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Synthesis and characterization of bimodal silver nanoparticles by using semi-batch method

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ABSTRACT

Synthesis of silver nanoparticles stabilized by myristic acids is reported. Bimodal shape of silver nanoparticles was formed by feed rate control using semi-batch method. The synthesized nanoparticles were re-dispersible in solution such as α-terpineol. The α-terpineol solution of these nanoparticles exhibited a surface plasmon resonance in the range around 430 nm. This broad absorption band depicted that the silver nanoparticles have an enhanced stability with increasing chain length of the fatty acid. The size of nanoparticles was influenced by the experimental conditions such as temperature, feed rate and reaction time. The nanoparticles were characterized by TEM, UV and XRD analyses.

1. Introduction

Metallic nanoparticles have been widely investigated in recent years due to their unusual physical and chemical properties, which largely differ from their bulk properties [1–3]. Particles in the nanometer size range have attracted increasing attention with the growing interest in nanotechnological disciplines because it is an important substance of conductive inks, pastes and adhesives for various electronic devices [4]. The intrinsic properties of metal nanoparticles are mainly decided by their size, shape, composition, crystallinity, and structure. Colloidal inorganic nanoparticles exhibit size and shape dependent phenomena that are expected to lead to superstructures with a range of practical applications [3,5]. Crystalline re-dispersible silver nanoparticles have application in electronics in addition to their potential use in optoelectronics, in catalysis, and as thermal pastes [6]. The size and shape uniformity of the nanoparticles is important because the thermal conductivity strongly depends on the density of nanoparticles packed into the superstructure that results after drying the ink vehicle from a printed trace [7]. In order to control particle size, most wet chemical methods were performed using homogeneous solutions containing low metal concentration and large amounts of stabilizer to avoid rapid aggregation of the metal core [8–11]. Silver nanoparticles synthesized via thermal decomposition of alkylcarboxylate, and utilization of reductants also acting as capping or stabilizing agents for the control of particle size to ensure a relatively stable suspension. The re-dispersed silver nanoparticles will be used to make interconnects in integrated circuit (IC) devices by screen printing. In this work, we present a new synthesis of bimodal silver nanoparticles.

2. Experimental

2.1. Starting materials

The following chemicals were purchased from various companies and used without further purification: Silver nitrate ($AgNO_3$, 99.9%; KOJIMA Co. Ltd), Myristic acid ($C_{14}H_{28}O_2$, 97%; ACROSS), Sodium hydroxide (NaOH, 98%; SAMJUNG) and Triethylamine ($C_6H_{15}N$, 98%; SAMJUNG).

2.2. Preparation of intermediate synthesis

A 50 mL of NaOH solution in water was put in a beaker. Then 200 mL of a 0.2 M $AgNO_3$ solution was added and sodium hydroxide solution fad individual rate thoroughly. Preparation of silver myristate was carried out in a semi-batch process. The general apparatus used were stirrer drive, impeller, three-neck flask, water bath, and syringe pump. The mole ratio was $AgNO_3$ 0.2 M, NaOH 0.2 M, and myristic acid 0.2 M. For reducing the effect of intermediate synthesis factor, temperature, feed rate, feed material and reaction time were decided as main parameters.

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Individual conditions were mixed in DI water on three-neck flask. A slowly changing white color indicates that complex compound was coordinated with silver ion with myristic acid. We obtained the white color intermediate that Ag-ligand formation while heating and stirrer. Silver myristate was washed using DI water and filtered by quantitative paper. Finally, it was dried in a vacuum oven at 50 °C for 24 h.

2.3. Reduction of silver myristate using triethlylamine (TEA)

Finely grounded silver myristate (31.91 g) was poured into 268 mL of triethlylamine and slowly heated to 80 °C while stirring was maintained. When white Ag-myristate changed to brown solids, this colloidal silver with heating was continued for 2 h. This reaction was based on a new concept in which the ligands of the precursor act as the stabilizer to avoid the aggregation of metal. With respect to the production of silver nanoparticles, the amine may play an important role in the reaction process. Silver myristate did not dissolve in triethylamine at room temperature, but the reaction proceeded at 80 °C, affording a highly dispersive liquid of silver nanoparticles in a short time. The brown solution was quickly filtered through Whatmann 42 filter paper to get clear nanoparticles solution. On the other hand, secondary and primary amines easily reacted with silver myristate at room temperature, but further reactions affording silver nanoparticles required higher temperature for secondary (100 °C) and primary amines (130 °C), respectively. This suggests that the intermediate, i.e. the silver myristate–amine adduct is formed in the reaction procedure and its reactivity strongly depends on the nature of the amine. Therefore, isolation of the intermediate adduct formed by the reaction of silver myristate with n-octylamine was attempted. As a result, the formation of the silver myristate–amine 1:2 adduct, $[Ag(n\text{-}C_8H_{17}NH_2)_2][C_{13}H_{27}CO_2]$, was confirmed [12,13], indicating that the silver nanoparticles are produced via the 1:2 adduct; the first step is the formation of the adduct and the second step is its thermal decomposition. Thus, thermal decomposition of the silver myristate–triethylamine adduct formed on the surface of insoluble silver myristate in triethylamine was so rapid that the silver nanoparticles were released just after formation of adduct, with the myristate ligand strongly protecting the nanoparticles to avoid further aggregation of nanoparticles. In practice, the particle size was scarcely affected by the reaction time. Therefore, particle size is determined by thermal decomposition of the silver adduct formed on the surface of silver myristate and is affected by changing the alkyl chain lengths of the carboxylate ligands and the tertiary amines. A similar result was reported for the preparation of silver nanoparticles by the reduction of insoluble silver halide by $NaBH_4$ in the presence of thiol. Therefore, this is a novel reaction, affording monodispersed silver nanoparticles capped by myristate ligands from insoluble silver myristate in tertiaryamine [14,15]. Using TEA (triethlylamine) caused a reduction reaction with silver myristate. Silver myristate suspended in TEA was heated at individual conditions with purge an N_2 gas. The surface of the white silver myristate powder gradually turned brown and the insoluble precursor finally disappeared, producing a highly homogeneous dispersion of silver nanoparticles in solution. Addition of excess methanol to the solution afforded a precipitate, which was collected by filtration, washed with a small portion of acetone and dried in a vacuum. The final solution was cooled and centrifuged at 12,000 rpm for 5 min. The liquid at the top of the centrifuge tube became colorless. The centrifugation was repeated for 7-8 cycles to remove the excess reagents. The silver nanoparticles isolated as a powder (15.04 g, 89% yield based on silver) was readily redispersed in solvents such as DMF and α-terpineol.

3. Results and discussion

3.1. Bimodal shape of silver nanoparticles mechanism

This research is a new preparative procedure for bimodal shape myristate-protected silver nanoparticles under mild condition at 80 °C for 2 h, using an insoluble silver myristate ($Ag\text{-}OOC(CH_2)_{12}CH_3$) in triethlylamine solvent. It is remarkable that in this procedure the intermediate, feed rate control has influence on particle diameter. The size of the particles is greatly influenced by experimental conditions. In this work, two stages of four experiments are carried

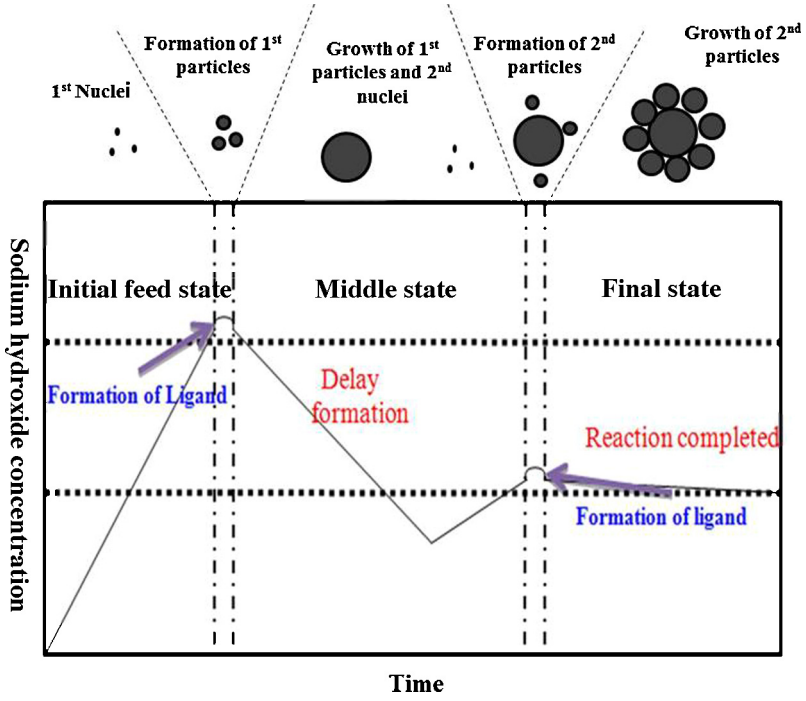

Fig. 1. The diagram of sodium hydroxide concentration change as time (initial feed state, middle state, final state).