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REVIEW ARTICLE

Synthesis and applications of silver nanoparticles

Kholoud M.M. Abou El-Nour [a], **Ala'a Eftaiha** [b], **Abdulrhman Al-Warthan** [b,*], **Reda A.A. Ammar** [b]

[a] *Chemistry Department, College of Science, King Faisal University, Hufof-31982, P.O. Box 4710, Al-Ahsa, Saudi Arabia*
[b] *Chemistry Department, College of Science, King Saud University, Riyadh, Saudi Arabia*

Abstract   Over the past few decades, nanoparticles of noble metals such as silver exhibited significantly distinct physical, chemical and biological properties from their bulk counterparts. Nano-size particles of less than 100 nm in diameter are currently attracting increasing attention for the wide range of new applications in various fields of industry. Such powders can exhibit properties that differ substantially from those of bulk materials, as a result of small particle dimension, high surface area, quantum confinement and other effects. Most of the unique properties of nanoparticles require not only the particles to be of nano-sized, but also the particles be dispersed without agglomeration. Discoveries in the past decade have clearly demonstrated that the electromagnetic, optical and catalytic properties of silver nanoparticles are strongly influenced by shape, size and size distribution, which are often varied by varying the synthetic methods, reducing agents and stabilizers. Accordingly, this review presents different methods of preparation silver nanoparticles and application of these nanoparticles in different fields.

Contents

* Corresponding author.
E-mail address: awarthan@KSU.EDU.SA (A. Al-Warthan).

1. Introduction

Nanoscience has been established recently as a new interdisciplinary science. It can be defined as a whole knowledge on fundamental properties of nano-size objects (Sergeev, 2006, 2003; Sergeev and Shabatina, 2008). The prefix 'nano' indicates one billionth or 10^{-9} units. The nature of this unit being determined by the word that follows. It is widely accepted in the context of nanoscience and nanotechnologies, the units should only be those of dimensions, rather than of any other unit of scientific measurement. It is widely agreed that nanoparticles are clusters of atoms in the size range of 1–100 nm (Williams, 2008).

The results of nanoscience are realized in nanotechnology as new materials and functional facilities. At present time nanochemistry becomes one of the main growing directions of nanoscience (Sergeev and Shabatina, 2008). Frequently, nanometer-size metallic particles show unique and considerably changed physical, chemical and biological properties compared to their macro scaled counterparts, due to their high surface-to-volume ratio. Thus, these nanoparticles have been the subject of substantial research in recent years (Li et al., 2001; Sharma et al., 2008; Iglesias-Silva et al., 2007; Huang and Yang, 2008).

Metallic nanoparticles exhibit size and shape-dependent properties that are of interest for applications ranging from catalysts and sensing to optics, antibacterial activity and data storage (Sudrik et al., 2006; Choi et al., 2007; Yoosaf et al., 2007; Hutter and Fendler, 2004; Sun et al., 2000; Vilchis-Nestor et al., 2008). For instance, the antibacterial activity of different metal nanoparticles such as silver colloids is closely related to their size; that is, the smaller the silver nuclei, the higher the antibacterial activity. Moreover, the catalytic activity of these nanoparticles is also dependent on their size as well as their structure, shape, size distribution, and chemical–physical environment. Thus, control over the size and size distribution is an important task. Generally, specific control of shape, size, and size distribution is often achieved by varying the synthesis methods, reducing agents and stabilizers (Yeo et al., 2003; Zhang et al., 2004, 2006; Chimentao et al., 2004; He et al., 2004).

Metal nanoparticles can be prepared by two routes, the first one is a physical approach that utilizes several methods such as evaporation/condensation and laser ablation. The second one is a chemical approach in which the metal ions in solution is reduced in conditions favoring the subsequent formation of small metal clusters or aggregates (Khomutov and Gubin, 2002; Oliveira et al., 2005; Egorova and Revina, 2000).

With respect to the nature of reducing agent, chemical methods may be subdivided into classical chemical, using the well-known chemical reducing substances (hydrazine, sodium borohydride, hydrogen, etc.) and radiation-chemical where the reduction process is initiated by solvated electrons generated by the ionizing radiation (Pileni, 1997; Leff et al., 1995; Petit et al., 1993; Lisiecki and Pileni, 1995; Huang et al., 1997; Toporko et al., 1995, 1996; Butenko et al., 1990; Treuger et al., 1998; Linnert et al., 1990; Gutierrez and Henglein, 1993; Dokuchaev et al., 1997; Joerger et al., 2000; Shankar et al., 2003).

Furthermore, chemical methods may be divided into those using in nondeleterious solvent and naturally occurring reducing agent such as polysaccharides or plants extract or employs biological micro-organism such as bacteria and fungus as reductants and those working in reverse micellar systems where the aggregation process takes place in the aqueous core of reverse micelles and growing particles are surrounded by the surfactant molecules (Pileni, 1997; Petit et al., 1993; Lisiecki and Pileni, 1995; Dokuchaev et al., 1997).

Nanoparticles stabilization is usually discussed in terms of two general categories of stabilization, electrostatic and steric. Electrostatic stabilization is achieved by the coordination of anionic species, such as halides, carboxylates or polyoxoanions, to metal particles. This results in the formation of an electrical double layer (really a diffuse electrical multilayer), which causes coulombic repulsion between the nanoparticles. Steric stabilization is achieved by the presence of bulky, typically organic materials that, due to their bulk, impede the nanoparticles from diffusing together. Polymers and large cations such as alkylammonium are examples of steric stabilizers. The choice of stabilizer also allows one to tune the solubility of the nanoparticles (Hunter, 1986; Hirtzel and Rajagopalan, 1985; Bard and Faulkner, 1980; Liu and Toshima, 1992; Templeton et al., 2000).

2. Synthesis of silver nanoparticles

2.1. Physical approach

In physical processes, metal nanoparticles are generally synthesized by evaporation–condensation, which could be carried out using a tube furnace at atmospheric pressure. The source material within a boat centered at the furnace is vaporized into a carrier gas. Nanoparticles of various materials, such as Ag, Au, PbS and fullerene, have previously been produced using the evaporation/condensation technique (Gurav et al., 1994; Kruis et al., 2000; Magnusson et al., 1999; Schmidt-Ott, 1988).

However, the generation of silver nanoparticles (AgNPs) using a tube furnace has several drawbacks, because a tube furnace occupies a large space, consumes a great deal of energy while raising the environmental temperature around the source material, and requires a lot of time to achieve thermal stability. A typical tube furnace requires power consumption of more than several kilowatts and a preheating time of several tens of minutes to attain a stable operating temperature.

Jung et al. (2006) synthesized AgNPs via a small ceramic heater that has a local heating area. Because the temperature gradient in the vicinity of the heater surface is very steep in comparison with that of a tube furnace, the evaporated vapor can cool at a suitably rapid rate. This makes possible the synthesis of small nanoparticles in high concentration. This method might be suitable for a variety of applications, including utilization as a nanoparticle generator for long-term experiments for inhalation toxicity study and as a calibration device for nanoparticle measurement equipment (Jung et al., 2006).

Moreover, AgNPs have been synthesized with laser ablation of metallic bulk materials in solution (Mafune et al., 2000, 2001; Kabashin and Meunier, 2003; Sylvestre et al., 2004; Tsuji et al., 2002a, 2003; Compagnini et al., 2003; Chen and Yeh, 2002; Dolgaev et al., 2002). The characteristics of the metal particles formed and the ablation efficiency strongly depend upon many parameters such as the wavelength of the laser impinging the metallic target, the duration of the laser pulses (in the femto-, pico- and nanosecond regime), the laser fluence, the ablation time duration and the effective liquid medium, with or without the presence of surfactants (Hwang et al., 2000a, b; Kim et al., 2005; Becker et al., 1998; Link et al., 2000; Link and El-Sayed, 1999; Smakin et al., 2001; Lee et al., 2001; Tarasenko et al., 2006; Kawasaki and Nishimura, 2006; Tsuji et al., 2001; Nichols et al., 2006; Mafuné et al., 2003; Semerok et al., 1999).

The laser fluence is one of the most important parameters. Indeed, the ejection of metal particles from the target requires a minimum power (or fluence). The mean size of the nanoparticles has been found generally to increase with increasing laser fluence and is generally smallest for fluencies not too far above the laser breakdown threshold. Besides the laser fluence, the number of laser shots (i.e. the time spent during laser vaporization) influences the concentration and the morphology of metal particles released in a liquid. For longer times under the laser beam the metal particle concentration is expected to increase, but it can saturate due to light absorption in the colloid highly concentrated in metal particles.

Moreover, nanoparticles can be modified in size and shape due to their further interaction with the laser light passing through (Becker et al., 1998; Link et al., 2000; Smakin et al., 2001; Mafuné et al., 2003; Kazakevich et al., 2007; Mahfouz et al., 2008). Also, the formation of nanoparticles by laser ablation is terminated by the surfactant coating. The nanoparticles formed in a solution of high surfactant concentration are smaller than those formed in a solution of low surfactant concentration (Mafune et al., 2001).

One advantage of laser ablation compared to other conventional method for preparing metal colloids is the absence of chemical reagents in solutions. Therefore, pure colloids, which will be useful for further applications, can be produced by this method (Tsuji et al., 2002b).

2.2. Chemical approach

Chemical reduction is the most frequently applied method for the preparation of AgNPs as stable, colloidal dispersions in water or organic solvents. Commonly used reductants are borohydride, citrate, ascorbate and elemental hydrogen. The reduction of silver ions (Ag^+) in aqueous solution generally yields colloidal silver with particle diameters of several nanometers.

Initially, the reduction of various complexes with Ag^+ ions leads to the formation of silver atoms (Ag^0), which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of colloidal Ag particles (Tao et al., 2006; Wiley et al., 2005; Lee and Meisel, 1982; Shirtcliffe et al., 1999; Nickel et al., 2000; Chou and Ren, 2000; Evanoff and Chumanov, 2004; Sondi et al., 2003; Merga et al., 2007; Creighton et al., 1979; Ahmadi et al., 1996; Kapoor et al., 1994).

Previous studies showed that use of a strong reductant such as borohydride, resulted in small particles that were somewhat monodispersed, but the generation of larger particles was difficult to control. Use of a weaker reductant such as citrate, resulted in a slower reduction rate, but the size distribution was far from narrow (Lee and Meisel, 1982; Shirtcliffe et al., 1999; Creighton et al., 1994; Schneider et al., 1979; Emory and Nie, 1997).

It is important to use protective agents to stabilize dispersive nanoparticles during the course of metal nanoparticle preparation. The most common strategy is to protect the nanoparticles with protective agents that can be absorbed on or bind onto the nanoparticle surface, avoiding their agglomeration (Oliveira et al., 2005; Bai et al., 2007).

For instance, Oliveira et al. (2005) prepared dodecanethiol–capped AgNPs, based on Brust procedure (Brust and Kiely, 2002), that based on a phase transfer of an Au^{3+} complex from aqueous to organic solution in a two-phase liquid–liquid system, followed by a reduction with sodium borohydride in the presence of dodecanethiol as stabilization agent which bind onto the nanoparticles surface, avoiding their aggregation and making them soluble in certain solvents. They showed that small changes in synthetic parameters lead to dramatic modifications in nanoparticle structure, average size, size distribution width, stability and self-assembly patterns.

The most commonly used polymers were poly(vinylpyrolidone) (PVP), poly(ethylene glycol) (PEG), poly(methacrylic acid) (PMAA), polymethylmethacrylate (PMMA) and so on. For instance, Bai et al. used polyacrylamide as stabilizer and reducing reagent to synthesize gold nanoparticles (Bai et al., 2007; Brust et al., 1994; He et al., 2004; Pillai and Kamat, 2004; Mock et al., 2002; Bosbach et al., 2002; Hall, 2000; Buffat, 2003; Lee and Stein, 1987). Furthermore, Zhang et al. used a hyperbranched poly(methylene bisacrylamide aminoethyl piperazine) with terminal dimethylamine groups (HPAMAM-N(CH$_3$)$_2$) to produce colloids of gold and silver. The amide moieties, piperazine rings, tertiary amine groups and the hyperbranched structure in HPAMAM-N(CH$_3$)$_2$ are significant to its effective reducing and stabilizing abilities. The metallic nanoparticles with the smaller particle size and narrower distribution could be obtained with increasing the molar ratio of silver and gold in feed (Zhang et al., 2008).

Also, AgNPs can be prepared inside microemulsion. The synthesis of AgNPs in two-phase aqueous organic systems is based on the initial spatial separation of reactants (metal precursor and reducing agent) in two immiscible phases. The rate of subsequent interaction between the metal precursor and the reducing agent is controlled by the interface between the two liquids and by the intensity of interphase transport between the aqueous and organic phases, which is mediated by a quaternary alkylammonium salt. Metal clusters formed at the interface are stabilized, due to their surface being coated with stabilizer molecules occurring in the nonpolar aqueous medium,

and transferred to the organic medium by the interphase transporter (Krutyakov et al., 2008).

This method allows preparation of uniform and size controllable nanoparticles. However, a highly deleterious organic solvents is employed in this method. Thus large amounts of surfactant and organic solvent, which are added to the system, must be separated and removed from the final product. As a result, it is expensive to fabricate silver nanoparticles by this method. Nevertheless, Zhang et al. used dodecane as oily phase which is a low deleterious and even nontoxic solvent. Thus the prepared silver solution need not be separated from the reaction solution and it can be directly used for antibacterial activities (Petit et al., 1993; May and Ben-Shaul, 2001; Zhang et al., 2007).

On other hand, the advantages of forming particles which are readily dispersed in organic media are recognized by scientific workers in many fields. For example, colloidal nanoparticles prepared in nonaqueous media for conductive inks are well-dispersed in a low vapor pressure organic solvent, to readily wet the surface of polymeric substrate without any aggregation. The advantages can also be found in the applications of nanometal particles as catalysts to catalyze most organic reactions, which take place in nonpolar solvents. It is very important to transfer nanoparticles to different chemicophysical environments in the practical applications. However, the nanoparticles prepared in nonpolar solutions are infrequent and difficult (Andrews and Ozin, 1986; Nakao and Kaeriyama, 1989; Cozzoli et al., 2004). Moreover, UV-initiated photoreduction is a simple and effective method to produce silver and gold nanoparticles in the presence of citrate, PVP, PAA and collagen. DNA-complexed metal ions can be photoreduced into metal nanoparticle in aqueous media. For example, Huang and Yang synthesized AgNPs via photoreduction of $AgNO_3$ in layered inorganic clay suspensions (laponite, which serves as stabilizing agent that prevent nanoparticles from aggregation. The properties of silver nanoparticles were studied as a function of the UV irradiation time. A bimodal size distribution and relatively large silver nanoparticles were obtained when irradiated under UV for 3 h. Further irradiation disintegrated the AgNPs into smaller size with a single mode distribution until a relatively stable size and size distribution were achieved (Huang and Yang, 2008).

Recently, biosynthetic methods employing naturally occurring reducing agents such as polysaccharides, biological microorganism such as bacteria and fungus or plants extract, i.e. green chemistry, have emerged as a simple and viable alternative to more complex chemical synthetic procedures to obtain AgNPs.

Three main steps, which must be evaluated based on green chemistry perspectives, including selection of solvent medium, selection of environmentally benign reducing agent, and selection of nontoxic substances for the silver nanoparticles stability. For instance Raveendran et al. (2003) synthesized starch AgNPs using starch as a capping agent and β-D-glucose as a reducing agent in a gently heated system. The starch in the solution mixture avoids use of relatively toxic organic solvents. Additionally, the binding interactions between starch and AgNPs are weak and can be reversible at higher temperatures, allowing separation of the synthesized particles (Amanullah and Yu, 2005).

Vilchis-Nestor et al. (2008) used green tea (Camellia sinensis) extract as reducing and stabilizing agent to produce gold

silver nanoparticles in aqueous solution at ambient conditions. Furthermore, Kalishwaralal et al. (2008) reported the synthesis of AgNPs by reduction of aqueous Ag^+ ions with the culture supernatant of Bacillus licheniformis. The synthesized AgNPs are highly stable and this method has advantages over other methods as the organism used here is a nonpathogenic bacterium.

3. Characterization of silver nanoparticles

Characterization of nanoparticles is important to understand and control nanoparticles synthesis and applications. Characterization is performed using a variety of different techniques such as transmission and scanning electron microscopy (TEM, SEM), atomic force microscopy (AFM), dynamic light scattering (DLS), X-ray photoelectron spectroscopy (XPS), powder X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), and UV–Vis spectroscopy (Choi et al., 2007; Yoosaf et al., 2007; Hutter and Fendler, 2004; Sun et al., 2000; Vilchis-Nestor et al., 2008; Yeo et al., 2003; Zhang et al., 2004, 2006; Chimentao et al., 2004; He et al., 2004; Khomutov and Gubin, 2002).

These techniques are used for determination of different parameters such as particle size, shape, crystallinity, fractal dimensions, pore size and surface area. Moreover, orientation, intercalation and dispersion of nanoparticles and nanotubes in nanocomposite materials could be determined by these techniques.

For instance, the morphology and particle size could be determined by TEM, SEM and AFM. The advantage of AFM over traditional microscopes such as SEM and TEM is that AFM measures three-dimensional images so that particle height and volume can be calculated. Furthermore, dynamic light scattering is used for determination of particles size distribution. Moreover, X-ray diffraction is used for the determination of crystallinity, while UV–Vis spectroscopy is used to confirm sample formation by showing the plasmon resonance.

4. Applications

AgNPs have been used extensively as anti-bacterial agents in the health industry, food storage, textile coatings and a number of environmental applications. It is important to note that despite of decades of use, the evidence of toxicity of silver is still not clear. Products made with AgNPs have been approved by a range of accredited bodies, including the US FDA, US EPA, SIAA of Japan, Korea's Testing and Research Institute for Chemical Industry and FITI Testing and Research Institute (Azonano, xxxx; Zhong et al., 2007; Deng and Chen, 2007; Wang et al., 2006; Wei et al., 2007; Jia et al., 2008; Bhattacharya and Mukherjee, 2008).

As anti-bacterial agents, AgNPs were applied in a wide range of applications from disinfecting medical devices and home appliances to water treatment (Bosetti et al., 2002; Cho et al., 2005; Gupta and Silver, 1998; Jain and Pradeep, 2005; Li et al., 2008). Moreover, this encouraged the textile industry to use AgNPs in different textile fabrics. In this direction, silver nanocomposite fibers were prepared containing silver nanoparticles incorporated inside the fabric (Yeo et al., 2003). The cotton fibers containing AgNPs exhibited high anti-

bacterial activity against *Escherichia coli* (Yeo et al., 2003; Duran et al., 2007; Chen and Chiang, 2008).

Furthermore, the electrochemical properties of AgNPs incorporated them in nanoscale sensors that can offer faster response times and lower detection limits. For instance, Manno et al. (2008) electrodeposited AgNPs onto alumina plates gold micro-patterned electrode that showed a high sensitivity to hydrogen peroxide (Hahm and Lieber, 2004).

Catalytic activities of nanoparticles differ from the chemical properties of the bulk materials. For instance, Köhler et al. showed that the bleaching of the organic dyes by application of potassium peroxodisulphate in aqueous solution at room temperature is enhanced strongly by the application of silver containing nanoparticles (Köhler et al., 2008). Furthermore, AgNPs was found to catalyze the chemiluminescence from luminol–hydrogen peroxide system with catalytic activity better than Au and Pt colloid (Guo et al., 2008). Moreover, Liu and Zhao (2009) used silver nanoparticles supported halloysite nanotubes (Ag/HNTs), with Ag content of about 11% to catalyze the reduction of 4-nitrophenol with $NaBH_4$ in alkaline aqueous solutions.

The optical properties of a metallic nanoparticle depend mainly on its surface plasmon resonance, where the plasmon refers to the collective oscillation of the free electrons within the metallic nanoparticle. It is well known that the plasmon resonant peaks and line widths are sensitive to the size and shape of the nanoparticle, the metallic species and the surrounding medium. For instance, nanoclusters composed of 2–8 silver atoms could be the basis for a new type of optical data storage. Moreover, fluorescent emissions from the clusters could potentially also be used in biological labels and electroluminescent displays (Berciaud et al., 2005; El-Sayed, 2001; Kelly et al., 2003; Jin et al., 2001; Mulvaney, 1996; Kossyrev et al., 2005).

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