

The Use of Carrageenan and Deep Eutectic Solvents in the Production of Biodegradable Anisotropic Metal Nanoparticles

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Citation: Arun Kumar R (2022) The Use of Carrageenan and Deep Eutectic Solvents in the Production of Biodegradable Anisotropic Metal Nanoparticles. *Nanotechnol Nanomater Res*, Volume 3:2. 118. DOI: <https://doi.org/10.47275/2692-885X-118>

Received: September 04, 2022; **Accepted:** October 14, 2022; **Published:** October 19, 2022

Introduction

In numerous industries, such as extraction procedures, pharmaceuticals, medicine, metallurgy, electrodeposition, separation, gas recovery, biocatalysts, and nanotechnology, natural deep eutectic solvents (NDES) are employed as a novel green solvent. They are employed in many sectors primarily because of their qualities, including simplicity, environmental friendliness, biocompatibility, and multifunctionality. Plasmonic metals, like gold and silver, have peculiar physicochemical characteristics, including intriguing plasmonic, optical, and catalytic capabilities, as well as surface modification with easily controllable size and shape [1]. The capacity of nanoparticles made of gold and silver to produce surface plasmon resonance in the visible near-infrared range is the most notable of these characteristics. The size and form of the nanoparticles have a significant impact on their intrinsic surface plasmon resonance, which is a characteristic of photonic metallic nanoparticles, which are frequently utilized as therapeutic treatments [2]. Solvents, reaction media, stabilizing agents, nanoparticle modifiers, and many other areas of study can all benefit from the use of nanotechnology [3].

The term “deep eutectic solvents” (DES) was recently coined to describe a new category of solvents. Also, a novel form of DES, known as biomolecules DES (SUPRADAS), using cyclic oligosaccharides as hydrogen bond acceptors or hydrophilic DES, was discovered. Hydrophobic substances, including tetrabutylammonium bromide, menthol, and thymol, as well as fatty acids like hydrogen bond acceptors, long-chain alcohols, and carboxylic acids, act as hydrogen bond donors in solvents [4]. NDESs can function as a redox agent, stabilizer, supramolecular template, reaction substrate, or acidity value when utilized in the production of nanomaterials without the need for additional reagents. The viscosity, polarization, surface tension, hydrogen bonding, and surface characteristics of the nanomaterials are all impacted by the composition of the NDES, and these factors have a direct impact on the energy and mass transfer properties of the nanostructures. Moreover, by neutralizing charges and passivating single crystal faces, DES components can change the processes of nucleation and growth, which directs development in advantageous crystallographic orientations. It is conceivable to create cutting-

edge nanostructures in a non-aqueous environment by fusing their exceptional features and wide-ranging perspectives [5, 6]. Due to their biocompatibility, a number of polymers, lipids, and chitosan-based particles have undergone substantial research for use in the delivery of drugs and therapeutic applications. Due to their intrinsic toxicity, metallic nanoparticles for biomedical purposes have lately acquired popularity in green synthesis. Although these metal nanoparticles are biocompatible, they fall short of key requirements for effective use in biological contexts, including monodispersity, high yield, and regulated shape. Recent research has demonstrated the value of green synthesis for the development of catalytic, antibacterial, and medicinal nanoparticles such as zinc oxide nanoparticles, bimetallic copper-silver nanoparticles, and nickel-cobalt nanoparticles [7, 8]. Moreover, polymer-based nanoparticles have poor drug encapsulation and loading. Because of its acidity, poly (lactic-co-glycolic acid) renders the polymer more vulnerable to enzymatic breakdown and is inappropriate for several medicines and bioactive compounds. Recent research has also shown its use as a possible instrument for biomedical applications. The use of anisotropic materials in nanomaterials to regulate climate change and reduce carbon emissions several research studies present novel nanomaterial-based techniques for environmental cleanup.

Materials

The DESs are a new type of stable nonaqueous solvents that are similar to ionic liquids at ambient temperature (RTILs). Although there are notable variations in terms of price and ecological footprint, DESs and RTILs are relatively comparable. Secondly, unlike RTILs, which mostly contain ions, DESs are primarily made up of molecules. Moreover, DESs have the characteristics of green solvents since they are less complicated, more affordable, and waste-free to make (Table 1). They also don't need further purification. The reaction mixture for the synthesis did not contain any seeds or surfactants. Many researchers have created nanomaterials using DES while adhering to green chemistry principles (Figure 1). DES as solvents for the production of nanomaterials have been extensively studied for more than 10 years; however, they have not yet been investigated for biological applications. In an intriguing study that was just published, metal oxide nanoparticles were extracted using a NDES. Surface tension, polarity, viscosity, and hydrogen bonding are



only a few crucial factors that have a big impact on a species' reactivity. The mass transport characteristics of DES components influence the development of nanostructures, and it is also feasible to modify the viscosity of DESs, particularly NDESs, by altering the content ratio of hydrogen-bond donor to acceptor components [9]. Rhodophytes, or red algae, are the main source of the oligosaccharide known as carrageenan. These are galactose residue units connected to (1-3) sulfated linear oligosaccharides. -linked (14)-linked (1-1)-glucopyranose (unit G) and -linked (1-1)-glucopyranose (unit D). A straightforward reduction technique, in which the dispersion comprises a prior metal salt and a reducing agent, is a popular wet chemical method for the synthesis of nanomaterials. The usefulness and stability of the suggested program were also enhanced by the installation of a stabilizing or blocking agent. High controllability and repeatability are made possible by the wet chemical method, which also maintains high yield and polydisperse nanomaterials. Initially, polyamide film templates or porous alumina were used for shape control during the electrochemical synthesis of gold nanorods in the presence of surfactants.

Unquestionably, the most promising and popular strategy for creating anisotropic nanoparticles with enhanced plasmonic characteristics is seed-mediated synthesis using wet chemical methods. By using this method, the chemist may regulate the reaction's parameters and produce nanomaterials with the appropriate size and form. For homogeneous solid interaction in the solution phase, the approach employs a growth solution containing the matching metallic salt, a weak reduction agent, a framework agent (mostly quaternary

ammonium surfactants), and silver ions. The multi-step-controlled oxidation and reduction used in the seed-mediated method uses metal seed particles with a diameter of 1.5 to 4.0 nm. The prior gold salt was reduced using an excessive amount of a potent reducing agent, like sodium borohydride, to create the seed particles. Although seedless production of anisotropy photonic metallic nanoparticles has been documented, the absorption spectrum must be tuned using binary surfactants [11].

The destiny of particles and their interplay at the steel substrate membrane interface have been extensively studied in vitro using high-throughput methods, including the transmission electron microscope, inductively coupled plasma mass spectrometry, and microscopic techniques. Fundamental and mechanistic details of nanomaterials interaction and their penetration into cell organelles have been discovered using electron microscopy. Inductively coupled plasma mass spectrometry was used to ascertain how much metal was present in the cells. Nanoparticles' toxicity is determined by their size, shape, surface chemistry, and the testing cell type (Table 2). This is because during receptor-mediated endocytosis, antibody and receptor contact is at its highest level. To reduce the toxicity of CTAB deposited on the surface of nanorods, it is thought to be safe to PEGylate gold nanorods. When combined with polyethylene glycol, which is known to minimize non-specific binding to biological molecules, gold nanorods make an effective optoacoustic contrast agent for use in imaging. This prevents macrophage detection and phagocytosis, resulting in extended circulation that increases nanorod retention

Table 1: Different DESs and their application in the synthesis of nanomaterials.

DESs	NM type	Surface group	Morphology	Role
choline chloride/urea	alloys, iron	N/A, choline chloride-urea	dendrite-like and sharp-edged crystallites, nearly spherical	electrolyte for nanoparticle deposition, media for nanoparticle synthesis by a sputter deposition technique, solvent for chemical synthesis of nanomaterials
choline chloride/thiourea	chitin	acetic acid	whiskers	solvent for chemical synthesis of nanomaterials
choline chloride/1,3-dimethylurea	cobalt and nickel	N/A	coral-like	solvent for chemical synthesis of nanomaterials
choline chloride/malonic acid	cobalt	N/A	octahedral	solvent as well as structure-directing agent for chemical synthesis of nanomaterials
choline chloride/ethylene glycol	manganese	N/A	spherical	dispersant for nanoparticles and chemical synthesis of nanomaterials
choline chloride/acrylic acid	molybdenum, iron	Poly (acrylic acid)	2D sheets	dispersant for nanoparticles and chemical synthesis of nanomaterials
choline chloride/p-toluenesulfonic acid	titanium	N/A	spherical	solvent as well as a structure-directing agent for chemical synthesis of nanomaterials
choline chloride/tris(hydroxymethyl)propane	graphite	epoxy resin	platelets	dispersant for nanomaterials

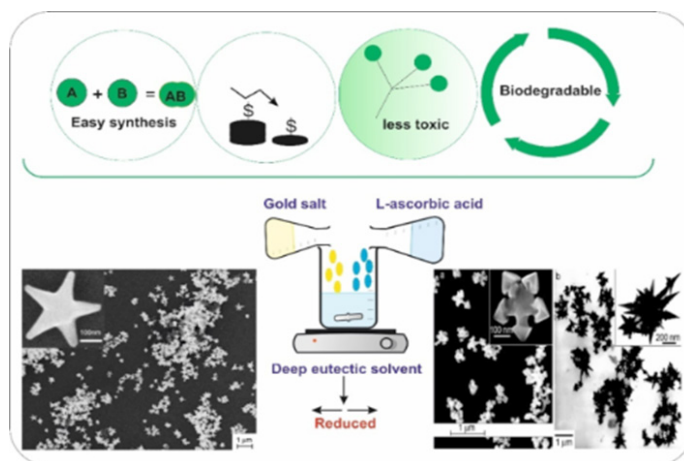


Figure 1: A DES as green solvent in the synthesis of anisotropic nanoparticles (flower shape) [10].



Table 2: *In vitro* and *in vivo* toxicity studies of gold nanoparticles of different shapes with different surface groups.

Nanoparticles	Morphology	Surface group	Model system	Remarks
Gold	spheres	PEG	<i>in vivo</i>	acute toxicity to liver and spleen
Gold	spheres	citrate	<i>in vitro</i>	dose-dependent cytotoxicity
Gold	nanospheres, nanostars, nanorods	chitosan	<i>in vitro</i>	toxicity trend: nanorods > nanostars > nanospheres
Gold	nanorods	CTAB	<i>in vitro</i>	cytotoxic
Gold	spheres	citrate	<i>in vivo</i>	size-dependent toxicity
Gold	spheres, triangles, rods, trigonal bipyramids	CTAB	<i>in vivo</i>	genotoxic

and permeability. In addition to PEGylation, phosphatidylcholine was also utilized as a capping agent to lessen the toxicity of CTAB-coated nanorods. In order to create DESs, high-melting solid organic precursors are mixed together. These precursors interact through hydrogen bonds to generate a liquid at ambient temperature that has a substantially lower freezing point than the sum of its parts. The parent chemicals' ability to recrystallize is constrained by these powerful hydrogen bonds [12]. Many publications on DES have been based on associations between hydrogen bond donors and acceptors in various combinations of chemicals. But, by selecting different components via permutations and combinations, more DESs may be created. The pharmacist can fully investigate the uses of DES due to the variety of components. Prior to their extensive usage in electroplating, DES were employed as solutions in electroplating to cleanse metals since they were non-toxic, biodegradable, and ecologically acceptable. Another appealing approach for the creation of micro-scale propulsion systems is electrolytic breakdown. DESs are well-known and show promise for the solubilization of many highly polar species, including amino acid residues, metal salts, glycerin, benzoic acid, citric acid, and glucose. They are also used in the pretreatment of cellulosic biomass [13]. The latest headlines on the electrolyte solution degradation of hydroxylammonium nitrate have demonstrated this.

Conclusion

Carrageenan and DES are two alternate but equally important ingredients used in the wet chemical production of plasmonic metal nanoparticles. Both parts use green chemistry principles to produce secure nanomaterials for biological purposes. In one of the investigations cited above, C12EDMAB was used instead of CTAB to create less hazardous nanorods. The surfactant's lower carbon tail length than CTAB is the cause of its decreased toxicity. The usage of DES and carrageenan is significant since existing biocompatible compounds utilized in the creation of secure nanoparticles do not go beyond simple biocompatibility. Several of them can also be broken down by enzymes. In contrast, the physicochemical qualities of metal nanoparticles are enhanced by the features of DES and carrageenan. When DESs were utilized as solvents during the creation of nanoparticles, inherent characteristics such as the capacity to influence structure were seen. Moreover, carrageenan's antibacterial, antiviral, and stabilizing qualities might inspire a multifaceted strategy for the synthesis of nanomaterials for cutting-edge biomedical applications. Carrageenan and surfactants completely dissolved as a result of the increased degree of solvation seen in DESs. A living system with increased conductivity is greatly influenced by the breakdown of several chemicals. Since DES hydrogen

bond donor and acceptor components may be combined in n different ways, this special hybrid model offers a platform for the synthesis of n different nanoparticles with 2 combinatorial possibilities.

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