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REVIEW

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Nanodiamonds for energy

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Abstract

Carbon materials have been playing important roles in advancing energy-related technologies and offering great promise to addressing the rising global energy demands and environmental issues. Nanodiamonds, an exciting class of carbon materials, with excellent mechanical, chemical, electronic, and optical properties, have great potentials in energy-related applications. In this contribution, we summarized some of the recent progress on nanodiamonds for energy storage, conversion, and other related applications in sustainable energy research. We discussed the promising opportunities and outlooks for nanodiamonds in energy-related fields.

KEYWORDS

energy, energy conversion, energy storage, nanodiamond

1 | INTRODUCTION

Since the first report of nanodiamonds (NDs) in 1963, material synthesis and application of NDs has progressed significantly.[1] The unique extended C-sp^3 structure of NDs gives them excellent mechanical, thermal, and optical properties, as well as high surface area and tunable surface structure.[2] NDs have been successfully synthesized through many approaches including: detonation synthesis,[3] laser ablation,[4] ball milling at high pressure and temperature,[5] energy-assisted chemical vapor deposition,[6] ion irradiation of graphite,[7] ultrasound cavitation,[8] and other methods.[9-11] NDs have been widely used in the fields of drug delivery,[12] magnetic sensing,[13] nanocomposites,[14] bioimaging, and cellular marking[15] because of their chemical and physical properties.[16] Recently, the superior catalytic activity, high surface area, and excellent chemical stability of NDs has drawn considerable interest from energy-related fields.[17]

Development of harvesting and using clean and sustainable energy techniques has become one of the most challenging in energy management to meet the growing global energy demands.[18] New nanotechnologies and materials have been demonstrated for energy-related fields including energy storage (eg, batteries) and conversion (eg, electrocatalysis) during the past decades. In this contribution, we will review recent progress on the application of NDs to energy-related fields. These applications include supercapacitors and batteries, electrochemical catalysis, optoelectronic, thermoelectric, and other energy-related systems as shown in Figure 1. Instead of an exhaustive review of the field, this perspective aims to demonstrate the promising opportunities for NDs in energy-related fields and provides an outlook and further opportunities for the application of NDs in energy.

2 | NDS IN ENERGY STORAGE

NDs have been used in energy storage devices because of their high surface area, good mechanical properties, high chemical stability, and relatively high conductivity. Appropriate doping or surface modification of NDs could

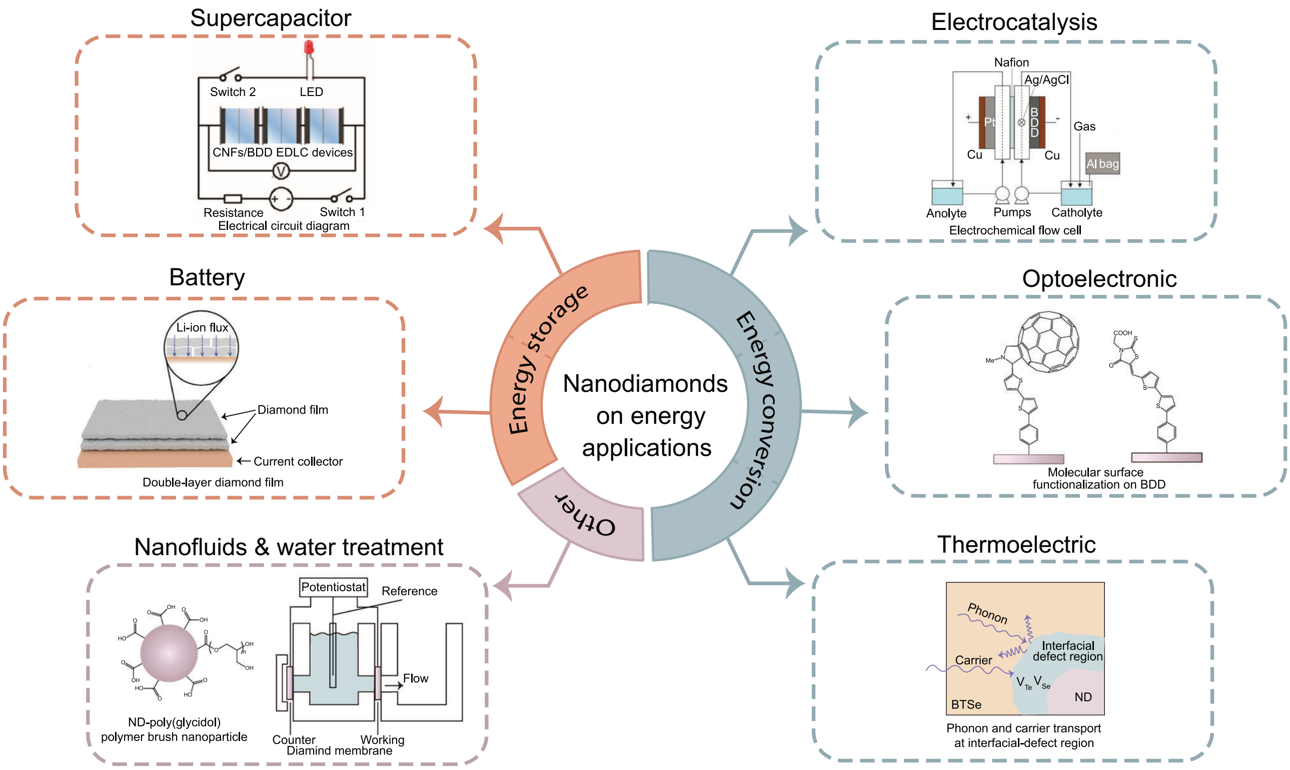

FIGURE 1 Applications of nanodiamonds on energy-related fields (eg, supercapacitor,[19] battery,[20] electrocatalysis,[21] optoelectronic,[22,23] thermoelectronic,[24] nanofluids,[25] and water treatment[26])

alter their electronic structure, which could facilitate their application into supercapacitors and batteries.

2.1 | Supercapacitors

Supercapacitors have high power densities, fast charge/discharge rates, long cycle lives, and wide ranges of operating temperature, which make them one of the most promising electrochemical energy storage devices.[27,28]

Vacuum annealing of NDs at temperatures 1170 to 2170 K forms onion-like carbon materials with a specific capacitance of 70 to 100 F g^{-1}.[29] Conductive doped diamond films have been used as an electrode material for supercapacitors in recent years. For example, boron-doped diamond (BDD) with p-type conductivity has a high current capacity.[30] Detailed studies of the morphology and size of the crystals, surface termination, doping level, redox behavior of diamond electrode, electrochemical pretreatment effects, and other electrochemical factors of BDD have been investigated. N-type diamond doped with nitrogen[31] or phosphorus[30,32] was also reported, but there are limited studies of their physical characteristics as the doping concentration is low compared with BDD.

NDs can exhibit improved specific capacitance with 640 F g^{-1} and up to 10 000 galvanostatic cycles when they are integrated with electrochemically active polymers, such as polyaniline.[33] Particularly, incorporation of NDs into 1-D, 2-D, and 3-D networks of carbon nanotubes,[34] graphene oxide,[35] and porous titanium carbide[36] offers larger surface area and greater potential for energy storage. Furthermore, an ND substrate can be incorporated with ruthenium oxides,[37] nickel hydroxide,[38] manganese oxide,[39] as well as redox-active couples,[40] which improves the capacitance and other related properties.

2.2 | Batteries

Lithium (Li) ion batteries have been developed for commercial electronics, electric vehicles, and storage of energy on the grid. The large surface area, chemical inertness, and high Li adsorption capacity of NDs make them a promising alternative cathode material[41] and anode material.[42-44] Introducing detonation NDs (DNDs) into an aggregated graphene nanosheet anode increased the capacity and cycling performance compared to the anode without DNDs.[42] An Li-ion battery anode composed of multiwalled carbon nanotubes embedded into a 400-nm diameter porous nanohoneycomb diamond structure improved the specific capacity to 894 mAh g^{-1}.[44] A film of ultrananocrystalline diamonds with nitrogen grain-boundaries (N-UNCD) provides a chemically robust coating for natural graphite (NG)–Cu composite anode, which suppressed the cointercalation of electrolyte in NG and enhanced the capacity retention.[43]

One critical issue hindering the development of Li batteries is the stability of the interface between Li metal and the electrolyte. A double-layer NDs film enhanced the defect tolerance, which resulted in a uniform flux of ions and strong mechanical properties.[20] The introduction of NDs into Li metal batteries not only improved the electrochemical stability, but the extremely high modulus (>200 GPa) of NDs suppressed the formation of Li dendrites. The double-layer interface improved the Coulombic efficiency of Li metal to more than 99.4% at an areal charge/discharge rate of $1\,mA\,cm^{-1}$. Additionally, the interface had excellent stability in both Li half-cell and Li-S full-cell configurations (more than 400 stable cycles).

NDs have also been used as an electrolyte additive to codeposit with Li ions and suppress the growth of Li dendrites.[45] In this study, ND particles served as heterogeneous nucleation seeds and adsorbed Li ions during Li plating, which caused uniform deposition of Li and improved stability and cycling performance.

NDs have also been used in nuclear batteries, as their bandgap is larger than many other semiconducting materials.[46] The reported nuclear micropower battery had no degradation after 1400 hours of radiation exposure from a high-activity ^{90}Sr-^{90}Y source. The maximum output power density was $2.4\,\mu m\,Wcm^{-2}$ using ^{238}Pu α source.

3 | NDS IN ENERGY CONVERSION

NDs have been applied to energy conversion fields owing to the superior electric features such as electrochemical properties, optoelectronic properties, as well as thermoelectric behaviors.

3.1 | Electrocatalysis

Electrochemical techniques offer a robust and environmentally benign path to accomplish target energy conversion, which makes the development of efficient electrocatalysts critical. The large surface area, unique surface morphology, and electrochemical stability make NDs strong candidates for the electrocatalytic conversion of electrical energy into chemical energy. The multiscale tenability of NDs also makes NDs a strong candidate for use as an electrode material. Doping with heteroatoms also improves conductivity, corrosion resistance, and catalytic performance.

Electrochemical and photoelectrochemical reduction of carbon dioxide (CO_2) into useful chemicals is an alternative method of energy conversion.[47-50] Photoelectrochemical reduction of CO_2 by one-electron activation to carbon monoxide (CO) with high selectivity and minimal formation of hydrogen has been demonstrated by NDs.[51,52]

The wide potential window in aqueous solution, chemical inertness, and mechanical durability of BDD, makes it a potential material for CO_2 reduction. The selectivity of formate formation from CO_2 reached 99% with BDD as the electrode in a flow cell; the production of formate is $473\,\mu mol\,m^{-2}\,s^{-1}$ at a current density of $15\,mA\,cm^{-2}$ with a faradic efficiency of 61%. In addition, the BDD has no obvious decay after 24 hours of operation.[21] Furthermore, the formation of a CO side product slightly increases with increased doping of boron, suggesting the binding energy of CO_2 and its intermediates could be altered by doping levels.[53] Besides formate, a 74% Faradic efficiency (FE) of formaldehyde formation has been achieved in methanol, aqueous NaCl, and seawater electrolyte.[54]

In addition to the above C_1 products, nitrogen-doped nanodiamond has been reported to convert CO_2 to acetate with a FE of about 90% at −0.8 to 1.0 V. The improved FE is attributed to the high overpotential for hydrogen evolution and highly active N-sp^3C species for CO_2 reduction.[55] The synergistic effect of B and N codoping gives boron and nitrogen codoped NDs (BND) good ethanol selectivity with high FE of 93.2% at −1.0 V vs RHE.[56] BND also outperformed the kinetic current density, stability, and methanol tolerance of oxygen reduction reaction under alkaline conditions of commercial Pt/C catalyst.[17]

The p-type conductive crystalline BDD surface with covalently linked cobalt complexes has good stability and electrocatalytic activity for CO_2 reduction to CO in acetonitrile electrolyte.[57] Ruthenium dioxide deposited on BDD also produces formate and methanol with 40% and 7.7% FE, respectively.

3.2 | Optoelectronic application

NDs have tetrahedral network structures, large grain-boundary density, and low negative-electron affinity, which makes them suitable for optoelectronic applications. Diamond has a wide bandgap (5.4-5.6 eV). The effect of the semiconducting properties of diamond on photoelectrochemical behavior has been known for over three decades.[58] After annealing, electrochemical impedance, photocurrent, and photopotential properties of undoped polycrystalline diamond suggest that the photo effects are caused by structural defects. In particular, dislocations in diamond crystallites near intercrystalline boundaries formed during the high-temperature annealing.[59] The photocurrent of doping with boron or nitrogen increased dramatically compared with undoped one.[60,61]

Surface functionalization of NDs with molecules[22,23] and hybridization of nanoparticles with NDs[62] have gained significant attention in solar cell devices. Coupled with two donor-acceptor molecules by Suzuki cross-coupling reaction, bithiophene-C_{60} and bithiophene-dicyano and BDD thin films had high photoconversion efficiency and photostability compared with tin-doped indium oxide (ITO) and fluoride-doped tin oxide (FTO) substrates. The improved performance was attributed to the matching energy levels and strong C–C bonding at the organic-diamond interface.[22] Modifying organic dyes on the surface of BDD foam gives a cathodic photocurrent density of ca. 500 to 700 nA cm^{-2} at −0.2 V which is approximately three times larger than those on the flat diamond and ca. 15 to 22 μA cm^{-2} within 1- to 2-days long-term illumination with chopped white light at 1 sun intensity and −0.3 V bias.[23] Gold nanoparticle-UNCD hybrid material[62] had improved electrical conductivity of 230 Ω^{-1} cm^{-1}, enhanced electron field emission (EFE) properties (viz, a low turn-on field of 2.1 V μm^{-1} with a high-EFE current density of 5.3 mA cm^{-2} at applied field of 4.9 V μm^{-1}), and a stable life-time up to a period of 372 minutes. The above studies open new prospects in flat panel displays and photovoltaic devices.

3.3 | Thermoelectric energy conversion

Doped NDs have been demonstrated thermoelectric transport properties using a set of eight substrate-free boron-doped nanocrystalline diamond foils,[63] although NDs have outstanding thermal conductivity and electrical insulation properties. Nevertheless, the thermoelectric figure of merit zT did not exceed 0.01 even at 900°C, due to low mobility of charge carriers (about 1 cm^2 V^{-1} s^{-1}) and high thermal conductivity (between 20 and 60 W m^{-1} K^{-1}). It turned out both the nature of the grain boundaries and gain size influenced the transport charge carriers and phonons. Nanodiamond-dispersed $Bi_2Te_{2.7}Se_{0.3}$ (ND/BTSe) composites display improved thermoelectric performances[24] with maximum zT of 0.97 at 473 K compared to pristine BTSe. The interfacial defect region at ND/BTSe interface acts as phonon-scattering sites and the electrical conductivity significantly increases, elucidating that incorporation of NDs into n-type BTSe matrix is an effective and promising approach to improve thermoelectric performance.

4 | OTHER APPLICATIONS IN SUSTAINABLE ENERGY RESEARCH

Other than energy storage and conversion applications, the addition of NDs into nanofluids caused enhanced heat transfer due to their high thermal conductivity, high hardness, relatively low density, and very low electrical conductivity.[25,64-66] Tuning surface chemistry allowed NDs membrane exhibiting distinct and specific chemical properties for selective removal of the contaminant in wastewater.[26] These diverse efforts open new avenues for the application of NDs.

5 | SUMMARY AND OUTLOOK

In this contribution, we have summarized recent progress on the application of NDs to energy-related fields, including supercapacitors and batteries on energy storage; electrochemical catalysis, optoelectronic, and thermoelectric on energy conversion; nanofluids and water treatment on other energy-related systems. NDs hold great potential for applications in energy storage and conversion-related fields with outstanding electrochemical properties. Nonetheless, the practical application of NDs is in the early stages and many critical issues have to be properly addressed. The understanding of physical, chemical, and electronic properties of NDs with different structure as well as surface chemistry need to be further investigated. Moreover, the control of size, shape, surface modulating, and doping level with high-quality NDs will enable further advantages of its electrochemistry to be realized. Overcoming those challenges would make NDs more possibilities in the energy-related fields.

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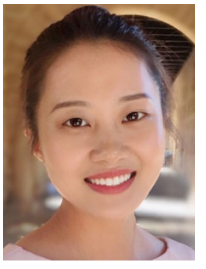

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