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SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF METAL OXIDE NANOPARTICLES IN SURFACTANT ASSISTED MEDIA

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ABSTRACT

The synthesis of metal oxide nanoparticles is described in terms of precursor formation, nucleation, growth, and aging processes. The main parameters governing these processes are the solution properties, including the solvent viscosity, dielectric constant and the presence of adsorbing anions, the solubility of the metal oxide, and the metal oxide surface energy. In the last few years, the progress made in the field of nanotechnology has allowed researchers to develop and synthesize nanosized materials with unique physicochemical characteristics, suitable for various biomedical applications. Amongst these nanomaterials, metal oxide nanoparticles (MONPs) have gained increasing interest due to their excellent properties, which to a great extent differ from their bulk counterpart. However, despite such positive advantages, a substantial body of literature reports on their cytotoxic effects, which are directly correlated to the nanoparticles' physicochemical properties, therefore, better control over the synthetic parameters will not only lead to favorable surface characteristics but may also increase biocompatibility and consequently lower cytotoxicity. Taking into consideration the enormous biomedical potential of MONPs, the present review will discuss the most recent developments in this field referring mainly to synthesis methods, physical and chemical characterization and biological effects, including the pro-regenerative and antitumor potentials as well as antibacterial activity. Moreover, the last section of the review will tackle the pressing issue of the toxic effects of MONPs on various tissues/organs and cell lines.

Keywords: *Metal oxide nanoparticles; nanotechnology, Media*

INTRODUCTION

In the last few decades, the field of nanotechnology has become one of the most active areas of customizable materials science, with wide practicability in various clinical applications, due mainly to the specific size-dependent properties exhibited by the resulting nanomaterials as a direct consequence of a controlled synthesis procedure. Amongst the already in use nanomaterials, nanoparticles (NPs) have received a great deal of attention due to their small size and large surface area , properties which provide researchers with novel ways of diagnosing and treating diseases that prior to this were thought to be unapproachable due to the size limitations. With multiple advantages such as high stability, simple preparation methods, excellent engineering control over aspects ranging from size, shape, porosity, etc. and cellular penetration capability, MONPs have grown into valuable materials for the drug and health-related industry. Through the design and development of engineered MONPs, the limitations imposed by their bulk counterparts could be finally overcome, allowing

researchers to make astounding breakthroughs in fields such as specific drug delivery, bio-imaging, biomolecule sensors, etc. Moreover, due to their reduced size, metal oxide nanoparticles can interact on a more in-depth level with various cellular structures compared to their bulk counterparts, and, more importantly, they do not cause systemic toxicity due to

their much enhanced compatibility with living systems. Several different kinds of MONPs are now being researched and developed for application in therapeutic settings as antibacterial and wound healing dressings, biosensors, and anticancer and image contrast agents.Of these, zinc oxide NPs (ZnO NPs), cerium oxide NPs (CeO2 NPs), iron oxide NPs (Fe2O3 NPs), silver oxide NPs (AgO NPs), magnesium oxide NPs (MgO NPs), titanium oxide NPs (TiO2 NPs), nickel oxide NPs (NiO NPs), zirconium oxide NPs (ZrO NPs) and cadmium oxide NPs (CdO NPs) are the most promising candidates for biomedicine, with a considerable amount of research data available in recent literature regarding their biological in vitro and in vivo activity.

A summary of the many different synthesis techniques that may be used for producing metal oxide nanoparticles is shown in Figure 1.

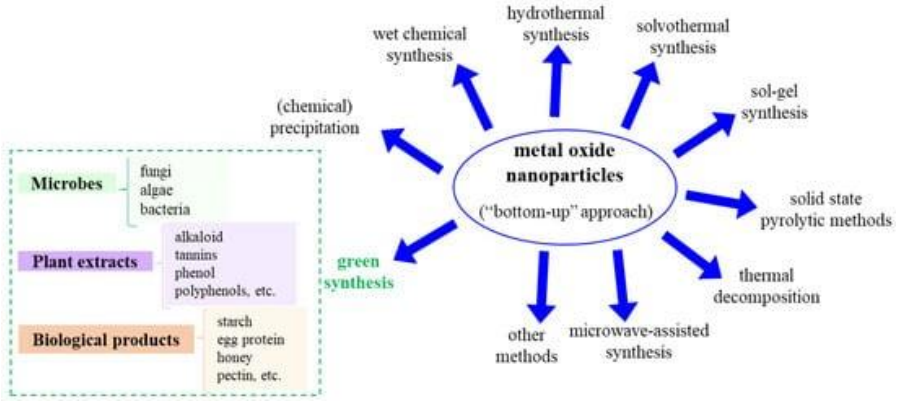

Figure 1 Possible metal oxide nanoparticle synthesis methods ("bottom-up" approach).

Solvent-mediated synthesis

Synthesis facilitated by N,N-dimethylformamide (DMF)

DMF is used widely as a solvent for preparing metal colloids. It is also used in chemical reactions involving organic compounds because of its higher boiling point. In addition, it exhibits good chemical/thermal stability and high polarity. Finally, it is an excellent solvent for both organic and inorganic compounds. Liz-Marz á n and coworkers have pioneered the use of DMF for reducing metal ions such as those of silver and gold at high temperatures. The point to note is that DMF can work as both a solvent and a reducing agent in the preparation of metal colloids. The ability to reduce metal ions (i.e., their reduction rate) increases significantly at a temperature > 100 ° C. The ability of DMF to reduce AuCl 4 - ions to Au 0 has been reported to be lower than that for Ag + ions . It has been suggested that catalysis by either polyvinylpyrrolidone (PVP) or by the seeds of the metal, itself, is required for the reduction of gold ions, although the formation of Au nanoparticles both in the absence and in the presence of the metal seeds has been reported. Therefore, it has been proposed that the use of AuCl 3 in place of HAuCl 4 may be preferable for the synthesis of Au nanoparticles via the DMF-

based reduction method. This is because AuCl 3 can be more readily reduced than HAuCl 4 , owing to the difference in the reduction potentials of Au 3 + and AuCl .

Several mechanisms have been proposed for the reduction of gold and silver ions by DMF. However, all of these mechanisms involve the formation of carbamic acid and H + ions. For example, Tom et al. proposed the following reaction, which is similar to that for silver ions

3HCONMe 2 + 2AuCl - 4 + 3H 2 O → 2 Au 0 + 3Me 2 NCOOH + 6H + + 8Cl

- (1) The resultant carbamic acid is unstable in DMF andreadily decomposes into (CH 3) 2 NH and CO 2 .

Recently, the surfactant-free synthesis of gold nanoclusters (Au NCs) via DMF-based reduction has been reported by several groups. In the synthesis of Au NCs, there is no need to protect ligands such as thiolate and phosphine compounds, surfactants, and polymers. Liu et al. first deve loped a surfactant-free method for synthesizing highly fluorescent blue light-emitting Au NCs by using DMF-based reduction methods. In a typical synthesis process, an aqueous solution of HAuCl 4 was mixed with DMF at room temperature, and the mixture was refluxed at 140 ° C for 4 h under vigorous stirring. The obtained DMF-stabilized Au NCs were highly fluorescent, and they could be further functionalized using various ligands. Moreover, Kawasaki et al. synthesized DMF-stabilized Au NCs using a modified version of the method developed by Liu et al. The asprepared DMF-stabilized Au NCs consisted of a mixture of nanoclusters of various core sizes, with each NCs containing < 20 gold atoms. The DMF-stabilized Au NCs were highly soluble in various solvents, having different pH

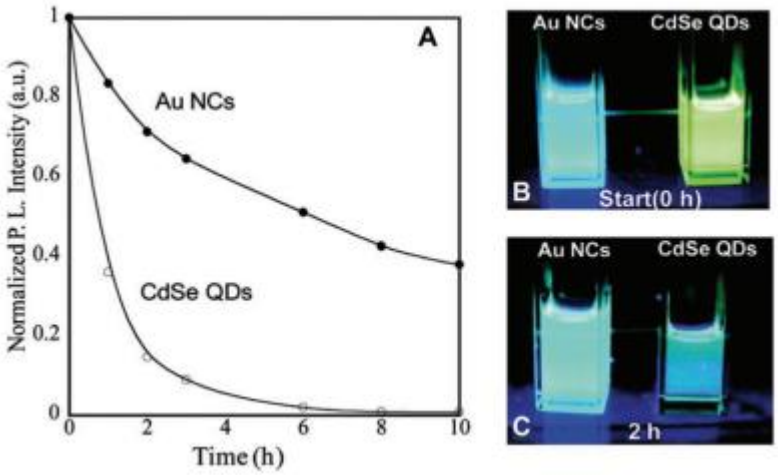

Figure 2 (A) Normalized photoluminescence intensities at 445 nm of DMF-protected Au clusters and those at 505 nm of CdSe QDs as a function of the UV irradiation time (356 nm, 1.3 mW/cm 2 Figure 1). Photographs of the DMF-protected Au clusters and the CdSe QDs in toluene (B) before and (C) after the UV irradiation for 2 h. Reprinted from Ref. with permission from the American Chemical Society.

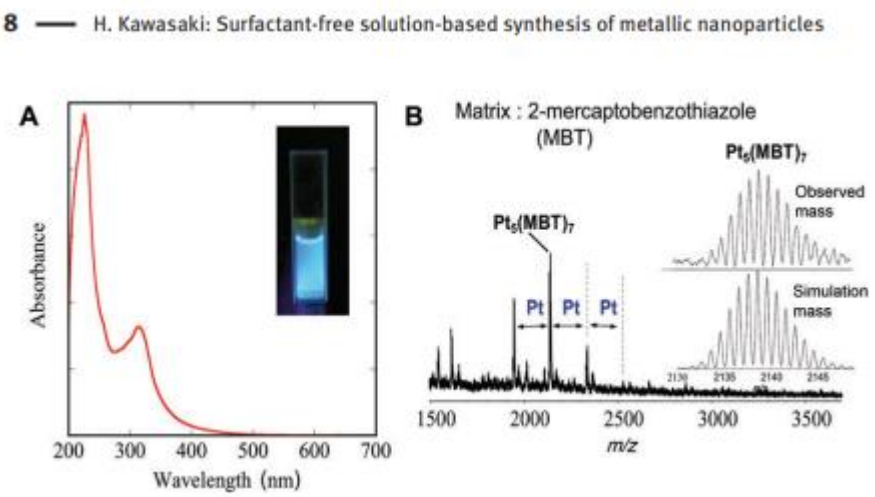

Figure 3 (A) UV-Vis spectrum of the MBT-stabilized Pt 5 NCs and (B) their MALDI-MS spectra. Reprinted from .

solutions became pale yellow, indicating the formation of Ag nanoparticles with sizes of 4.6 ± 0.59 nm. The Ag nanoparticles obtained using DMA had a smaller average size than those obtained using DMF. This difference in size was attributed to the interaction of DMA with the Ag(I) ions being stronger than that of DMF.

OBJECTIVE

1. To Applications Of Metal Oxide Nanoparticles.
2. To photochemical synthesis of stable, unprotected gold nanoparticles.

Simple ion-mediated synthesis

Citrate-mediated synthesis

Citrate ions, which are commonly used as a reductant in the synthesis of metal colloids via the oxidation of citrate into acetonedicarboxylic acid, interact with the surfaces of gold or silver nanoparticles, as described by Turkevich et al. . In the citrate reduction-based synthesis of gold colloids, citrate ions play the dual role of a reducing agent and a stabilizer. The citrate ions form a charged layer around the surfaces of the nanoparticles, resulting in electrical repulsive forces between them in aqueous media. Strong interactions between the amino or thiol group and the surfaces of the gold nanoparticles displace the weaker bound citrate ions from the surfaces of the metal nanoparticles. In a typical synthesis procedure, gold ions in an aqueous medium can be reduced by citrate at 100 ° C, as has been reported by Turkevich et al.. The ratio of the number of gold ions to that of the reducing agent influences the particle size. In general, the smaller the ratio was, the smaller was the size of the gold nanoparticles. There have been numerous reports on the synthesis of metal nanoparticles in aqueous media through modified methods based on that of Turkevich et al. These have aimed to control the sizes and shapes of the metal nanoparticles Kimling et al. reported that Au nanoparticles could be produced in a wide range of sizes, from 9 to 120 nm, via the citrate-mediated synthesis method . The lowest absolute concentration of gold ions for obtaining stable nanoparticles was < 2 m m . At concentrations lower than 1 m m , the suspensions were stable even after a few months, whereas at higher concentrations, precipitation on the

walls of the container occurred within days after the preparation of the solutions. More recently, monodispersed sub-10 nm gold (5.7 ± 0.8 nm) and silver (average size of 1.6 nm) nanoparticles could be obtained via modified Turkevich methods.

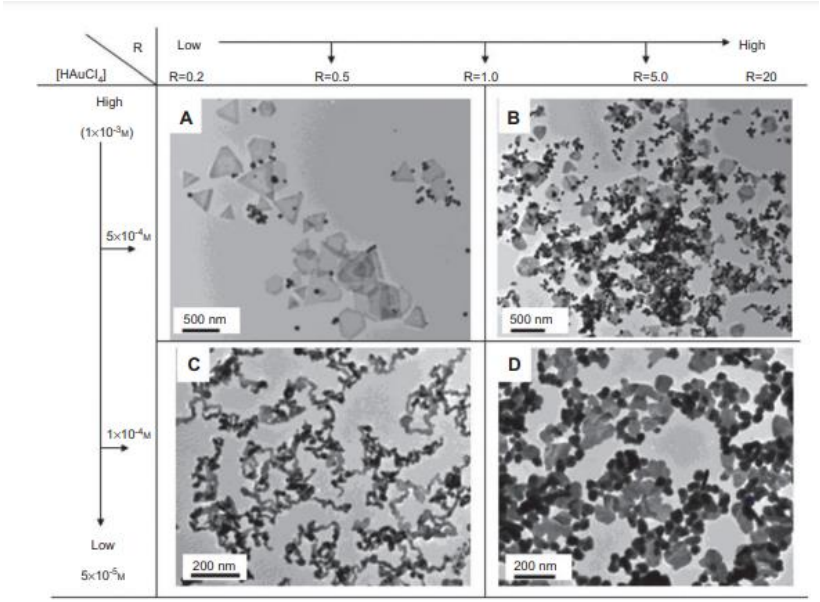

Figure 4 Two-dimensional maps of the gold nanostructures synthesized using different combinations of gold precursor concentrations and Figure 5 R ([Asp]/[HAuCl 4]) ratios with the TEM images showing the reaction products synthesized at the selected reaction conditions: (A) R = 0.5 and [HAuCl 4] = 0.50 m m , (B) R = 5.0 and [HAuCl 4] = 0.50 m m , (C) R = 0.5 and [HAuCl 4] = 0.10 m m , and (D) R = 5.0 and [HAuCl 4] = 0.10 m m . Reprinted from with permission from the American Chemical Society.

Physical process-mediated synthesis methods

Photochemically mediated synthesis

The photochemical synthesis of stable, unprotected gold nanoparticles without the need for any of the conventional (S, N, or P) stabilizing ligands was reported by McGilvray et al. In this synthesis method, 1-[4-(2-hydroxyethoxy) phenyl]-2-hydroxy-2-methyl-1-propane-1-one (Irgacure-2959) was used. On being excited with radiation with a wavelength of 350 nm, I-2959 yields ketyl radicals via Norrish type I R-cleavage; these ketyl radicals function as reducing agents that are capable of reducing Au 3 + to Au 0 , resulting in the formation of Au nanoparticles (Figure 7). The photochemical synthesis of Au nanoparticles in an

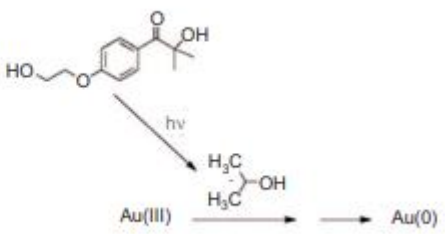

Figure 5 (S, N, or P) stabilizing ligands. Reprinted from Ref. [85]with permission from the American Chemical Society..

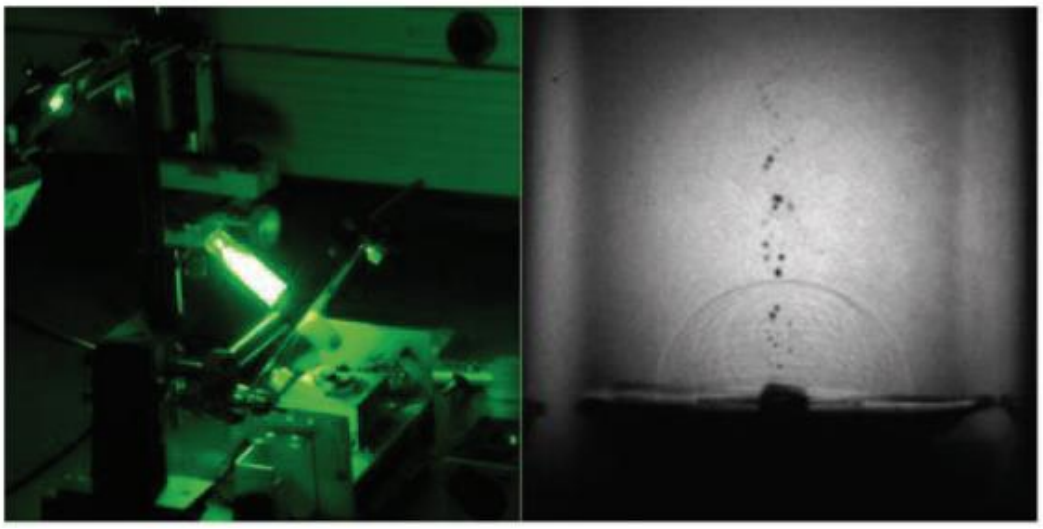

Figure 6 Photographs showing laser ablation in a liquid. The photographs provided by Dr. Takeshi Tsuji, Kyushu University, Japan.

CONCLUSIONS

Mentation of the complementary in vitro and in vivo protocols used to evaluate specific NPs responses would be beneficial and more than likely eliminate the limitations imposed by their toxicity, especially if it would present both as a standardized method of synthesis and as testing protocols. From the point of view of synthesis and functionalization, firstly, due to the variety of synthesis methods, there is difficulty in evaluating the influence of the NPs size and morphology, and, secondly, as a result of differences in the chemical and surface properties of the same metal oxide NPs synthesized by different methods, there is a disparity in the performance and actual functionalization of such NPs Each MONP synthesis method comes with its own advantages, and from the different bottom-up approaches discussed in the present review, typically precipitation, sol-gel, hydrothermal and various biosynthesis methods are extensively used in both laboratory and industrial synthesis. Furthermore, biosynthesis or green synthesis possesses a huge potential for the advancement of green research in the field of MONPs with biomedical applications due to its effectiveness, low costs, sustainability and environmental and human health safety benefit.

REFERENCES

1. Chaudhury, K.; Kandasamy, J.; Kumar, H.S.V.; RoyChoudhury, S. Regenerative nanomedicine: Current perspectives and future directions. *Int. J. Nanomed.* **2014**, *9*, 4153–4167.

2. Chung, E.J.; Rinaldi, C.; Leon, L. (Eds.) *Nanoparticles for Biomedical Applications*; Elsevier: Amsterdam, The Netherlands, 2020; ISBN 9780128166628.

3. Rizvi, S.A.A.; Saleh, A.M. Applications of nanoparticle systems in drug delivery technology. *Saudi Pharm. J.* **2018**, *26*, 64–70.

4. Sánchez-Moreno, P.; Ortega-Vinuesa, J.L.; Peula-García, J.M.; Marchal, J.A.; Boulaiz, H. Smart Drug-Delivery Systems for Cancer Nanotherapy. *Curr. Drug Targets* **2018**, *19*, 339–359.

5. Rostami, M.; Nasab, A.S.; Fasihi-Ramandi, M.; Badiei, A.; Rahimi-Nasrabadi, M.; Ahmadi, F. The ZnFe 2 O 4 @mZnO–N/RGO nano-composite as a carrier and an intelligent releaser drug with dual pH- and ultrasound-triggered control.

6. *New J. Chem.* **2021**, *45*, 4280–4291. Biswas, S.; Bellare, J. Bioactivity, Biocompatibility, and Toxicity of Metal Oxides. In *Metal Oxides for Biomedical and Biosensor Applications*; Elsevier: Amsterdam, The Netherlands, 2022; pp. 3–33.]

7. Augustine, R.; Hasan, A. Emerging applications of biocompatible phytosynthesized metal/metal oxide nanoparticles in healthcare. *J. Drug Deliv. Sci. Technol.* **2020**, *56*, 101516.

8. Mirzaei, H.; Darroudi, M. Zinc oxide nanoparticles: Biological synthesis and biomedical applications. *Ceram. Int.* **2017**, *43*, 907–914.

9. Shen, C.; James, S.A.; de Jonge, M.D.; Turney, T.W.; Wright, P.F.A.; Feltis, B.N. Relating Cytotoxicity, Zinc Ions, and Reactive Oxygen in ZnO Nanoparticle–Exposed Human Immune Cells. *Toxicol. Sci.* **2013**, *136*, 120–130.

10. Korsvik, C.; Patil, S.; Seal, S.; Self, W.T. Superoxide dismutase mimetic properties exhibited by vacancy engineered ceria nanoparticles. *Chem. Commun.* **2007**, *10*, 1056–1058.

11. Deshpande, S.; Patil, S.; Kuchibhatla, S.V.; Seal, S. Size dependency variation in lattice parameter and valency states in nanocrystalline cerium oxide. *Appl. Phys. Lett.* **2005**, *87*, 133113.

12. Asati, A.; Santra, S.; Kaittanis, C.; Nath, S.; Perez, J.M. Oxidase-Like Activity of Polymer-Coated Cerium Oxide Nanoparticles. *Angew. Chem. Int. Ed.* **2009**, *48*, 2308–2312.

13. Karakoti, A.S.; Tsigkou, O.; Yue, S.; Lee, P.D.; Stevens, M.M.; Jones, J.R.; Seal, S. Rare earth oxides as nanoadditives in 3-D nanocomposite scaffolds for bone regeneration. *J. Mater. Chem.* **2010**, *20*, 8912–8919.

14. okel, R.A.; Hussain, S.; Garantziotis, S.; Demokritou, P.; Castranova, V.; Cassee, F.R. The yin: An adverse health perspective of nanoceria: Uptake, distribution, accumulation, and mechanisms of its toxicity. *Environ. Sci. Nano* **2014**, *1*, 406–428.

15. [Haugen, H.J.; Monjo, M.; Rubert, M.; Verket, A.; Lyngstadaas, S.P.; Ellingsen, J.E.; Rønold, H.J.; Wohlfahrt, J.C. Porous ceramic titanium dioxide scaffolds promote bone formation in rabbit peri-implant cortical defect model. *Acta Biomater.* **2013**, *9*, 5390–5399.

16. Martin, P.; Leibovich, S.J. Inflammatory cells during wound repair: The good, the bad and the ugly. *Trends Cell Biol.* **2005**, *15*, 599–607. Fu, G.; Vary, P.S.; Lin, C.-T. Anatase TiO 2 Nanocomposites for Antimicrobial Coatings. *J. Phys. Chem. B* **2005**, *109*, 8889–8898.

17. Kaviyarasu, K.; Geetha, N.; Kanimozhi, K.; Magdalane, C.M.; Sivaranjani, S.; Ayeshamariam, A.; Kennedy, J.; Maaza, M. In vitro cytotoxicity effect and antibacterial performance of human lung epithelial cells A549 activity of Zinc oxide doped TiO 2 nanocrystals: Investigation of bio-medical application by chemical method. *Mater. Sci. Eng. C* **2017**, *74*, 325–333.