Journal of Alloys and Compounds 643 (2015) S51–S61

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Shape-and size-controlled Ag nanoparticles stabilized by *in situ* generated secondary amines

E. Ramírez-Meneses [a,*], V. Montiel-Palma [b], M.A. Domínguez-Crespo [c], M.G. Izaguirre-López [c], E. Palacios-Gonzalez [d], H. Dorantes-Rosales [e]

[a] *Departamento de Ingeniería y Ciencias Químicas, Universidad Iberoamericana, Prolongación Paseo de la Reforma 880, Lomas de Santa Fe, Distrito Federal C.P. 01219, Mexico*
[b] *Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001 Col. Chamilpa, Cuernavaca, Morelos C.P. 62209, Mexico*
[c] *Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada-IPN, Unidad Altamira. Km 14.5 Carretera Tampico-Puerto Industrial, 89600 Altamira, Tamaulipas, Mexico*
[d] *Laboratorio de Microscopia de Ultra alta Resolución, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas No. 152, C.P. 07730 México D.F., Mexico*
[e] *Departamento de Metalurgia, E.S.I.Q.I.E.-I.P.N., Unidad Profesional Adolfo López Mateos, Zacatenco, Delegación. Gustavo A. Madero, C.P. 07738 México D.F., Mexico*

ARTICLE INFO

Article history:
Available online 17 January 2015

Keywords:
Ag nanoparticles
Chemical synthesis
Amines
Stabilizers

ABSTRACT

Silver amides such as AgN^iPr_2 and $AgN(SiMe_3)_2$ have been employed successfully as precursors for the yield synthesis of silver nanoparticles under mild conditions of dihydrogen gas reduction (2 atm) in organic media. Transmission electron microscopy (TEM) showed the formation of silver nanoparticles with FCC structure, variously sized from 26 to 35 nm for AgN^iPr_2 and from 14 to 86 nm for $AgN(SiMe_3)_2$, the synthesis could take place in absence of added stabilizers due to the *in situ* formation of secondary amines from the reaction of dihydrogen gas with the amide ligands of the silver precursor. Indeed, the presence of HNR_2 (R = $i$$Pr_2$, $N(SiMe_3)_2$) on the surface of the nanoparticle was confirmed by spectroscopic means.

Finally, the addition of ethylenediamine as additional capping agent allowed not only the control of the structural characteristics of the resulting Ag nanoparticles (well-dispersed with spherical shape), but that regarding the nanoparticle size as it inhibited overgrowth, limiting it to *ca.* 25 nm.

1. Introduction

Metal nanoparticles (MNPs) with unusual chemical physical properties, often significantly different from those of their bulk counterparts, are undoubtedly the synthetic targets for nanoscience and engineering technology [1–8]. Furthermore, the focus of attention has not only been the synthesis of monodispersed nanoparticles, but also their self-organization into 2-dimensional (2-D) arrays [9–15]. Thus, one of the principal objectives of various synthetic strategies concerning metallic nanomaterials is to achieve a precise control of their size, shape and dispersion [16]. Among all metals, silver and gold are promising materials for their application in nonlinear optics as chemical sensors and optoelectronic nanodevices [17]. Ionic or metallic silver features low toxicity to human cells, high thermal stability and low volatility; such properties can be exploited in medicine for burning treatment and dental materials, and in the manufacturing industry as coatings for stainless steel materials, textile fabrics, water treatment, sunscreen lotions, etc. For the production of metallic silver from the cationic species, a variety of different reduction methods have been proposed such as γ-rays [18,19], ultraviolet or visible light [20], microwaves [21,22], ultrasonic radiation [23], electrochemical deposition [24], laser irradiation [25], thermal decomposition [26] and recently, hydrothermal methods [27]. As for the last methods, numerous reducing agents such as sodium borohydride ($NaBH_4$), formaldehyde, sodium citrate, hydrazine, ascorbic acid, glucose polysaccharides and even biological microorganisms [28–35] have been employed. To prevent the agglomeration and precipitation of silver nanoparticles, capping agents, either in organic or aqueous media, such as poly(vinylpyrrolidone) (PVP), poly(ethylene glycol) (PEG), oleic acid, dodecanoic acid, sodium citrate dehydrate, some surfactants and amines have been used [36–40].

In some cases, amines can serve as both reducing and capping agents. For instance, Mishra et al. [41] reported the synthesis of Ag nanomaterials with elongated structures in a two-phase system using hexadecylamine, whereas Chen et al. [42] obtained monodispersed silver nanoparticles (~12 nm) on a large scale in a simple oleylamine–liquid paraffin system. Oleylamine was also used as stabilizer by Hiramatsu and co-workers to obtain nearly monodispersed silver nanoparticles with variable size in the mixture of

---

* Corresponding author. Tel.: +52 (55) 9177 4400, +52 5950 4000x4057; fax: +52 (55) 5950 4279.

E-mail address: esther.ramirez@ibero.mx (E. Ramírez-Meneses).

http://dx.doi.org/10.1016/j.jallcom.2015.01.035
0925-8388/

oleylamine and toluene or hexane or dichlorobenzene [43]. Kashiwagi et al. [44] reported the synthesis of monodispersed silver NPs by heating a suspension of insoluble silver myristate in tertiary alkylamines at 80 °C. Alternatively, hexamethylenetetramine has been used as an efficient reducing agent [45]. More recently, triethylamine have been used as a promoted and directing agent for silver nanoparticles [46]. Others works have employed amines such as tetraethylenepentamine [8] and poly-amino compounds [47] as stabilizers.

Despite these advances regarding the accessibility of silver NPs, the use of alternative precursors to AgCl and $AgNO_3$ is much less developed with only a handful of reports using $AgClO_4$ [48], $Ag(CO_2C_6H_5CO_2)$ [18], $Ag(CH_3COO)$ [49], Ag(acac) [50], [Ag(μ-mesityl)]$_4$ [51] and more recently the organometallic $[Ag(C_6F_5)]$ [52]. However, it is evident that the selection of starting molecular precursors is crucial and often the most difficult task when targeting the controlled synthesis of nanoparticles. As for precursors, imposed requirements such as thermal stability, chemical selectivity and even solubility in non-polar organic media are often difficult to achieve from commercial or easily available precursors. Hence, apart from using organometallic compounds as nanoparticle sources, simple metal and metalloid amides, and in general element-nitrogen precursors, have very recently been proposed as alternative metal sources. Indeed, during the submission of this manuscript, a comprehensive review on the synthesis of colloidal nanocrystals and nanoparticles from metal and metalloid amides was published [53].

In this work, AgN^iPr_2 and $AgN(SiMe_3)_2$ have been proposed as practical alternative precursors to conventional $AgNO_3$ to form silver NPs under dihydrogen atmosphere either at room temperature or at 60 °C. The agglomeration of the nanoparticles was prevented by the *in situ* formation of the corresponding amines. The effect of the additional presence of capping agents such as ethylenediamine, $NH_2(CH_2)_2NH_2$ or hexamethyldisilazane and $HN(SiMe_3)_2$ on the size, shape and dispersion of the attained nanostructures was also studied. Although this is the first time silver amide precursors are used for this purpose, Chaudret et al. [54] employed previously analogous $Co[N(SiMe_3)_2]_2$ for the synthesis of Co nanoparticles.

2. Experimental

2.1. Synthesis of AgN^iPr_2 and $AgN(SiMe_3)_2$ precursors

The synthesis of AgN^iPr_2 was first reported by Lappert et al. [55] to proceed from the reaction of AgNCO and $M'[N(SiMe_3)_2]$ (were M′ = Sn, Pb, Yb). As for the present research work, AgN^iPr_2 and $AgN(SiMe_3)_2$ were prepared from either AgCl or $AgNO_3$ (Aldrich) using standard Schlenk and glove box techniques. Although $LiNR_2$ (R = $SiMe_3$) is commercially available, its fresh preparation (R = ^iPr) from the corresponding secondary amine (either diisopropilamine or hexamethyldisilazane) and stoichiometric amounts of a titrated n-BuLi (n-BuLi = C_4H_9Li) in hexanes was preferred. The white precipitate (either LiN^iPr_2 or $LiN(SiMe_3)_2$) was then filtered and dried under vacuum. Subsequently, a suspension of $LiNR_2$ (R = ^iPr, $N(SiMe_3)$) and one equivalent mol of AgCl in THF were vigorously stirred for 24 h at room temperature in darkness. The solution was filtered off the residue, concentrated to eliminate the remaining LiCl and recrystallized from THF. The general synthesis reaction of $AgNR_2$ precursors is presented in Fig. 1. The resulting compounds were insoluble in most common organic solvents, but gave satisfactory microanalytical data and FT-IR analysis.

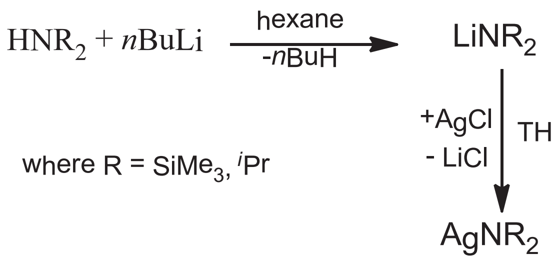

Fig. 1. General reaction of synthesis of $AgNR_2$ precursors.

2.2. Synthesis of Ag nanoparticles from AgN^iPr_2 and $AgN(SiMe_3)_2$

The synthesis of silver NPs was carried out in the darkness in a Fischer–Porter bottle either at room temperature or at 60 °C. A typical procedure is described below. AgN^iPr_2 or $AgN(SiMe_3)_2$ (40 mg) were introduced in a Fisher–Porter bottle under argon atmosphere and a mixture of freshly distilled and degassed tetrahydrofuran, THF (20 mL), and toluene (20 mL) was added. When an additional capping agent was needed, either 1 or 5 equivalents of it (either ethylenediamine or hexamethyldisilizane) were added at this point by means of a syringe. The obtained dark gray solutions were then pressurized under dihydrogen atmosphere (2 bar) for 16 h under stirring. After this time, homogeneous brown colloidal solutions were obtained. Schematic illustrations of the proposed stabilization of the silver NPs obtained from the AgN^iPr_2 and $AgN(SiMe_3)_2$ precursors are shown in Figs. 2 and 3, respectively.

2.3. Characterization of the as-synthesized silver nanoparticles

TEM specimens were prepared by slow evaporation of a drop of each crude colloidal solution deposited onto a holey carbon covered copper grid. Then, the colloidal solutions were purified by hexane washings (to eliminate the impurities). Finally, the resulting gray solution was evaporated in vacuum until the residue was completely dry. Size and morphology of the as-synthesized silver NPs were investigated by means of a JEOL-2000 FX II electron microscope, operating at 200 kV. The presence and bonding mode of the capping molecules after the purification step were studied through Fourier Transform-infrared spectroscopy (FT-IR, Spectrum One Perkin Elmer). KBr pellets (Aldrich, 99% IR grade) were employed to carry out this analysis.

3. Results and discussion

3.1. Ag nanoparticles from AgN^iPr_2 reduction

Fig. 4 illustrates typical transmission electron microscopy (TEM) images and their corresponding selected area electron diffraction (SAED) pattern of the silver nanoparticles obtained from the reaction of AgN^iPr_2 under H_2 atmosphere (2 bar) in the absence of additional capping agents either at room temperature or at 60 °C. From the TEM images, it can be observed spherical particles with no elongated or rod-shape. Regardless of the reaction temperature, the particle size distribution ranged from 20 to 50 nm. It is well documented that high reaction temperatures provoke important effects on the shape and size of nanoparticles, generally increasing the latter [42,56]. In our system, small Ag nanoparticles (<20 nm) were produced, displaying a very slight tendency to agglomerate at higher temperatures, i.e. the TEM micrograph in Fig. 4a shows the dispersion obtained when the synthesis was carried out at room temperature, which is slightly better than that obtained at 60 °C, where some aggregates of particles are formed (Fig. 4c). This behavior is in agreement with the stabilization of the silver NPs likely resulting from the coordination of solvent (THF) as well as of the *in situ* generated HN^iPr_2, both of which are volatile and will therefore be less efficient in preventing aggregation at higher temperatures. The corresponding SAED of the particles was identified and confirmed the silver FCC (face centered cubic) structure (JCPDS 04-0783), Fig. 4b. The average distances between the fringes and the corresponding crystallographic planes are presented in Table 1.

The Ag particles obtained at 60 °C show a different crystallographic plane (420) that is not observed in the case of the particles obtained at room temperature, Fig. 4d. These different lattice planes of the Ag crystals in the Ag nanoparticles could be attributed to alternative growth mechanisms dependent on temperature and the presence of the *in situ* generated HN^iPr_2. Thus, according to previous works, reaction temperature variations affect the particle growth mechanisms [57]. In our case, the synthesis carried out at 60 °C showed that the initial solution exhibited a color change from white to gray during the first 30 min and at room temperature, change