

Green Synthesis of Copper, Silver and Iron Nanoparticles- A Review

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Abstract: In recent years, the development of efficient green chemistry methods for synthesis of metal nanoparticles has become a major focus of researchers. The investigations carried out are in an attempt to find an eco-friendly technique for the production of well-characterized nanoparticles. One of the most considered methods is production of metal nanoparticles using cost efficient and environment favoring methods like green synthesis. A review with the perspective of synthesis of Copper, Silver and Iron nano particles have been presented here. Synthesis of high-quality nanoparticles with respect to chemical purity, phase selectivity, crystallinity and homogeneity in particle size with controlled state of agglomeration in a cost-effective procedure is still a challenge to material chemists. Consequently, many efforts have been devoted to the finding of sustainable reactions from the feedstocks to solvents, to synthesis and to processing. Green chemistry actively seeks ways to produce materials in a way that is more benign to human health and the environment. It encompasses a series of considerations in the design of environmentally benign protocols. A major point in the design of greener and more sustainable processes relates to the efficiency of the process, which has to take into account several parameters including energy, material consumption (preferably use of bio-renewable resources) and man-power.

Keywords: Green Chemistry, Nanoparticles, Cost-effective, Green synthesis, eco- friendly

I. Introduction

Organic synthesis is continuously being challenged by new inventions and discoveries which ought to be pursued deliberately for their own sake or as goals leading towards the synthesis of a target molecule. The main objective of organic synthesis is to assemble a target compound from starting materials and reagents that are readily available in the most efficient way. This process is initiated with the design of a strategy involving various synthetic reactions to address individual synthetic objectives in a particular sequence. The creation of molecular diversity and complexity from simple and readily available substrates is one of the major current challenges of organic syntheses. Chemical industries plays a major role in human development. An increased pressure has been put on chemists to develop sustainable processes. The unavoidable responsibilities of the chemists reside in resolving the issues such as the adverse effect of certain chemicals on the health and safety of the environment, the diminishing non-renewable resources and the need for sustainable development. Most of the reactions are found to be hazardous for the environment and also to human beings. In order to overcome these issues, a new science for the research and commitment has been coined by Paul T. Anastas in the year 1991 as “Green Chemistry”.

It has been widely acknowledged that there is a growing need for more environmentally acceptable processes in the chemical industry. The concept of Green Chemistry has been defined as the design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances and was developed in principles to guide the chemists in their search towards greenness. Green Chemistry with its 12 principles would like to see changes in the conventional ways that were used for decades to make synthetic organic chemical substances and the use of less toxic starting materials. Thus, Green chemistry is the practice of chemical science and manufacturing in a manner that is sustainable, safe, and non-polluting and that consumes minimum amounts of materials and energy while producing little or no waste material. Green chemistry begins with recognition of the production, processing, usage, and eventual disposal of chemical products that may harm when

performed in an incorrect manner. In order to achieve its objectives, green chemistry and green chemical engineering may modify or totally redesign chemical products and processes with the objective of minimizing wastes and the use or generation of particularly 4 dangerous materials. And it does so in a manner that is economically feasible and cost effective. It is found that, green chemistry is the most efficient possible practice of chemistry and the least costly when all of the costs of the practice of chemistry, including hazards and potential environmental damage are taken into account. A brief account on the synthesis of Copper oxide, Silver and Iron oxide nanoparticles are reviewed in order to understand the variations in the methods of syntheses.

II. Synthesis of Copper (I) Oxide Nanoparticles

Synthesis of high-quality nanoparticles with respect to chemical purity, phase selectivity, crystallinity and homogeneity in particle size with controlled state of agglomeration in a cost-effective procedure is still a challenge to material chemists. There is a growing interest to synthesize Cu_2O nanostructures in recent years, not only for the development of synthetic strategies, but also for the examination of their sensing, catalytic, surface and electrical properties. Cu_2O nanocrystals are relatively easy to make, safe and economical because of abundant copper ion sources and consumption of less energy. They can also form a wide variety of morphologies. Generally, Cu_2O nanostructures are either gained via oxidation of pure copper or obtained via reduction of Cu^{2+} . In the second method, a certain reducer is additionally introduced to the reaction system to obtain Cu_2O crystals. Up to now, a variety of approaches are available including catalytic reduction, seed mediated synthesis, micro emulsions, sonochemical preparation, alkoxide based preparation, microwave irradiation, precipitation- pyrolysis, thermal decomposition, thermal relaxation, liquid phase reduction, vacuum evaporation, sol-gel, flame spray, vapor-phase reaction, aqueous precipitation, template method, sacrificial anode technique, laser ablation in vacuum etc [1-7]. Various interesting copper oxide nanostructures such as cubes, cuboctahedra, octahedra, multipods, nanowires and hollow structures have been synthesized. The usual methods of their preparation are wet chemical reduction, electro deposition and solvothermal synthesis methods. Copper Oxide is also a prospective identity for low-cost photovoltaic applications due to its high optical absorption coefficient, lower band gap energy, simplicity of preparation, scalability, the non-toxic nature, the abundance and the economics of the material. Therefore, it is of fundamental interest to prepare high-quality, mono disperse copper oxide nanocrystals to examine their structure and characterize their optical properties. Cuprite (or copper oxide) is the oldest material of semiconductor electronics [8]. It has been the subject of numerous theoretical and experimental studies, but still its electronic and atomic structures continue to puzzle the researchers. New applications of Cu_2O in nanoelectronics, spintronics and photovoltaics are emerging. Copper Oxide is a non-stoichiometric defect p-type [9] semiconductor and its potential for the design of solar cells have been recognized since 1920. This was before silicon, germanium and other potential semiconducting materials were discovered. Cu_2O has a direct band-gap of 2 eV which is suitable for photovoltaic conversion. Though theoretical calculations have predicted an electrical power conversion efficiency of approximately 12%, the practical electrical power conversion efficiencies obtained by researchers, in the past, are below 2%. However, recently an efficiency of 2% has been reported [10]. Copper Oxide films are reported to have high transparency, with a slightly yellowish appearance and absorb usually at wavelengths below 600 nm, whilst CuO absorbs strongly throughout the visible spectrum and is black in appearance. The current potential application areas of copper oxide thin films include solar cells and electro-chromic devices. Richardson [11] has also highlighted the potential of copper oxide films as spectrally selective variable reflectance coatings for radiant energy control in architectural and aerospace applications. Copper oxide is a perspective material with applications in magnetic storage media, catalysts, semiconductors, sensor, negative electrode material for lithium-ion batteries, templated, metal-insulator-metal resistive switching memory, electrochromism, antibacterial activity, organic catalysis, CO oxidation, photocatalysis, photochemical evolution of H_2 from water, photocurrent generation, organic synthesis, photo catalytic degradation of organic pollutants etc [12-17]. The electrical properties of each Cu_2O nanowires synthesized by hydrothermal conditions in the presence of poly (2, 5-dimethoxyaniline) have also been examined [18]. A solar cell consisting of vertically oriented n-type ZnO nanowires, also surrounded by a p-type Cu_2O film constructed from nanoparticles has been recently fabricated [19].

III. Synthesis of Silver Nanoparticles

Numerous pathways have been employed for the synthesis of silver nanoparticles with different morphologies as well as size distributions including NaBH_4 reduction, polyol process, use of plant extracts, photo reduction, thermal decomposition of silver compounds, radiation assisted, electrochemical, sonochemical, microwave assisted process, chemical and photochemical reactions in reverse micelles and recently via green chemistry route [20-24].

Synthesis using biological methods have shown way to the 'greener synthesis' of nanoparticles. These methods have proven to be better due to slower kinetics that offers better manipulation and controls over crystal growth and their stabilization. This has motivated an upsurge in research on the synthesis routes that allow better control on shape and size for various nanotechnological applications. The use of environmentally benign materials like plant extract, bacteria, fungi and enzymes for the synthesis of silver nanoparticles offers numerous benefits of eco-friendliness and compatibility for pharmaceutical and other biomedical applications as they do not use toxic chemicals for the synthesis protocol. Chemical synthesis methods lead to presence of some toxic chemical absorbed on the surface that may cause adverse effect in the medical applications.

Group of researchers extensively synthesized silver nanoparticles by using various plant leaf extracts such as *Camellia sinensis*, *Magnolia kobus*, *Diopyros kaki*, *Geranium*, *Acalypha indica*, *Coriandrum sativum*, *Sorbus aucuparia*, *Gliricidia sepium*, *Rose*, *Cinnamomum camphora*, *Cardiospermum helicacabum* and *Neem* [25-29]. The uses of Silver in medicines have been recorded since 1000 B.C. Silver adds to the health in traditional Chinese as well as Indian Ayurvedic medicine. Its performance as an antibiotic is due to the fact that it is a non-selective toxic 'biocide'. Antimicrobial biocides based on Silver are used as wood preservatives. In applications of water technology, silver and copper based disinfectants are used in hospital and hotel distribution systems to control infectious agents. Silver along with copper, is commonly used to inhibit bacterial and fungal growth in chicken farms and in post harvested cleaning of oysters. Silver is also used to sterilize recycled water in MRI space station and in the NASA space shuttle. The use of silver nanoparticles as antibacterial agent is relatively new. Because of their high reactivity due to the large surface to volume ratio, nanoparticles play a crucial role in inhibiting bacterial growth in aqueous and solid media. Silver containing materials can be employed to eliminate microorganisms on textile fabrics [30] or they can be used for water treatment [31]. Contrary to bactericidal effects of ionic silver, the antimicrobial activity of colloid silver particles are influenced by the dimensions of the particles; the smaller the particles, the greater will be the antimicrobial effect.

In Japan, a new compound (Amenitop, silica gel microspheres containing a silver-thiosulfate complex) is mixed into plastics for lasting antibacterial protection [32]. Silver halide is often incorporated into prescription of eye glasses for reversible 'photo chromatic' protection, as it decreases transmitted visible light. In the late 1970s, Robert O. Becker discovered that silver ions promote bone growth and kill surrounding bacteria. Silver kills some 650 different disease organisms. Silver based topical dressing has been widely used as a treatment for infections in burns, open wounds and chronic ulcers. The silver nanoparticles and Ag^+ carriers can be beneficial in delayed diabetic wound healing as diabetic wounds are affected by many secondary infections. These nanoparticles can help the diabetic patients in early wound healing with minimal scars. Silver nitrate is still a common antimicrobial used in the treatment of chronic wounds [33]. Noble metal nanoparticles are well known to their important applications in the fields of electronic, magnetic, optoelectronics, and information storage. It is now understood that the intrinsic properties of a noble metal nanoparticles are determined by its size, shape, composition, crystallinity and structure (solid or hollow). Silver nanoparticles, as a significant member of the noble metal nanoparticles, are excellent substrates for Surface Enhanced Raman scattering (SERS) to probe single molecules and are excellent as catalysts for accelerating some chemical reactions. Silver is widely known as a catalyst for the oxidation of methanol to formaldehyde and ethylene to ethylene oxide.

IV. Synthesis of Iron (II, III) Oxide Nanoparticles

Various chemical synthetic routes have been employed to produce magnetite nanoparticles with desired physical and chemical properties such as coprecipitation of aqueous ferrous (Fe^{2+}) and ferric (Fe^{3+}) salt solution by the addition of a base, microemulsion technique, hydrothermal synthesis,

sonochemical approach, nonaqueous route, thermal decomposition of an organic iron precursor including $\text{Fe}(\text{CO})_5$ or $\text{Fe}(\text{acac})_3$, sol-gel technique, γ -ray radiation, thermal decomposition of organic metals, microwave plasma synthesis, thermal decomposition of alkaline solution of Fe^{3+} chelate in the presence of hydrazine, the reduction of hematite by CO etc [34-37]. With the concern for environmental contaminations, 'green' methods for the synthesis of nanoparticles are also heightened as the chemical procedures generate a large amount of hazardous by products. As an alternative to conventional methods, biosynthesis involving organisms ranging from bacteria to fungi and plants are considered safe and ecologically sound for the nanomaterial fabrication [38,39]. In spite of the method of synthesis, the preparation conditions (e.g., surfactants, concentrations, pH, reaction temperature, stirring rate, etc.) strongly influence the chemical composition, particle size, size distribution, particle morphology, crystal structure and consequently the properties and applications of the products [40]. Based on the unique mesoscopic physical, chemical, thermal, and mechanical properties of super paramagnetic Fe_3O_4 nanoparticles offer a high potential for several biomedical applications, such as cellular therapy, cell labelling, targeting and as a tool for cell-biology research to separate and purify cell populations, tissue repair, drug delivery, magnetic resonance imaging (MRI), hyperthermia and magnetofection etc. Magnetite (Fe_3O_4) is one of the iron oxides with a non-normal spinel structure which can offer great potential applications in different fields such as recording materials, photocatalysis, ferro fluid technology, magneto caloric refrigeration, drug delivery, pigment, magnetic storage, magnetic ink printing, microwave absorption, biosensors, bioseparation, in-vivo drug delivery, immune magnetic array, magnetic resonance imaging contrast agents, hyperthermia treatment of cancer, etc [41,42]. Its particle dispersions have been widely used as ferro fluid for example, in rotary shaft sealing, oscillation damping, and position sensing. The use of properly coated magnetite nanoparticles in clinical medicine has also been intensified. With proper surface coating, these magnetic nanoparticles can be dispersed into water forming water-based suspensions; such a suspension can interact with an external magnetic field and can be positioned to a specific area, facilitating magnetic resonance imaging for medical diagnosis and AC magnetic field- assisted cancer therapy . In chemotherapy, the application of anti-cancer drugs such as adriamycin is limited in clinics due to their toxicity for both normal cells and cancer cells. During these years, people are attempting to improve the distribution of drug in human body to reduce the toxicity of these anti-cancer drugs. Thus, drug delivery systems become a technique to increase the density of drug in target area and reduce the nervousness to normal tissue. Among various drug delivery systems, the magnetic targeted-drug delivery system [43] is considered to be the most popular and efficient. In this technique, the drug carrying magnetic materials like Fe_3O_4 will lead to the cancer areas by outside magnetic field after taken orally or injected through vein. Moreover, Fe_3O_4 as magnetic material is widely used in human treatment because of its stable quality, high magnetic responses and easy achievement. After absorption by human body, the remaining magnetic particles can be safely excreted through skin, bile, kidney, etc. So the most important in the targeted treatment is to obtain extremely small and uniform Fe_3O_4 magnetic nanoparticles with high magnetic response.

V. Conclusion

Many cost- effective and eco-friendly methods to synthesis metal nanoparticles like Copper, silver and Iron are available in the literature. The above conventional methods may be modified by the use of solid acids and bases as catalysts. The use of solid acids and bases (recyclable catalysts) such as zeolite, mesoporous materials, metal oxides, etc., as catalysts provides innumerable benefits like facilitated separation and recycling, easy handling, avoidance of the contamination of products etc. Development of solvent-free alternative processes can also be implemented in the near future.

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