reported. The field of lithium ion battery electrodes or electrolytes with nanodiamond nanomaterials also demands extensive research efforts to expand the related potential. In this regard, the most effective methods to enhance the future advancements of lithium ion battery performance were suggested as pre-lithiation of nanodiamond and subsequent incorporation in the battery electrodes [160]. The prelithiation technique as well as nanodiamond modification can be beneficial to enhance the energy density properties of future high-tech batteries [161].

Limited research has been observed on the nanodiamond based supercapacitor electrodes so far. Here, the incorporation of zero dimensional nanodiamond in two dimensional graphene nanosheets can be suggested to enhance the electron/charge transfer capability of nanodiamond hybrids, in turn increasing the specific capacitance [162]. In addition, doped nanodiamond and surface modified nanodiamond have been recommended to enhance the electrochemical and supercapacitance of future energy storage devices [163].

On the whole, nanodiamond and derived nanostructures have superior surface area, charge or electron conduction, and electrochemical properties for improved energy competences [164]. Various simple techniques have been applied to construct the nanodiamond and derived nanomaterials. Superior structural design, compatibility, electrostatic, hydrogen binding, or staking, and electron or charge transport have been investigated. Especially, in the form of nanocomposite, adding nanodiamond led to microstructural variations, such as uniform nanoparticle dispersions and matrix-nanofiller interfacial contacts, to support fine ion/electron transfer through the medium. Furthermore, nanodiamond have the advantages of low cost and the least ecologically toxic effects when used in energy systems. Despite the beneficially advanced uses, challenges in nanodiamond fabrication and resulting advanced properties need to be resolved for advanced energy device applications. Still, there is a need to produce more efficient nanodiamond based solar cells, fuel cells, and batteries, relative to graphene or fullerene based systems. The stability of nanodiamond nanocomposites, controlled formation of nanodiamond sizes and nanocomposite nanostructures must be focused on all kinds of above discussed energy device systems. Therefore, continuous efforts seemed to be indispensable to explore the worth of nanodiamond nanomaterials in energy devices, compared with graphene or other nanocarbon based systems.

Since, traditional solar cells, fuel cells, batteries, and supercapacitors employ simple materials and techniques to easily synthesize on a large scale. However, for commercial viability, fabrication of advanced defect free and high surface area nanomaterials has been demanded for fine control over synthesis parameters. In this regard, nanomaterials like nanodiamond, modified nanodiamond, or nanodiamond have superior physical features, nevertheless intricate multi-step synthesis and purification processes may demand cost consumption. Herein, the low cost and availability of nanodiamond nanomaterials, relative to conventional materials, can be beneficial for energy devices. Here, producing sophisticated nanomaterials with facile processing and controlled parameters seems indispensable to achieve high uniformity, purity, high yield and throughput. Initial researches on nanodiamond based energy devices were performed on lab scale devices, but mass production of advanced nanodiamond nanomaterials for commercial scale may bring about revolutions in this field. Incidentally, engineering and manufacturing challenges must be resolved to attain industrial scale nanodiamond based designs. On a commercial scale, adding nanodiamond in supercapacitors and lithium batteries not only upgraded the electrochemical stability but also resulted in high modulus (> 200 GPa) [165]. In this regard, coulombic efficiency of lithium and charge/discharge rate of about 99.4% and 1 $mA \cdot cm^{-1}$, respectively were observed due to a double-layer interface structure. Furthermore, the interface caused excellent stability of the over 400 cyclic performances. For solar cells, practically nanodiamond based protective layers have been efficiently used on a commercial level, however, as discussed in the above sections, further improvements in the nanodiamond designs seem to be indispensable for future advanced energy device uses. Moreover, in energy applications, incorporating nanodiamond nanomaterials may face environmental challenges regarding fabrication, toxicity, and recycling. Owing to nano-sizes, nanodiamond nanomaterials may enter living cells/tissue and may cause damage with exposure beyond certain levels. Hence, environmental and toxicity impacts of nanodiamond must be considered for commercial scale energy applications.

8. Conclusions

This review focuses on developments in the area of nanodiamond based architectures for energy systems. Accordingly, nanodiamond nanomaterials have been developed for efficient solar cells, fuel cells, and lithium ion batteries. Here, facile methods have been used to develop the advanced nanodiamond hybrids. Consequently, the conductive nanodiamond nanocomposites depicted high photovoltage near 100 mV in solar cell applications. In addition, the conjugated polyaniline/nanodiamond and graphene/nanodiamond systems were effective towards superior electrocatalytic activity due to the high surface area in a direct methanol fuel cells. Using zirconium dioxide/nanodiamond in direct methanol fuel cell exhibited a peak current of 3 ~ 5.00 × 10^{-4} A. For lithium ion battery electrodes, nanodiamond nanocomposites with silica and conducting polymers caused significantly high specific capacity (> 600 mAh/g) and cyclic performance. Moreover, conjugated polymers (polyaniline, polypyrrole) have been efficiently used with nanodiamond to portray high specific capacitance > 600 $F \cdot g^{-1}$. The performance of nanodiamond based nanocomposites in different energy systems can be attributed to effective nanostructural designs based on the combination of nanodiamond with polymers, nanocarbons, or inorganic materials. Subsequently, uniform nanoparticle dispersion, matrix-nanofiller interactions, compatibility, electrochemical performance, electron/charge, conductivity, capacity, specific capacitance, and proton conductivity have been analyzed for the energy systems. Furthermore, the structure-property-performance relationships of nanodiamond nanocomposites have been scrutinized for advanced energy production and storage applications. However, there is an intense need for future research efforts targeting high performance nanodiamond nanocomposites for energy systems. Ultimately, the challenges of applying nanodiamond and derived nanocomposites in energy devices can be overcome through continuous efforts in this field.

Conflict of interest

The author declares that they have no conflict of interest.

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