Graphical abstract

Green Nanomaterials: On Track for a Sustainable Future

Yuan Lu, Soydan Ozcan*

Materials Science and Technology Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, TN. 37831

*Address correspondence to Dr. Soydan Ozcan, email: ozcans@ornl.gov

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Summary

Nanotechnology is one of the most significant scientific and industrial breakthroughs of the twenty-first century. With applications that cross scientific boundaries—from electronics to medicine, to advanced manufacturing, to cosmetics—nanotechnology has the potential to dramatically change lifestyles, jobs, and whole economies [1]. However, many of the materials and processes currently used not only are dependent on nonrenewable resources but also create hazardous wastes. The combination of green chemistry techniques with nanotechnology applications has thus become a key component of the nanotechnology future. The use of natural ingredients to synthesize nanomaterials and design environmentally benign synthetic processes has been extensively explored. While many of these so-called “green nanotechnologies” are now finding their way from the laboratory to commercial application, green nanotechnology still faces significant challenges. This article presents the recent advances and challenges in green nanotechnology, and suggests ways to improve the commercial readiness of these technologies.

Keywords: green nanotechnology, natural sources, environmentally friendly green synthesis

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4 In the past few decades, nanomaterials have demonstrated superior performance in numerous
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7 applications, including medicine, energy, and advanced manufacturing. However, many of the
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10 materials and processes currently used are not only dependent on nonrenewable resources but
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13 also create hazardous wastes. Green nanotechnology, the combination of nanotechnology and the
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16 principles and practices of green chemistry, may hold the key to building an environmentally
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19 sustainable society in the twenty-first century [1]. Green chemistry is a set of principles or rather
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22 a chemical philosophy that encourages the design of products and processes that reduce or
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25 eliminate the use and generation of hazardous substances [2-5]. Current green nanotechnology
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28 practices often involve the use of natural sources, nonhazardous solvents, and energy-efficient
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31 processes in the preparation of nanomaterials.
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33 34 35 **Natural, renewable sources of reducing agents** 36

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39 Nature provides us with numerous chemical substances that serve as suitable reducing agents for
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42 the synthesis of nanoparticles, including plant extracts, biopolymers, vitamins, proteins, peptides
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45 (e.g., glutathione), and sugars (e.g., glucose, fructose) [1, 6]. Plant extracts are the most studied
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48 category to date. Given their abundance, plant extracts are regarded as one of the most promising
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51 natural reducing agents [7]. One area of particular success is the synthesis of metal nanoparticles,
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54 useful in electronics and medical applications, using plant extracts as reducing agents [3].
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57 Biomedical applications such as drug and gene delivery using gold and silver nanoparticles have
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recently become a very active research area. To improve the biocompatibility, nontoxic green reduction agents plants, algae, bacteria and fungi are used. Elia *et.al.* synthesized gold nanoparticles by using of four different type of plant extracts, *salvia officinalis*, *lippia citriodora*, *pelargonium graveolens*, *punica granatum*, as a reducing and stabilization agent [8].

Biopolymers are another family of natural sources used as reducing and stabilizing agents for metal nanoparticle synthesis. These polymeric carbohydrate molecules have already been used in various industries and thus are readily available for the large-scale production of nanoparticles. Examples of **biopolymers** for nanoparticle synthesis are cellulose, chitosan, and dextran, which are isolated from plants, the exoskeleton of crustaceans, and sugar cane, respectively [9-11].

Vitamin C is a well-known natural reducing agent or antioxidant. Similar to other natural reducing agents, vitamin C can reduce metal ions in an aqueous solution to produce metal nanoparticles [12]. Interestingly, it can also be used to synthesize Fe_3O_4 nanoparticles by reducing colloidal iron hydroxide under hydrothermal conditions [13]. Other vitamins used for metal nanoparticle synthesis include vitamins B and E [14]. Despite the widespread commercial availability of vitamins, their relatively **cost effectiveness** may be a hurdle for commercial application. Other natural sources, such as proteins and peptides, also suffer from cost-related challenges and thus are ill-suited for the large-scale production of nanomaterials [15-17].

Natural sources as precursors for carbon nanomaterials

One emerging area of green nanotechnology research is the use of natural sources as precursors for carbon nanomaterials, useful in a host of applications due to their unique properties. For example, vegetable oil has proven itself to be a viable precursor for high-quality carbon nanotubes using a spray pyrolysis approach. Using different catalysts, both single-walled and multi-walled carbon nanotubes can be produced by this method[18]. In another example, sugars and biopolymers have been used as precursors for carbon quantum dots via a microwave approach. Given the abundance of carbon-rich natural sources, it is expected that their use as precursors for carbon nanomaterials will increase rapidly in the next few years [18].

Nanocellulose—a green nanomaterial

As shown in the previous sections, a significant portion of green nanotechnology is the development of green chemistry to synthesize nanomaterials. However, recently much attention has been devoted to the use of natural nanomaterials as alternatives to synthetic products. One example is nanocellulose materials, which are nanosized cellulose fibers or crystals produced by bacteria or derived from plants. These materials exhibit exceptional strength characteristics, light weight, transparency, and excellent biocompatibility. Compared to some other nanomaterials, nanocellulose is renewable and less expensive to produce. Because of this, nanocellulose has shown great promise as an alternative to synthetic nanoparticles in areas such as polymer

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4 nanocomposites and drug delivery [19-22]. Nanocellulose aerogel has also been used as a
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7 sacrificial templating material for metal oxide nanotubes [23]. Interest in green nanomaterials is
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10 increasing, as evidenced by the growing number of publications in this area and the recent
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13 initiative of the government and private sectors on its commercialization.
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Figure 1. Natural, renewable, sources for green nanotechnology

Green processesing

In addition to using natural starting and processing materials for nanoparticle synthesis, the other half of green nanotechnology is developing environmentally friendly, sustainable processes. In this regard, water and supercritical carbon dioxide have been investigated as alternatives to organic solvents [24, 25]. Of particular interest are various alternative approaches to conventional heating [26]. The most popular green strategy is what is known as the

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4 “hydrothermal approach,” where water is the reaction medium. In another interesting
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7 development, Abdelaziz and his collaborators recently reported using the Leidenfrost effect to
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10 create an overheated and charged green chemical reactor to fabricate nanoparticles and coatings
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13 on complex objects [27].
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17 Microwave energy [26] and focused sunlight [28] have also been explored as alternative heat
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20 sources for the synthesis of nanoparticles. Although these approaches are effective at the
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23 laboratory scale, there are enormous challenges when using these technologies in commercial
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26 production. For example, the short reaction times in microwave heating are restricted to small
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29 scale reactions. The use of focused sunlight is limited by inconsistent light intensity and the
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32 necessity of a lens. Recently, flow chemical processes have been developed for the improvement
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35 of cost effectiveness of green chemistry. [29]
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38 39 **Ongoing challenges** 40

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43 To date, most green nanotechnologies are only conducted on a laboratory scale. Initiatives are
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46 necessary to evaluate the feasibility of adapting the existing technologies to commercial-scale
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49 production. The financial and regulatory barriers due to the unclear toxicology of nanomaterials
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52 may be the greatest hurdles for most green nanotechnologies [30]. Green nanotechnology often
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55 requires entirely new processes, making it initially expensive to move into production. The key
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58 to overcome this barrier is to represent enough of a potential cost savings to outweigh upfront
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costs. For example, Pfizer has saved millions of dollars to date from the green process to synthesize sertraline. The implementation of this green chemistry has resulted in revenue increase enough to overcome the costs, including capital investment and all of the costs associated with recertifying the drug with the U.S. Food and Drug Administration [30]. In the past few decades, environmental regulations implemented by the government have had a significant impact on the chemical enterprise. Most of these regulations focus on reducing the health and environmental risks by reducing the exposure. Therefore, many firms have to use their resources on mandated actions and end-of-pipe technologies, instead of investing in green process to ensure inherently safer products and processes. This is evidence by the fact that chemical manufacturing spent more than any other industrial sector on pollution abatement [30]. Obviously, a regulatory focus on risk control, rather than risk prevention, poses a serious barrier. To overcome these barriers, the collaboration of academic researchers and the private sector is key to successfully moving green technologies from the laboratory to the manufacturing facility. Indeed, the government has promoted such collaborations by providing financial support to commercializing green nanotechnologies. Relevant government guidelines and regulations on the green production of nanomaterials could provide an effective boost to the development and implementation of green nanotechnologies on a commercial scale.

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Biography

Yuan Lu is a Postdoctoral Researcher in the Carbon and Composites Group at the Oak Ridge National Laboratory (ORNL), US. He received his doctoral degree in chemistry from the University of North Carolina at Chapel Hill working on nanotechnology for biomedical applications. His current research focus at ORNL is development of green nanocomposites and green synthesis of metal oxide nanoparticles for energy applications.

Soydan Ozcan is a scientist in the Materials Science and Technology Division of the Oak Ridge National Laboratory since 2010. His main research interest includes formation of fibers, multifunctional smart composites materials. His current research activities also involve development of bio-based material and green synthesis methods as well as hierarchical approach to composite structures. He received his B.S. (2001) in Physics from Ankara University, Turkey, and Ph.D. (2008) in Engineering Science with an emphasis on materials from Southern Illinois University.