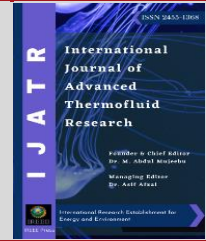


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Editorial

Green Nanomaterials and Nanotechnologies for Energy Applications

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Abstract

Nanomaterials and nanotechnologies have conquered almost all domains of science and technology. However, the environmental and health impacts associated with the synthesis of nanoparticles, and the use of nanoproducts and technologies have been a serious concern. Thus, the emerging trend is to adopt green approaches wherein clean, non-toxic, and eco-friendly reagents and procedures are employed for the synthesis of nanoparticles. Proper linkage of nanotechnology with green chemistry could pave the way for an environmentally sustainable society, which is an ongoing challenge. Abundant literature is available on the green nanomaterials and nanotechnologies, and a brief review of the application of green nanomaterials and technologies for energy applications is presented in this article. There is a wide scope for extensive research in this domain for the effective utilization of green nanomaterials towards realizing efficient and sustainable energy technologies for the future.

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1. Introduction

The concerns over depletion of fossil fuels and the drastically escalating environmental pollution have necessitated wide-spread adoption of clean, renewable, and sustainable technologies for the exchange, conversion, harvesting, and storage of energy. While proposing viable solutions, a trade-off between energy-efficiency, sustainability, and affordability is the main challenge, which is being tackled by researchers and the industry. In this regard, the remarkable contributions of nanoscience and nanotechnology have been well-demonstrated (Wang and Zhiquan 2014), and this domain undergoes continuous research and development. A wide variety of nanomaterials, products, and technologies have been explored and proposed for clean energy applications.

The term nanoscience refers to the manipulation and characterization of matter at the nanoscale, while nanotechnology deals with the design, characterization, production, and application of structures, devices, and systems at the nanoscale (Guisbiers et al. 2012; Sudha et al. 2018); nanomaterials link both these areas together (Guisbiers et al. 2012). Nanotechnology is a multidisciplinary field that encompasses various disciplines such as physics, chemistry, biology, medicine, materials science, and engineering (Madkour 2019).

Parallel to the dramatic development of nanomaterials and technologies, their harmful impacts on the environment and human health have been a serious concern. This has resulted in the emergence of “green nanotechnology”, which has three major goals: i) promoting clean technologies that use nanotechnology, (ii) minimizing the environmental and human health risks involved in the manufacture and use of nanomaterials and products, and (c) replacing existing products with new environment-friendly nanoproducts (Schmidt 2007). In order to eliminate the generation of harmful by-products from the synthesis of nanomaterials, sustainable and eco-friendly synthesis approaches, known as ‘green synthesis routes’, have been proposed; green synthesis uses ideal (non-toxic) solvent systems and natural resources (Singh et al. 2018). There are many reviews available on various aspects of green nanomaterials and green nanotechnology, e.g. (Das and Mandal 2015; Duan et al. 2015; Duarte et al. 2018; Eckelman et al. 2008; Lu and Ozcan 2015; Patwardhan et al. 2018; Saratale et al. 2018; Varma 2012; Villaseñor and Ríos 2018). However, this short review specifically focuses on the prospects of green nanomaterials in the energy sector.

2. Green synthesis of nanomaterials

Compliance with the basic principles of green chemistry and green engineering is essential to ensure effective applications of nanomaterials with minimal or no impact on the environment (Eckelman et al. 2008). In green synthesis, the nanomaterials are synthesized through green routes (using plants, plant extracts, agricultural residues, micro-organisms, etc.) that eliminate generation of unwanted or harmful by-products (Fig.1). In other words, use of eco-friendly solvent system and reducing agents, and nonhazardous capping agents is the main strategy of green synthesis (Varma 2012; Devatha and Thalla 2018). Thus, Green synthesis of nanomaterials is simple, nontoxic, energy-saving, affordable, and clean, compared to the conventional methods (Dahoumane et al. 2016; Singh et al. 2018; Wadhwani et al. 2016; Velusamy et al. 2016). Saratale et al. (2018) provided an exhaustive review of the various green synthesis routes, materials involved, and applications of green nanomaterials.

Another method of green synthesis of nanoparticles is the use of supercritical fluids such as water. Supercritical water forms a homogeneous phase with inorganic and organic substances, and water itself works as an acid or base catalyst. Synthesis by supercritical water is termed as supercritical hydrothermal synthesis, and various metal oxide nanoparticles synthesized by this method have been proposed for solar energy devices (Adschiri et al. 2011). However, proper choice of the precursor is important to control the associated GHG emissions (Caramazana et al. 2018). Apart from the biological and hydrothermal methods, the microwave-assisted synthesis has also been regarded as green, owing to its substantial energy-saving benefit compared to the other heating methods (Butt and Bandarenka 2016) (Shukla and Iravani 2017; Gour and Jain 2019; Singh et al. 2019).

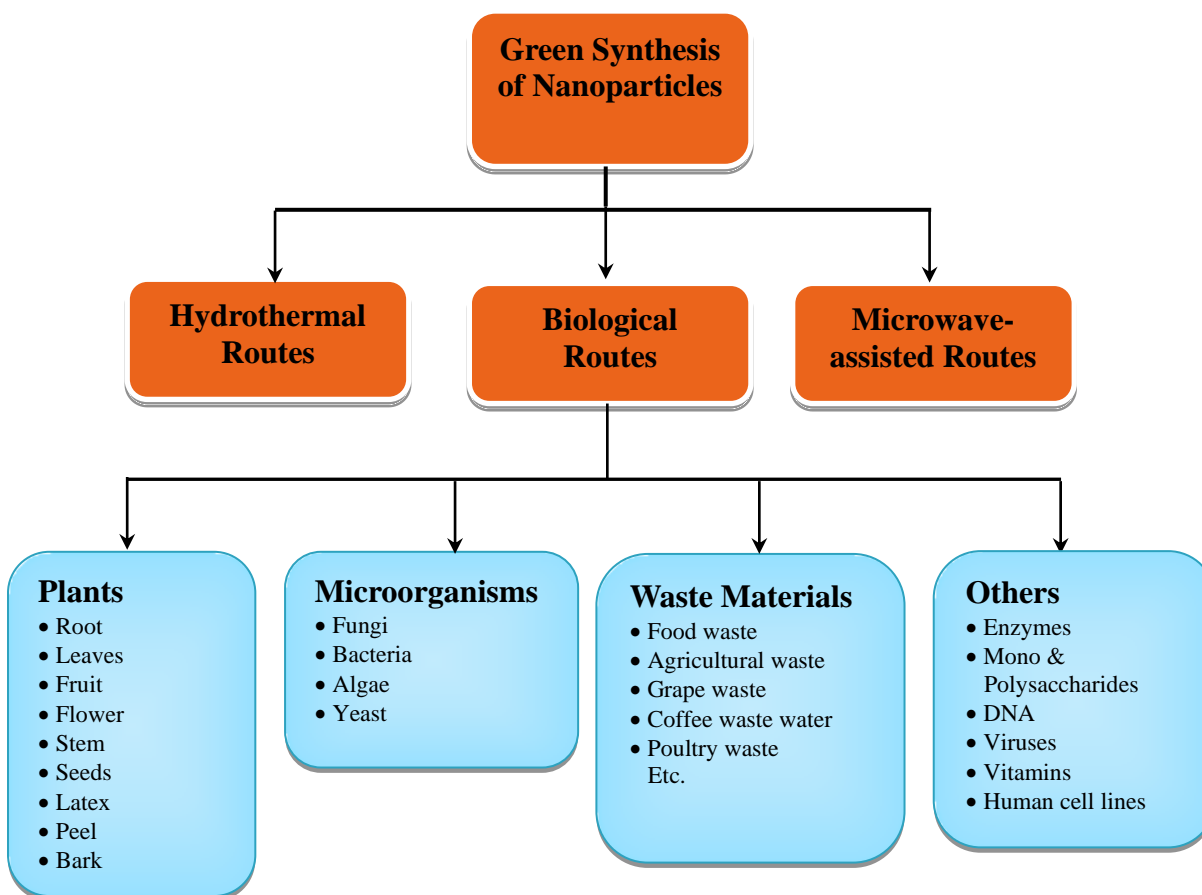


Fig.1: Green synthesis routes for nanoparticles (Singh et al. 2018; Velusamy et al. 2016; Adschiri et al. 2011; Shukla and Iravani 2017; Devatha and Thalla 2018; Gour and Jain 2019; Shabir Ahmad et al. 2019; Hussain et al. 2016; Sharma et al. 2019).

3. Green nanomaterials for energy applications

Green nanomaterials cover two types: 1) any conventional nanomaterial synthesized by green routes, and ii) nanomaterials produced from natural bioresources (Fig. 2). Therefore, according to the first category, all energy applications where a normal nanomaterial is used are relevant in this context, provided there is a scope for green synthesis of the nanomaterial involved. The most common organic nanomaterials used for green energy harvesting are carbon nanotubes, fullerenes, and graphene, while the inorganic category includes platinum, silver, gold, aluminum, titanium dioxide (TiO_2), copper oxide, nickel oxide, cerium oxide, molybdenum trioxide, cadmium sulfide, cadmium selenide, cadmium telluride, and bismuth sulfide; Holkar et al. (Holkar et al. 2018) categorized these materials for different applications (such as solar, wind, and hydro) with their roles. Wang et al. (2020) provided a comprehensive review of multifunctional inorganic nanomaterials for clean energy applications. Researches are in progress to develop nanomaterials of different shapes and sizes, such as nanoparticles, nanowires, nanotubes, quantum dots, nanosheets, nanorods, nanofibers, and nanopores (Bhanvase and Pawade 2018). Plenty of literatures are available on the application of nanomaterials for conversion, storage, exchange, and harvesting of energy, e.g. (Niemann et al. 2008; Dai et al. 2012; Abdin et al. 2013; Gurjar and Tyagi 2015; Hussein 2015; Qin 2016; Liu et al. 2017; Holkar et al. 2018; De et al. 2019; Madkour 2019); though a comprehensive review of these works is

beyond the scope of this article, few recent developments in green nanomaterials for energy applications are mentioned here.

Carbon nanomaterials have unique characteristics that make them promising candidates for energy-conversion and storage (Su and Schlögl 2010; Dai et al. 2012; Candelaria et al. 2012; Q. Zhang et al. 2013; Yang et al. 2015; Bayatsarmadi et al. 2017; Guo et al. 2017; Liu et al. 2018; Perathoner and Centi 2018). Carbon nanomaterials and nanofibres are much more energy intensive than alumina. Graphene – a 2D carbon nanomaterial isolated from graphite (Nicol 2019) or developed from hydrocarbons (COROŞ et al. 2019), has been identified to be excellent for energy conversion and storage applications (Pumera 2011; Liu et al. 2012; Sarkar and Bhattacharyya 2012; Sahoo et al. 2012; Sun and Shi 2013; Li et al. 2014; Dollfus et al. 2017; Amollo et al. 2018). However, the environmental and health impacts associated with its synthesis and applications have been a challenge (Jastrzębska and Olszyna 2015; Lalwani et al. 2016), and hence there has been a growing interest to develop green synthesis routes for graphene (Agharkar et al. 2014; COROŞ et al. 2019; Kumar et al. 2019). Titania-reduced graphene oxide nanocomposites synthesized in a greenway exhibited enhanced photocatalytic properties, which are promising for solar cells and energy storage devices (Shah et al. 2012).

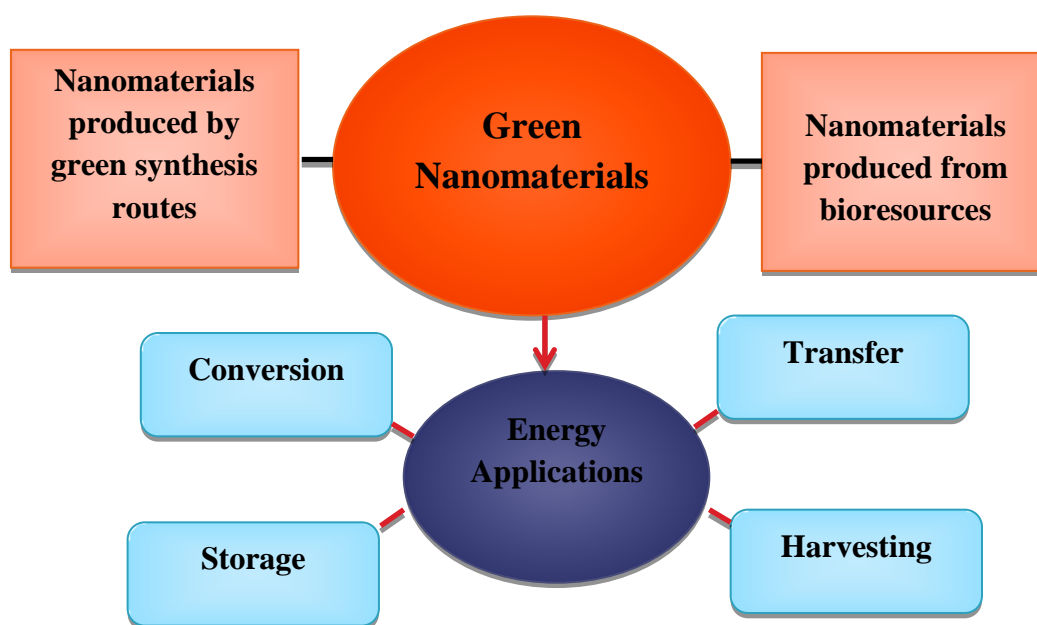


Fig.2: Green nanomaterials and energy applications.

Apart from pure graphene, a wide variety of organic nanostructures have been experimented to enhance the conversion efficiency of thermoelectric (TE) power generators. Even though thermoelectric conversion is a green technology, one of the drawbacks of the widely used conventional inorganic TE materials is toxicity. This could be addressed by the introduction of nanostructures containing organic conducting polymers and carbon nanoparticles as green TE materials (Bharti et al. 2017; C. Gao and Chen 2016; Song et al. 2017). Conducting polymer nanostructures of all dimensions (1D, 2D and 3D) have been proposed for various energy applications (Yin and Zheng 2012; Shi et al. 2015). Single-walled carbon nanohorns are structures of single-graphene tubules with highly strained conical ends; they are excellent for fuel cells, solar cells, supercapacitors, and lithium ion batteries (Zhang et al. 2015). 3D graphene-based composites have been proposed for energy applications, owing to their unique features such as non-agglomerated 3D

inter-networked morphology, large pore volume, high accessible surface area, controlled inter-sheet connectivity, and high stability and mechanical strength (Mao et al. 2015)

Since the advent of graphene, there has been a growing interest to develop atomically thin (single or a few atoms thickness) 2D single- and multi- layered nanomaterials (also known as nanosheets) (Pottathara et al. 2019). Their unique properties such as high packing density and volumetric capacitance make them highly attractive for energy storage applications (Mendoza-Sánchez and Gogotsi 2016). Layered double hydroxides (LDHs) are good for energy applications, as electrode, dielectric, and even semiconductor (Chew et al. 2015). Inorganic 2D nanomaterials have excellent electrochemical properties that make them ideal for energy storage and conversion (Feng et al. 2015).

A major breakthrough in the development of green nanomaterials is the advent of nanocellulose, a purely natural nanomaterial extracted from the lignocellulosic bioresources by chemical, mechanical, or enzymatic methods. Nanocellulose has unique properties that make them excellent substitutes for synthetic nanoparticles (Mondal 2017; Nasir et al. 2017). Among the diverse potential applications of nanocellulose, recent studies have reported its amazing benefits for energy domain (storage, harvesting, conversion, and conservation of energy) (Erlandsson et al. 2016; Sabo et al. 2016; Julkapli and Bagheri 2017; Du et al. 2017; Wang et al. 2017; Lay et al. 2017; Dutta et al. 2017; Chen and Hu 2018; Kim et al. 2019; Tayeb and H. Tayeb 2019; Lasrado et al. 2020). Use of nanocellulose as transparent, conductive substrate for the development of light-weight, foldable solar cells (Fig. 3) was reported (Nogi et al. 2015). Nanocellulose-only and Nanocellulose-based hydrogels, aerogels, and foams have been proposed for energy storage and thermal insulation applications (De France et al. 2017; Zu et al. 2016; Lavoine and Bergström 2017; Zaman et al. 2020; Geng et al. 2020). Carbon nanostructures derived from biomass and agricultural wastes, known as nanostructured biocarbons, are promising sustainable alternatives for energy conversion, storage, and harvesting (Santhiago et al. 2018). A robust, flexible, multilayered triboelectric nanogenerator (FM-TENG) with nanostructured biocarbon as the cathode material was proposed for self-powering electrochemical process, as an excellent replacement for the conventional fossil fuel-powered electrochemical method (Chen et al. 2017).



Fig. 3. Nanocellulose-based foldable solar cell (reproduced from Nogi et al. (2015) as per creative commons attribution norms).

Super-hard cutting tools and super-smooth hydraulic pumps made of boride-based nanocomposites can save energy, water, and materials; nano-boride coatings make cutting tools cut faster and wear out slower

compared to the conventional ones, and decrease friction in hydraulic pumps (Lubick 2009). Carbon-based and polymer-based nanocomposites have been explored and proposed to enhance the performance of pyroelectric, piezoelectric, photovoltaic, and thermoelectric devices for energy-harvesting from pavements and roadways (Ahmad et al. 2019). Perovskite nanomaterials synthesized by green approach (using genetically modified viruses) exhibited very high photocatalytic and photovoltaic performance, which were also proposed for solar energy conversion application (Nuraje et al. 2012).

The miscellaneous nanomaterials/nanostructures (or their class) reported for energy conversion and/or storage include but not limited to, earth-abundant inorganic electrocatalysts and their nanostructures (Faber and Jin 2014), manganese dioxide (Julien and Mauger 2017), electrospun nanomaterials (Sun et al. 2016; Santangelo 2019), nanostructured CeO₂-based materials (Sun et al. 2012), nickel nanowires for hybrid supercapacitors (Xu et al. 2016; Naveenkumar and Kalaignan 2018), highly crystalline mesoporous C₆₀ with ordered pores (Benzigar et al. 2018), 3D graphene-based composites (Mao et al. 2015), hierarchically porous carbons (Dutta et al. 2014), 3D carbon-based nanostructures (Jiang et al. 2013), nanostructured metal chalcogenides (Gao et al. 2013), branched nanowires (Bierman and Jin 2009; Cheng and Fan 2012), Zinc oxide film with hierarchical nanoparticles (Chou et al. 2007), hollow nanostructures (Yu et al. 2016 & 2017), carbon aerogels (Biener et al. 2011), crumpled graphene-based nanocrystals (Mao et al. 2012), colloidal metal and metal alloy nanoparticles (You et al. 2013), semiconductor nanomaterials such as TiO₂ (Chen 2009; Ye et al. 2014), oriented and controlled nanostructures (Liu et al. 2008), 1D nanomaterials (Han et al. 2011; Han and Ho 2014; Ma et al. 2016; Chen et al. 2018), metal-organic frameworks (also known as porous coordination polymers) (Wang et al. 2017), protein-based nanomaterials (Lee et al. 2013), and hybrid nanostructured electrode materials (Yu et al. 2013). However, the green synthesis of most of these materials needs extensive research.

Green Nanofluids

Nanofluids are produced by dispersion of nanoparticles in a base fluid, which significantly enhances the thermal conductivity of conventional heat transfer fluids (Das et al. 2008) (Ganji et al. 2018; Sheikholeslami 2019). Nanofluids play important role in various energy exchange and energy conversion applications (Jama et al. 2016; Nagarajan et al. 2014; Said et al. 2014; Reddy et al. 2017; Hussain et al. 2019; Muñoz-Sánchez et al. 2018; Bhalla and Tyagi 2017; Islam et al. 2015). An interesting breakthrough in nanofluids is the advent of hybrid nanofluids wherein two or more nanoparticles are immersed in the base fluid, which has shown further enhancement of the thermal and rheological properties (Kumar and Arasu 2018). However, as already mentioned, the emerging trend is to adopt green approaches for the synthesis of nanoparticles (Genuino et al. 2013; Ghulam 2016); the resulting nanofluids are termed as green nanofluids (Narayanan and Rakesh 2019). Several researchers have reported development and characterization of green and eco-friendly nanofluids, such as silver and gold nanofluids (Mollick et al. 2014; John et al. 2015), graphene-based nanofluids (Mehrali et al. 2016), and coconut fiber-based nanofluids (Adewumi et al. 2018). These green nanofluids would be promising alternatives for their conventional counterparts, for various energy conversion applications. Holkar et al. (2018) listed different nanofluids employed for energy harvesting (with the methods of immersion of nanoparticles in the base fluid) and their advantages. Apart from these, cupric oxide nanofluid was proposed to improve the heat transfer performance of asphalt solar collectors that harvest solar energy from roads (Hashim 2014).

4. Conclusion

As nanomaterials and nanotechnologies have found tremendous applications in all domains including the energy sector, the associated environmental and health concerns have necessitated development of green approaches for the synthesis of nanomaterials. Moreover, a global awareness has been created to adopt all possible means to eliminate or minimize the detrimental impacts of the wide-spread applications of

nanomaterials and products, in compliance with the principles of green chemistry and green engineering. Thus, the green nanotechnology has paved a way to preserve the environment and human health, thereby significantly contributing to a sustainable future. Even though the adoption of green nanotechnology in the energy sector is associated with health and safety risks coupled with a number of barriers in the political, economic and cultural framework, the benefits of a paradigm shift to green nanotechnology would be far greater than these risks and barriers. Most of the green nanotechnologies are at the exploratory stage, so extended research is required to study their technical, economic, and commercial feasibilities. A lifecycle assessment of any green option is essential in order to ensure its 'greenness'. Moreover, a lifecycle costing would reveal the true financial benefit of an option in the long run, though most of the options may have a high initial cost. Development of commercially viable products and technologies based on natural green nanoparticles such as nanocellulose for energy applications needs specific attention. Along with the governmental supports to promote green nanomaterials and technologies, there must be stringent policies to regulate and monitor their production and application, in order to ensure their benefits with no or minimal risks.

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