



Preparation of Silver Nanoparticles through Alcohol Reduction with Organoalkoxysilanes

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Abstract. Silver nanoparticles of narrow size distribution were prepared through the chemical reduction in an alcohol solution with several organoalkoxysilanes. In this system, organoalkoxysilanes served as a stabilizer, protecting silver nanoparticles from aggregation. The changes in size and morphology of colloidal silver nanoparticles were investigated with the addition of organoalkoxysilanes such as 3-aminopropyltriethoxysilane (APS), methyltriethoxysilane (MTS), phenyltrimethoxysilane (PTS), vinyltriethoxysilane (VTS), and 3-glycidoxypropyltrimethoxysilane (GPS) as stabilizers. The organic functional groups of organoalkoxysilanes interact with silver ions and clusters, which stabilize silver nanoparticles in the system. The silver nanoparticles obtained were characterized with transmission electron microscopy (TEM), UV-vis spectroscopy, etc.

Keywords: alcohol reduction, nanoparticle, silanes, silver, stabilization

1. Introduction

Nanoparticles of metals have been investigated extensively in recent years. Among them, silver nanoparticles have been widely studied due to their useful optical, electrical, and catalytic properties [1–3], and as the substrates for surface-enhanced Raman spectroscopy [4]. A variety of reduction processes have been used to prepare stable silver nanoparticles, which include chemical reduction in aqueous media without and with stabilizers, radiation chemical reduction, thermal decomposition in organic solvents, Langmuir-Blodgett films, and etc [5–9]. The stabilizer in chemical reduction process plays an important role in protecting smaller metal nanoparticles from the aggregation that results in the formation of larger particles. The earlier literatures have reported

on the stabilization of nanoparticles in the presence of various stabilizers including surfactants [10], tetraalkylammonium halide [11], glucose [12], and polymers like poly(vinylalcohol) (PVA), poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(acrylonitrile) (PAN), and others [13–17].

In this work, the stabilization of silver nanoparticles with organoalkoxysilanes was investigated. The interaction of silver nanoparticles with organic functional groups of silane compounds led to prevent nanoparticles from being aggregated. The smaller silver nanoparticles were thus obtained than without organoalkoxysilanes.

2. Experimental

Organoalkoxysilanes such as 3-aminopropyltriethoxysilane (APS), methyltriethoxysilane (MTS), phenyltrimethoxysilane (PTS), vinyltriethoxysilane (VTS),

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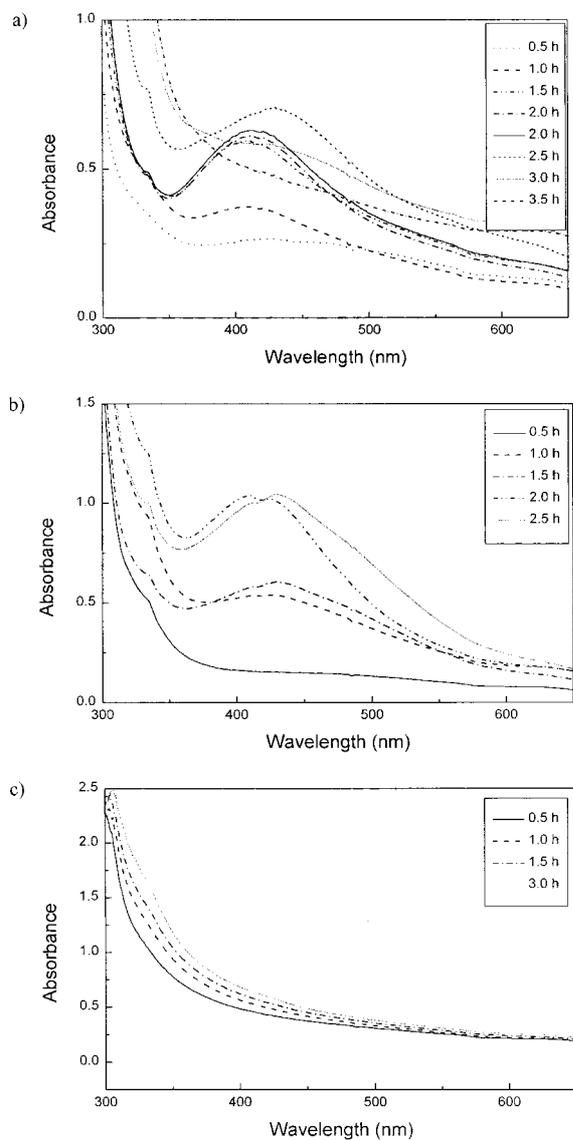


Figure 1. UV-vis spectra of the silver nanoparticles with organoalkoxysilanes at various times under refluxing condition. (a) UV-vis spectra of the silver nanoparticles with APS, (b) VTS, and (c) MTS.

and 3-glycidoxypropyltrimethoxysilane (GPS) were purchased from Aldrich. Ethyl alcohol was obtained from J.T. Baker and AgNO_3 from Kojima Co., respectively. All materials were used as received.

Silver nanoparticles could be prepared from AgNO_3 solution in ethanol without adding reducing agents. To 30 mL of ethanol was added to 2.20×10^{-5} mol of AgNO_3 , and the mixture solution was stirred until AgNO_3 was completely dissolved.

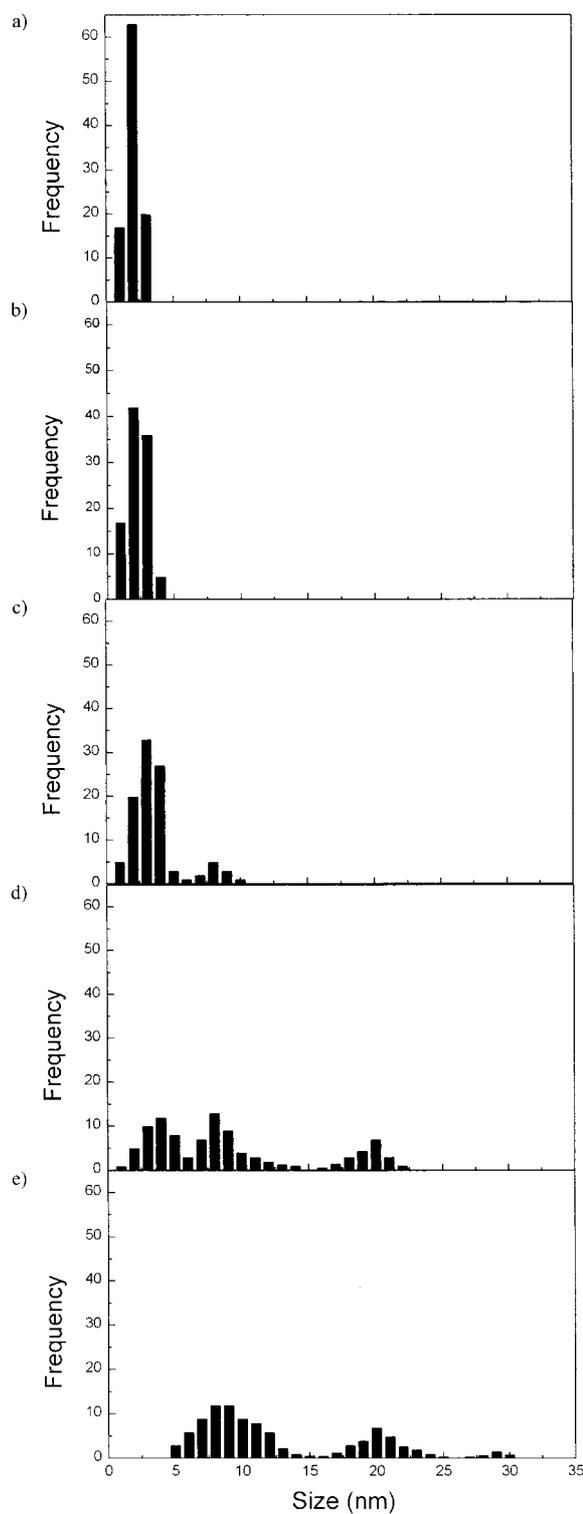


Figure 2. Size distributions of the silver nanoparticles with APS at various times under refluxing condition. (a) 0.5 h, (b) 1.0 h, (c) 1.5 h, (d) 2.0 h, and (e) 2.5 h.

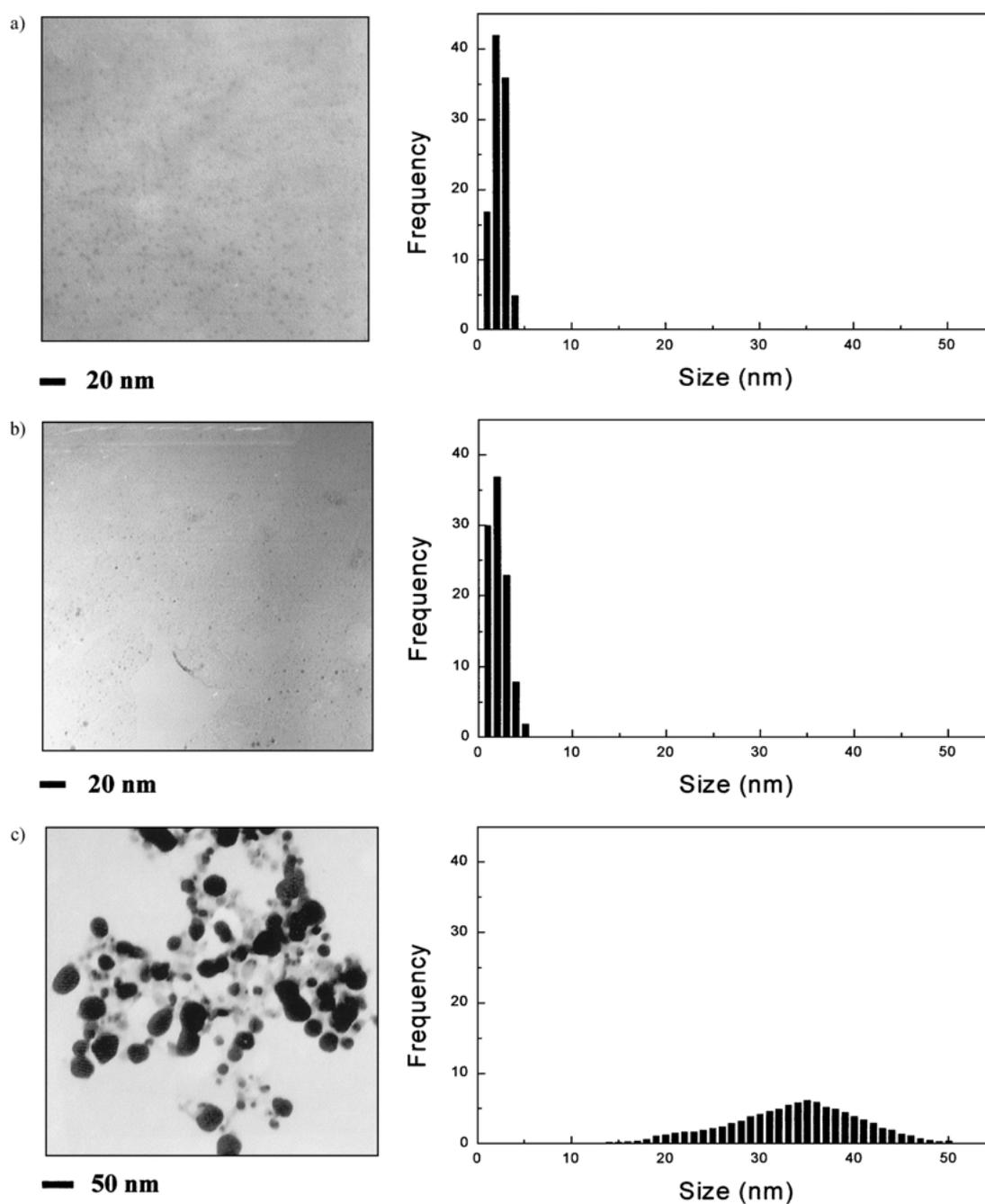


Figure 3. TEM images of the silver nanoparticles with organoalkoxysilanes at 1 h under refluxing condition. (a) TEM image of the silver nanoparticles with APS, (b) VTS, and (c) MTS.

Then 1.76×10^{-4} mol of organoalkoxysilane was added to the above solution under stirring. The mixture solution gradually changed to a yellowish color for refluxing condition (0.5 h–4 h). All procedures were performed in an inert atmosphere.

The UV-vis spectra of the silver nanoparticles were recorded using SCINCO S-2150. For electron microscopy, a few drops of the resulting ethanol solution was placed onto a carbon-coated copper grid and allowed to evaporate. Micrographs were recorded using

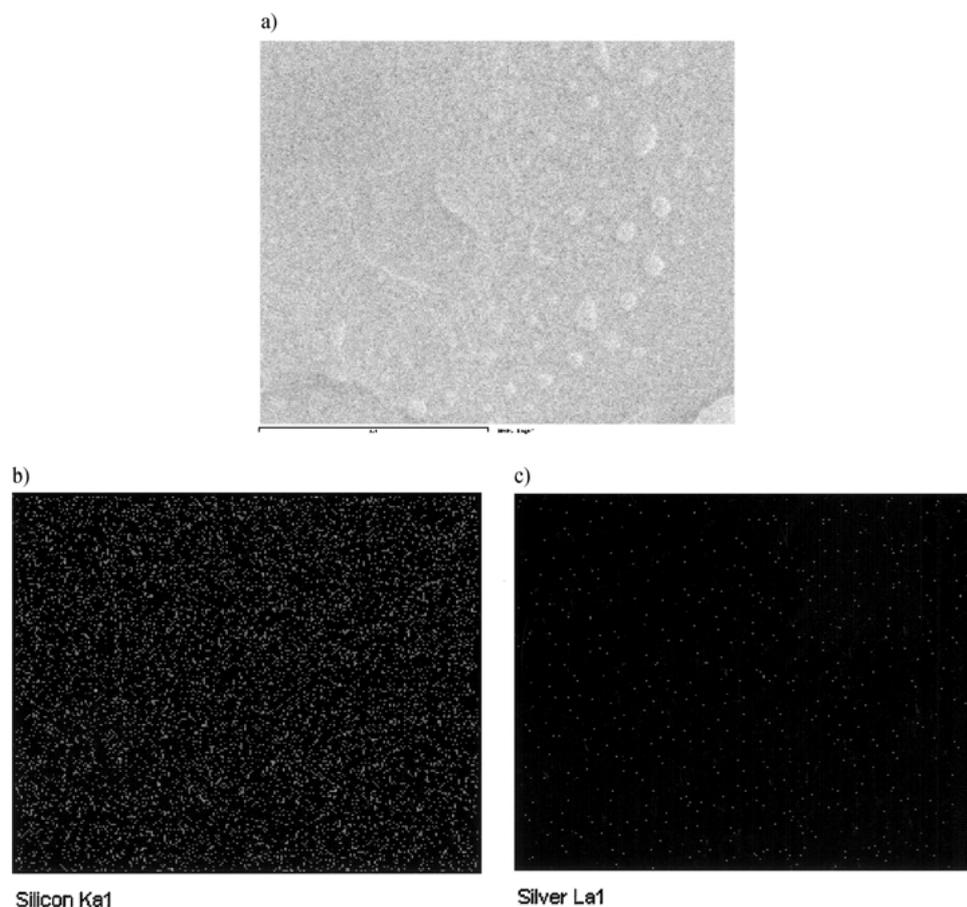


Figure 4. Elemental map of solution coated glass by EDX.

a JEOL JEM-2000EX II transmission electron micrograph (TEM) operating at 200 kV. The size distribution of samples was obtained by counting a total of 200 particles in each case. The elemental map was obtained using energy-dispersive X-ray microanalysis (EDX).

3. Results and Discussion

In the presence of water, the hydrolysis of organoalkoxysilanes and their following condensation occur, leading to formation of silica network. To protect the hydrolysis of organoalkoxysilanes, all experimental procedures were carried out in an inert atmosphere with schlenk technique and in the absence of water through further purification of all reagents used in this study. IR spectroscopy (not shown) elucidated the absence of the Si—O—Si bonds resulted from the condensation of hydrolyzed organoalkoxysilanes.

Figure 1 shows the UV-vis spectra of the silver nanoparticles at various times under refluxing condition. The spectrum of the silver particles contains a strong plasmon band close to 410 nm, which represents that Ag^+ ions are reduced to Ag^0 in an ethanol solution. The appearance of the absorption band is caused by $4d \rightarrow 5s, p$ interband transitions [2]. In the case of APS (Fig. 1(a)), the absorption band of the silver particles occurs at near 405 nm after 1 h, and the intensity of the band increases with time. The absorption band shifts to longer wavelengths gradually and to 429 nm at 2.5 h. This shift is most pronounced slowly. The strong absorption band at 429 nm corresponds to the plasmon peak associated with relatively large spherical silver nanoparticles [18]. The intensity of band after 3 h decreases with time, accompanied by the gradual red shift and severe broadening, showing the onset of the particle aggregation [19]. It is in good agreement with the size distribution of silver nanoparticles shown in Fig. 2.

The UV-vis spectra of silver nanoparticles with other organoalkoxysilanes except MTS exhibit similar trends to those with APS. The UV-vis spectra of the particles with VTS and MTS are shown in Fig. 1(b) and (c). As shown in the spectra in Fig. 1(c), the absorption band of silver nanoparticles with MTS was not observed regardless of time. This is because silver nanoparticles formed are in large range of size which does not exhibit the plasmon absorption band (Fig. 3). It is assumed that MTS is not a good stabilizer for silver nanoparticles due to weak or no interaction of the methyl groups in the silane with silver compounds such as Ag^+ , Ag_n^+ , and etc. The size and morphology of silver nanoparticles with organoalkoxysilanes (APS, VTS, and MTS) are shown in Fig. 3. The average diameters of stabilized silver nanoparticles with organoalkoxysilanes are in the range of 2–3 nm. For MTS case, silver particles with 35 nm in size are obtained.

The organic functional groups of organoalkoxysilanes such as amine, epoxy, phenyl, and vinyl groups are an important role in stabilizing silver nanoparticles. Their interaction with silver ions or clusters prohibits the aggregation to larger particles. Therefore, organoalkoxysilanes can be used as stabilizers for metal nanoparticles, as a substitute for organic stabilizers such as surfactants and polymers. In addition, it is possible to prepare nanocomposite materials containing metal nanoparticles with these silanes under given conditions. Shown in Fig. 4 is the elemental map of solution coated glass by EDX, and it is shown that silver nanoparticles is located on coating glass homogeneously. It is expected for organoalkoxysilanes-stabilized metal colloid to utilize in many application fields.

4. Conclusions

Silver nanoparticles were prepared through the chemical reduction in an ethanol solution, in the presence of organoalkoxysilanes. The UV-vis spectra of silver nanoparticles with other organoalkoxysilanes except MTS exhibit similar trends to those with APS. The average diameters of stabilized silver nanoparticles with organoalkoxysilanes are in the range of

2–3 nm. For MTS case, silver particles with 35 nm in size are obtained. The organic functional groups of organoalkoxysilanes such as amine, epoxy, phenyl, and vinyl groups are an important role in stabilizing silver nanoparticles. Therefore, organoalkoxysilanes can be used as stabilizers for metal nanoparticles, as a substitute for organic stabilizers such as surfactants and polymers.

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