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High Surface Clay-Supported Silver Nanohybrids

Jiang-Jen Lin^{1,2}, Rui-Xuan Dong¹ and Wei-Cheng Tsai² ¹Institute of Polymer Science and Engineering, National Taiwan University, Taipei, ²Department of Materials Science and Engineering, National Chung Hsing University, Taichung, Taiwan

Abstract

Conventionally, silver nanoparticles (AgNPs) have been prepared by using either physical methods such as electron beam- and photo-reductions or chemical methods with various reducing agents and organic stabilizers. Many researches have been conducted previously in the following areas: tailoring of particle size, polydispersity, geometric shape, and Low-molecular-weight surfactants or nucleation. functional polymers such as poly(vinylpyrrolidone) have also been commonly employed for stabilizing the generated AgNPs. The presence of organic stabilizers may provide soft templates for controlling the growth of the AgNPs with different shapes such as spherical, triangular, and fibrous. In this review, various syntheses involving the applications of inorganic supports such as alumina and aluminosilicate clays in place of organic stabilizers are discussed; in this manner, the synthesis of AgNPs supported on inorganic substrates is reviewed. The function of inorganic supports is primarily to stabilize the homogeneity of colloidal Ag⁰. In the absence of contamination by organic components during the synthesis, the prepared AgNPs were found to exhibit unique properties such as catalytic performance, high stability for longterm storage, low-temperature Ag melting, and high efficacy for antimicrobial properties. This new class of AgNP nanohybrids on inorganic supports is expected to have considerable impact on biomedical fields and on several applications such as optoelectronic devices.

1. Introduction

Inorganic materials on the nanometer scale may have different physical and chemical properties from their bulk analogs. In recent years, tremendous efforts have been made to develop new nanomaterials for various applications such as antimicrobial [1], magnetic recording materials [2], DNA detection [3], and photodetection [4]. The synthesis and manipulation of nanoparticles with various sizes and shapes are important research issues. Silver nanoparticles (AgNPs) are of particular interest because they have unique properties that can be applied to antibacterial applications [5], cryogenic superconducting materials [6], biosensor materials [7], and as additives in composite fibers [8]. In particular, recent

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developments in electronic devices have led to reductions in the thickness of conductive films and the width of printed circuits. This has led to the development of new AgNP materials having different physical forms such as conductive silver pastes [9]. As catalysts, the performance of AgNPs is highly dependent on their size distribution [10], structure [11], shape [12], and support species [13].

In this review, conventional synthesis methods of AgNPs using various organic surfactants and reducing agents are first discussed. Different organic species used in the process may have an effect on the sizes and shapes of nanoparticles. Further, in place of organic reagents, various inorganic alumina and silicates are found to be effective for stabilizing the in-situ generated AgNPs. Thus, a new class of Ag nanohybrids on inorganic supports has been characterized to have different compositions and morphologies. The nanohybrids possessing unique physical properties such as low melting temperatures have been reported. Lastly, new trends for expanding the scope of applications are discussed.

2. Synthesis of silver nanoparticles (AgNPs)

2.1. Conventional syntheses and stabilization of AgNPs in solution

Several methods have been reported for synthesizing AgNPs. Physical methods include metal ablation using a laser [14–17] and metal vapor deposition [18,19]. Physical vapor deposition is an efficient process, and it has been extensively employed in combination with the evaporation and sputtering of metals with plasma as well as with magnetron sputtering. The advantages of physical over chemical processes are the uniformity of nanoparticle distribution and the relative absence of solvent contamination in the prepared thin films. However, in the case of polymeric substrates, the adhesion between the deposited metal and polymer matrix is generally poor. On the other hand, the following chemical methods have been well documented—reduction of silver ions in aqueous solutions [20–24] or non-aqueous solutions [25,26], electrochemical reduction [32,33], microwave-assisted reduction [30,31], photoinduced or photocatalytic reduction [32,33], microwave-assisted synthesis [34–36], irradiation reduction [37–39], microemulsion [40–42], and biochemical reduction [43–45].

In general, by using a wet chemical process, AgNPs can be made into different shapes. The mechanism involves initial interactions of silver ions with organic stabilizers before their reduction into nanoparticles. Further aggregation leads to optimal sizes as well as the generation of a repelling layer. On the surface of small particles, the absorbed silver ions can be further reduced forming larger silver crystallites. However, the inherent problems of nanoparticle aggregation or coalescence might still be encountered. One of the key issues for synthesizing AgNPs is the stabilization and prevention of particle agglomeration. The presence of surfactants comprising functionalities such as amines, thiols, acids, and alcohols [46] for interactions with the particle surface can stabilize the particle growth. Polymeric compounds such as poly(vinylpyrrolidone) [23,24,29,30], poly(vinyl alcohol) [47], poly(ethylene glycol) [25], and various block copolymers [48] have been found to be effective stabilizers. These organic surfactants or functional polymers enable the protection of small particles from agglomeration or losing their surface properties. In addition, the presence of surfactants might also affect the growth process of nanocrystallites and allow control of AgNP shapes and sizes. By controlling the stability, size distribution, and shape, the surface activity and performance in the targeted applications can be influenced. Recent

literature reports on various synthetic methods with different process parameters, solvents, stabilizers, and organic templates are summarized in Table 1. Various morphologies including spherical, triangular, wire, cubic, and dendritic shapes have been reported.

Synthetic methods	Reducing agents	Organic stabilizers	Silver morphologies	Ref.
chemical reduction (water-system)	sodium citrate	citrate	nanowire or spheroid	[20,21]
	NaBH ₄	PVP and PVA	nanospheroids (7–20 nm)	[22]
	Polyol	PVP	nanowire or nanocubes	[23]
	ethylene glycol	PVP	nanocubes	[24]
chemical reduction (organic solvents)	dimethyl acetamide	PEG	nanospheroids	[25]
	acetonitrile	TTF	dendritic particles	[26]
electrochemical reduction	Cyclic voltammetry	polyphenylpyrr ole	nanospheroids (3–20 nm)	[27]
	zeolite film modified electrodes	zeolites	nanospheroids (1–18 nm)	[28]
	rotating platinum cathode	PVP	nanospheroids (10–20 nm)	[29]
ultrasonic- assisted reduction	sonoelectrodeposition	PVA	nanosphere, nanowire and	[30]
	sonoelectrochemistry reduction	NTA	nanosphere	[31]
photoinduced or photocatalytic reduction	dual-beam illumination	citrate and PSS	triangular nanoprisms (3–120 nm)	[32]
	PSS, polychromatic irradiation	PSS	nanospheroids (~8 nm)	[33]

microwave- assisted synthesis	sodium citrate	citrate	nanorods or spheroids	[34]
	ethylene glycol	PVP	nanospheroids	[35]
	formaldehyde	citrate	nanospheroids	[36]
irradiation reduction	γ-irradiation	mesoporous silica	nanospheroids (1–4 nm)	[37]
	γ-irradiation	PVP	nanospheroids (5–20 nm)	[38]
microemulsion method	Fs and ns laser ablation	No	nanospheroids (20–50 nm)	[39]
	Vc	CTAB and SDS	nanowires and dendrites	[40]
	KBH4	Ellipsoidal micelles	needle-shaped and wire- shaped	[41]
biochemical reduction	NaBH ₄	PFPE-NH ₄	particles nanospheroids	[42]
	Peptide	peptide	hexagonal, spherical and triangular	[43]
	Yeast strain	proteins	nanospheres (2–5 nm)	[44]
	Neem leaf extension	flavanones, terpenoids	polydisperse spheres (5-35 nm)	[45]

Table 1. Various methods for preparing silver structures with different morphologies

PVA: poly(vinylalcohol); PVP: poly(vinylpyrrolidone); PEG: polyethyleneglycol; TTF: tetrathiafulvalene; NTA: nitrilotriacetate; PSS: Poly(styrene sulfonate); CTAB: cetyltgrimethlammonium bromide; SDS: sodium dodecyl sulphate; PFPE: ammonium carboxylate perfluoropolyether

2.2. Chemical method—reduction of silver salts

In addition to the use of organic stabilizers for controlling the particle morphologies, the reduction process offers another possibility-tailoring of particle characteristics. Reducing agents such as sodium borohydride [22], sodium citrate [20,21], N, N-dimethylformamide (DMF) [49], polyols [50], ascorbate [51], Tollens reagent [52], and poly(ethylene glycol)-block copolymers [24,35] are popular. In general, strong reducing agents such as sodium borohydride can often afford fine particle sizes, as demonstrated by studies conducted with sodium citrate [21] and sodium borohydride [22]. Systematic studies were performed by varying the reductant/AgNO₃ ratios. The resultant colloids were characterized by UV-Vis spectroscopy immediately after the preparation as well as during its long-term stability studies. The AgNPs generated by the citrate method were large particles with diameters of around 40-60 nm; they were stable during storage. In contrast, the borohydride reduction afforded smaller AgNPs (3–10 nm). DMF is another example of a strong reducing agent for the silver ion reduction; it achieves fast reaction rate and nanoprism morphology [49]. AgNPs having diameters in the range of ~40 nm were prepared by using weak reducing agents such as polyols at elevated temperatures [50]. Large colloidal silver particles using ascorbic acid as the reducing agent have also been prepared in aqueous media [51]. The Tollens process has been recently recognized as a simple one-pot synthetic route for AgNPs with a narrow size distribution [52]. The basic reaction involves the reduction of silver solution from glucose. Stable aqueous dispersion of silver colloids having a size of 20–50 nm can be obtained. In this manner, the choice of reducing agents and synthetic conditions can significantly affect the size and stability of AgNPs. In Table 2, the commonly used reducing agents given in literature have been cited.

Reducing agents	References	
Sodium borohydride (NaBH4)	[22]	
N, N-dimethylformamide (DMF)	[49]	
Polyols	[50]	
Ascorbate	[51]	
Tollens reagent	[52]	
Poly(ethylene glycol)-based	[24,35]	

Table 2. Common reducing agents for converting silver salts to nanoparticles

2.3. Controlling factors for forming various shapes of silver nanoparticles

The activity and reaction selectivity of AgNPs are strongly dependent on their sizes, shapes, and surface composition [53]. Hence, a protective agent is essential for tailoring the shape formation of AgNPs; different shapes may be required for different targeted applications.

Organic surfactants can be provided as templates for altering the nanoparticle shapes to spherical [22,25], triangular [32,43], wire [20,23,40,41], cubical [24], and fibrous [54] morphologies. These strategies have proven to be useful for controlling the growth of anisotropic AgNPs with different shapes as a result of the effects of surfactants or polymers [34] that may induce and maintain directional growth. The molar ratio of the surfactant/AgNO₃ is also an important factor in determining the morphology of the final product [22]. Covalent linkage or surface capping with an organic molecule at an early stage of cluster growth usually yields smaller-sized clusters. Such controlling factors have been widely used to prepare specific shapes of AgNP nanocrystallites.

3. Inorganic supports for AgNPs without organic stabilizers

3.1. Preparation of AgNPs in the presence of inorganic supports

The synthesis of AgNPs using organic dispersants has several disadvantages. In addition to the possible contamination by toxic chemical agents, the presence of organic residues may reduce particle surface activity. In order to overcome the limitations of the chemical reduction method for manufacturing AgNPs with fine dispersion, inorganic dispersants are introduced. By using inorganic dispersants, nanoparticles with a specific diameter and morphology can be synthesized advantageously. The use of inorganic supports for AgNPs may lead to a new form of nanoparticles that are not contaminated by organic components [55-59]. In literature, there have been some reports on the synthesis of water-dispersible AgNPs in the absence of organic components. Some inorganic supports are effective for controlling the uniformity of particle size distribution and for stabilizing nanosized metal particles. For example, laponite clay was used for creating silver colloidal nanoparticles from silver ions by using the chemical reduction method with sodium borohydride as the reducing agent [57]. Controls in size growth and particle aggregation were achieved, and a high concentration of silver colloid with a narrow size distribution was obtained. The UVvis absorption for the nanoparticles is shown in Figure 1. Different molar ratios of NaBH₄ to AgNO₃ were used for generating the AgNPs. When less NaBH₄ was used, two broadabsorption UV peaks at around 390 and 535 nm were observed. The latter peak disappeared with increasing NaBH₄ concentration. Hence, the formation of AgNPs is highly sensitive to and influenced by the reducing conditions and process control. Transmission electron microscopy (TEM) micrograms (Figure 2) have demonstrated that the particle size and aggregated morphologies varied with the experimental conditions using the same reducing agent.



Fig. 1. UV-vis absorption of AgNPs as the function of NaBH₄ to AgNO₃ molar ratios at (a) 1/2, (b) 2, (c) 5, and (d) 10. Reproduced with permission from [57], J. Liu et al., Preparation of high concentration of silver colloidal nanoparticles in layered laponite solution. *Colloids Surf. A* 302, 276 (2007).



Fig. 2. TEM of AgNPs prepared with various $NaBH_4$ to AgNO₃ molar ratios at (a) 1/2, (b) 2, (c) 5, and (d) 10. Reproduced with permission from [57].

Another case of AgNP formation was examined by adding different silicate clays such as montmorillonite, bentonite, and mica [59]. The particle size was predominately affected by the AgNO₃/clay ratio and the species of the reducing agents (methanol, NaBH₄, etc.). Silicate clays with a lamellar geometric shape offered a high surface area for supporting AgNPs having a size of 17–88 nm, as shown in Figure 3. The particle size distribution was also influenced by the type of clay used. A narrow size distribution (polydispersity $D_w/D_n = 1.2$ when $D_n = 26$ nm; analysis by FE-SEM) was obtained.



equivalent ratio (Ag*/CEC)

Fig. 3. Particle size and composition of AgNPs on clay using various Ag⁺/CEC ionic ratios in the preparation. Reproduced with permission from [59], R. X. Dong et al., Synthesis of immobilized silver nanoparticles on ionic silicate clay and observed low-temperature melting. *J. Mater.Chem.* 19, 2184 (**2009**).

3.2. Properties of AgNPs on clay supports

3.2.1 AgNPs with a low-temperature melting property

The development of metal composites for miniature interconnection materials is important for applications to microelectronic packaging. For meeting the requirements of lowprocessing temperatures and environmentally benign conditions, low-temperature-melting AgNPs can be one of the suitable candidates. It is generally believed that the melting temperature depends on the particle size. Recent studies have demonstrated that fine sizes of ~5 nm can be synthesized by using polymeric dispersants. Figure 4 shows different morphologies for the creation of AgNPs having an average size of 5 nm at ambient temperatures; when water-soluble hyperbranched polyglycidol (HPG) is employed as the template, the AgNPs are obtained in the form of a silver tube at 165 °C. Ostwald ripening of small Ag crystals with surface interactions with HPG is probably the key to the controlled formation of tubes, as schematically illustrated in Scheme 1. The low-melting-temperature properties of the AgNPs might also have contributed to the easy melting into tubes. By using differential scanning calorimetry (DSC), it was found that the melting process began at approximately 120 °C to form the tube morphology within 40 h. This study has demonstrated the hierarchical derivation of AgNPs having tubular shapes involving organics as templates and low-melting-temperature behavior.



Fig. 4. Morphology of the hydrothermal products at 165 °C for different times of (A) 20, (B) 30, and (C) 40 h. Reproduced with permission from [60], X. Ding et al., Hyperbranched Polymer-Assisted Hydrothermal In situ Synthesis of Submicrometer Silver Tubes. *Crystal Growth & Design* 8, 2982 (2008).



Scheme 1. Ostwald Ripening of Small Ag crystals with Surface Passivated by HPG to Form Tubes. Reproduced with permission from [60], X. Ding et al., Hyperbranched Polymer-Assisted Hydrothermal In situ Synthesis of Submicrometer Silver Tubes. *Crystal Growth & Design* 8, 2982 (2008).

In a recent study, AgNPs having a size of 26 nm on a clay surface were prepared at 80 °C and examined by using a field emission-scanning electron microscope (FE-SEM) (Figure 5a); they were then sample dried and treated at 110 °C for 2 h (Figure 5b). A comparison

between Figures 5a and 5b reveals that AgNPs change into lumps, implying that they melted at 110 °C. Figure 6 illustrates the role of the clay supports in the initial formation of the AgNO₃/clay complex and reduction into AgNPs. When the clay supports were used, the AgNPs were stabilized and easily melted into an Ag matrix at low temperatures (110 °C).



Fig. 5. FE-SEM micrographs of (a) AgNP/clay, prepared at 80 °C and dried at 80 °C on glass, (b) prepared at 80 °C and dried at 110 °C. Reproduced with permission from [59], R. X. Dong et al., Synthesis of immobilized silver nanoparticles on ionic silicate clay and observed low-temperature melting. *J. Mater.Chem.* 19, 2184 (**2009**).



Fig. 6. Illustration of AgNP formation from AgNO₃/clay complex and the melting on the plate substrates. Reproduced with permission from [59], R. X. Dong et al., Synthesis of immobilized silver nanoparticles on ionic silicate clay and observed low-temperature melting. *J. Mater.Chem.* 19, 2184 (**2009**).

3.2.2 Antimicrobial properties of AgNPs/clay

AgNPs/clay has been shown to exhibit strong inhibition of bacterial growth. The plate-like clay of anionic surface charges provided a high surface support for AgNPs having a diameter of ~30 nm diameter. The AgNP nanohybrids have demonstrated the ability of inhibiting the growth of dermal pathogens such as *Staphylococcus aureus (S. aureus), Pseudomonas aeruginosa,* and *Streptococcus pyrogens,* as well as the methicillin- and oxacillin-resistant *S. aureus* (MRSA and ORSA). SEM has revealed the mechanism of nanohybrids adhering on the surface of individual bacteria (Figure 7). Cytotoxicity studies have indicated that surface contact with the reduced AgNPs on clay is the initial cause for cell death. Detailed mechanisms have been shown to involve a loss in membrane integrity due to reactive oxygen species (ROS) generation, as shown in Scheme 2. The AgNPs supported on clay surface are a new class of nanohybrids that can be applied to biomedical applications.



Fig. 7. AgNP/Clay inhibited bacterial proliferation. FE-SEM images showed the untreated (A) and the AgNP/Clay-encapsulated *S. aureus* (B). In contrast to the proliferative *E. coli* on clay. Reproduced with permission from [61], H. L. Su et al., The disruption of bacterial membrane integrity through ROS generation induced by nanohybrids of silver and clay. *Biomaterials* 30, 5979 (**2009**).



Scheme 2. Illustration of the AgNP/Clay synthesis and interaction with a bacterium: AgNPs are fabricated on the surface of platelet clay and electrostatic attraction to a bacterial cell wall. Reproduced with permission from [61], H. L. Su et al., The disruption of bacterial membrane integrity through ROS generation induced by nanohybrids of silver and clay. *Biomaterials* 30, 5979 (2009).

4. Conclusion

In the literature, various synthetic methods and stabilizers have been reported for AgNPs. By using different reducing agents and organic stabilizers, the fine particle diameter and changes in the morphology of AgNPs have been controlled. In addition to the influence by organic additives, the synthetic processes may alter the occurrence of chemical reduction from silver ions to silver metal with different morphologies. The particle sizes can be controlled by varying the species of reducing agent and its amount of addition. By using inorganic supports such as smectite clay, homogeneously dispersed AgNPs with a narrow size distribution on the clay surface can be synthesized. Furthermore, the presence of clay stabilized the AgNP stability for long storage durations and high surface "naked" activity. An unusual property is the low melting temperature at 110 °C; which might be useful in low-temperature fabrications of silver arrays, conductive wires, and biosensor devices. Furthermore, the AgNP nanohydrid also demonstrated its ability to inhibit bacterial growth by disruption of cell membranes and thus a high potency as an antimicrobial agent.

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