REVIEW: COMPARISON OF CAPPING AGENTS USED IN CHEMICAL AND GREEN SYNTHESIS OF ZINC OXIDE NANOPARTICLES

Author's Name: [1]M. Sabitha, [2]D. Helen
Affiliation: [1]Research scholar, 19113282032012, Women's Christian College, Affiliated to Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu, India
[2]Assistant Professor, Department of Chemistry, Women's Christian College, Nagercoil, Tamil Nadu, India
E-Mail: sabi.lookkas96@gmail.com

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Abstract

Capping agents play a vital role in the synthesis of nanoparticles. Capping agents are often used to prevent the aggregation, controlling the size, shape and properties of nanoparticles. Commonly used capping agents are polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene glycol, proteins and phenolic compounds. Among a variety of nanoparticles, zinc oxide nanoparticles has worldwide advantages because of its marvelous physical and chemical properties. ZnO nanoparticles are synthesized by various techniques. This novel review highlights the comparison between capping agents used in both chemical and biological synthesis of ZnO nanoparticles. This review provides important information about the role of capping agents on the size and morphology of ZnO nanoparticles also it is found that green synthesis leads to ecofriendly nanoparticle whereas chemical synthesis leads to toxic and non-ecofriendly nanoparticle.

***Keywords**: zinc oxide, capping agents, synthesis*

INTRODUCTION

Nanotechnology includes the usage and production of material at nanoscale dimensions [1] less than one hundred nanometers, [1, 2] so that they can show some atom-like properties. [3, 4] Nanoparticles plays a vital role in the field of modern science. The characteristic properties of nanoparticles exhibit completely new or improved properties such as increased surface area, distribution, size and morphology which are different and improved when compared with bulk counterparts. [5] Nowadays the unique properties of nanomaterials have motivated the researchers to develop many simpler and inexpensive techniques to produce nanostructures of technologically important materials. [6] Inorganic materials such as metal and metal oxides have attracted more attention over the past decade due to their ability to withstand harsh process conditions and are generally considered as safe materials to human beings and animals. [7] Among the inorganic nanoparticles, Zinc oxide nanoparticles are of particular interest because they can be prepared easily inexpensive and they are extensively used in the formulation of health care products. [8] Zinc oxide is an inorganic compound with the molecular formula ZnO. It appears as white powder and nearly insoluble in water. [2] ZnO is present in the earth crust as a zincite mineral; however ZnO used for commercial purposes is produced synthetically. [9] ZnO is one of the most exploited n-type semiconductor and it has a direct wide band gap (3.37 eV) and high exciton- binding energy (60 meV) [10] that would allow ZnO to be used for the multifarious applications. ZnO NPs has entered the scientific spotlight for its semiconducting properties, unique antibacterial, antifungal, wound healing and UV filtering properties, high catalytic and photochemical activity. [11] A number of approaches are available for the production of zinc oxide nanoparticles [5] which must be sufficiently reliable for large scale production. [12] Nanoparticles when interact they agglomerate and lose their size and shape. In order to avoid agglomeration and also control the size, capping agent is used in the synthesis of nanoparticles. Capping agents form bonding themselves and act as a cage. It prevents the interaction of nanoparticles with one another. Capping agent should be biodegradable, biocompatible and non-toxic in nature so that they can easily utilized in the living system. [13]

CHEMICAL SYNTHESIS

The synthesis methods of diverse zinc oxide nanostructures can be broadly classified as two main categories namely gas phase synthesis and solution phase synthesis. Vapour solid, vapour liquid solid, chemical or physical vapour deposition are commonly used gas phase methods. While solution phase techniques are the sol-gel, template assisted and spray pyrolysis. [14] Generally, this techniques need sophisticated equipment and tedious procedures. [15] Some reactions require high temperature and/ or high pressure for initiating the reaction, while some reactions require inert atmosphere protection, and / toxic matters such as H_2S, toxic template and stabilizer, and metallic precursors. [16] Some of the chemical synthesis techniques that used chemical compound as a capping/ stabilizing agents are listed in table: 1.

Table: 1 Chemical compound as a capping/ stabilizing agent.

Method	Precursor	Stabilizing /capping agent	Particle Size	Morphology	Reference
Hydrothermal method	$Zn(CH_3COO)_2.2H_2O$	Hexamethylenetetramine	55 - 110 nm	Spherical	[17]
Precipitation method	$Zn(CH_3COO)_2.2H_2O$	Polyethylene glycol (PEG)	30 nm	Spherical	[18]
Precipitation method	$Zn(NO_3)_2.6H_2O$	Starch	40 nm	Spherical	[19]
Co-precipitation method	$Zn(CH_3COO)_2.2H_2O$	Thioglycerol	12 - 16 nm	Hexagonal wurtize	[20]
Precipitation method	$Zn(CH_3COO)_2.2H_2O$	Polyvinyl alcohol (PVA)	2.5 nm	Hexagonal wurtize	[21]
Solvothermal method	$ZnSO_4.7H_2O$	Sodium carbonate (Na_2CO_3)	40 - 160 nm	Rod	[22]
Solvothermal method	$Zn(CH_3COO)_2.2H_2O$	Ethylene glycol (EG)	12 - 15 nm	Ellipsoidal, Spherical	[23]
Sonothermal method	$Zn(NO_3)_2.6H_2O$	Ethylene diamine (EDA)	4 - 8 nm	Hexagonal wurtize	[24]
Wet chemical method	$Zn(NO_3)_2.6H_2O$	Polyvinyl pyrrolidone (PVP)	8.5 nm	Spherical	[25]
Wet chemical method	$ZnCl_2$	Triethanolamine (TEA)	25 nm	Hexagonal shape nanopencil	[26]

Among the capping agents used in chemical synthesis, polyvinyl alcohol is water soluble and biodegradable. [27] Polyvinyl pyrrolidone is a water soluble polymer. It possesses low toxicity and is biocompatible. [28] Polyethylene glycol is a hydrophilic, biocompatible and biodegradable material. [29] Thioglycerol is harmful by inhalation or skin absorption. Hexamethylenetetramine is also highly soluble in water but it is highly combustible and harmful. [30]

GREEN SYNTHESIS

Green synthesis are required to avoid the production of unwanted or harmful by-product through the reliable, sustainable and eco-friendly synthesis procedures. [31] The use of environmentally benign materials like plant extract, bacteria, fungi, algae [3] and enzymes for the synthesis of nanoparticles could be an alternative as compared to chemical and physical methods [15] which offers numerous benefits for pharmaceutical and other biological applications where toxic chemicals are not used for the synthesis protocol. [3] Among the available green methods of synthesis for nanoparticles, utilization of plant extract is rather simple and easy process relative to bacteria and/ or fungi mediated synthesis. [31] The microorganisms based synthesis is not of industrial viability [32] because it involves elaborate process of maintaining intracellular synthesis, cell culture and multiple purification steps.[2, 33] But the usage of plant for the nanoparticle synthesis does not require the maintenance of cell culture and it supports the large- scale production. [34] The plant phytochemical with antioxidant properties are accountable for the preparation of metal and metal oxide nanoparticles. [33] Plant extract contain different concentrations and combination of biological compound [50] namely flavonoids, saponin, alkaloids, tannin, glycosides, steroids, [35] polyols, carbohydrates, terpenoids, [33] inositol, resins, quinine [2] enzymes, proteins [36] phenols, ketones, [37] aldehydes, amine, amide which act both as a reducing and capping agent for rapid biosynthesis of nanoparticles and different proteins aid in the stabilization of synthesized nanoparticles. [38] Some of the green synthesis methods that used phytochemical as capping/ stabilizing agents are listed in table. 2.

Table: 2 Phytochemical as capping/ stabilizing agents

Plant	Precursor	Stabilization/ Capping agent	Morphology	Size	Reference
Andrographis paniculata	$Zn(NO_3)_2.6H_2O$	Protein	Hexagonal, spherical	96-115 nm	[39]
Atalantia monophylla	$Zn(CH_3COO)_2.2H_2O$	Amide group of protein	Spherical	30 nm	[40]
Deverra tortuosa	$Zn(NO_3)_2.6H_2O$	Protein	Hexagonal	15.22 nm	[41]
Calotropis procera	$Zn(NO_3)_2.6H_2O$	Aldehydes, amines, terpenoids, phenolic compounds	Spherical	15 - 25 nm	[42]
Coccinia abyssinica	$Zn(CH_3COO)_2.2H_2O$	Proteins, phenolic compounds, alcoholic compounds	Hexagonal	10.4 nm	[43]
Coriandrum sativum	$Zn(CH_3COO)_2.2H_2O$	Polyphenolic tannins	Wurtzite	60 nm	[32]
Moringa oleifera	$Zn(NO_3)_2.6H_2O$	Ascorbic acid	Spherical, granular	16 - 20 nm	[44]
Parthenium hysterophorus	$Zn(NO_3)_2.6H_2O$	Enzymes, proteins	Radial, cylindrical	16 - 45 nm	[45]
Solanum nigrum	$Zn(NO_3)_2.6H_2O$	Proteins	Quasi- spherical	20 - 30 nm	[46]
Azadirachta indica	$Zn(CH_3COO)_2.2H_2O$	Amide group of protein and functional group of hetero cyclic	Spherical	20 - 40 nm	[4]

		compounds such as –C=C-, -CO-C and –C-O			

CONCLUSION

In chemical synthesis the small change in ratio results into a large variation in the morphology of nanostructures [6] and the chemicals used for the synthesis of nanoparticles and for their stabilization are toxic which may be hazardous in nature and may lead formation of non-eco-friendly byproducts. [47] The chemical synthesis methods result in the presence of some toxic chemicals adsorbed on the surface of ZnO NPs that may have adverse effects in medical application. [33, 6] Also physio- chemical methods require sophisticated equipment, tedious procedures and rigorous experimental condition. [48] Green synthesis of nanoparticles can overcome the problems related to physical and chemical methods. Moreover, green synthesis methods does not require any harmful chemicals as reducing and capping agents. [47] Phytochemicals present in the plant extract itself acts as a reducing and capping agent. Nanoparticles produced by plants are more stable and the rate of synthesis is faster, [49] also the properties of leaf extract enhances the properties of synthesized nanoparticles.

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