Journal of Industrial and Engineering Chemistry 20 (2014) 3157–3162

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Regeneration of aged-AgNPs via density gradient ultracentrifugal nanoseparation

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ARTICLE INFO

Article history:
Received 29 October 2013
Accepted 28 November 2013
Available online 4 December 2013

Keywords:
Nanoseparation
Silver nanoparticles
Centrifugation
Density gradient
Recycling

ABSTRACT

To reuse aged-silver nanoparticles (AgNPs) and recover the mono-dispersed AgNPs separately, we attempted to recycle the aged-AgNPs with high polydispersity in particle size distribution using the density gradient ultracentrifugation rate (DGUR) separation with five media. Results for the microscopic and spectroscopic showed that Tween series media, which have low density compared to other media, are suitable for the application of DGUR separation for recycling aged-AgNPs. This method might be helpful to regenerate and recycle the precious metal nanoparticles with polydispersity due to long-term storage.

1. Introduction

Silver nanoparticles (AgNPs) have attracted considerable attention due to their significant applicability as catalyst, sterilizer, and sensing materials [1]. Especially, the unique properties of AgNPs, colorimetric sensing based localized surface plasmon resonance (LSPR) is of particular importance for molecular detection [2]. Because the SPR of AgNPs depends strongly on the initial size and shape of the AgNPs, it is important to maintain their initial state during storage. The ability to tailor mono-dispersed particles is also important in catalysis where catalytic activity of NPs depends on the particle size and shape [3].

Colloidal stability is a function of many factors including the type of capping agents, the surrounding environmental conditions (temperature, pH, and irradiation of light), and the background electrolyte composition (type and concentration of salts) [4]. When citrate coated AgNPs (ABC Nanotech, Korea) with ca. a diameter of 40 nm was exposed to several environmental conditions, the initial particle size and dispersion stability was changed, as described in a previous paper [5]. Among the destabilizing factors, the effect of salt in solution was shown to be the largest. That is, the size of AgNPs in PBS (phosphate buffered saline) solution was increased 23-fold upon the aggregation of AgNPs. At temperatures above ambient temperature, increasing Brownian motion of AgNPs increased the possibility of collision between neighboring particles [5]. The light exposure of AgNPs leads to photo-oxidation of adsorbed citrate, destroying the strong citrate double-layer kinetic stabilization, which may change the size and shape of the AgNPs [6].

Although we diminished the destabilizing factors, long-term storage over 1 year might induce the aggregation and sedimentation of AgNPs, and show polydispersed AgNPs. In order to synthesize nanostructured devices and materials with well-defined properties and functions, it is desirable to reduce the polydispersity of nanoparticles. As shown in Fig. 1, even though AgNPs solution was stored at a low temperature and in a dark condition, aggregated and large particles were clearly observed during long-term storage. Therefore, aged-AgNPs cannot be used in the application of nanostructured devices.

To reuse aged-AgNPs after overcoming this drawback and recovering mono-dispersed AgNPs separately, we attempted to recycle the polydispersity aged-AgNPs using the density gradient ultracentrifugation: isopycnic and rate zonal centrifugation [7]. Isopycnic centrifugation, which is often used for biomacromolecule separation, has been applied for diameter and electronic-dependent separation of single-walled carbon nanotubes (SWCNT) [7,8]. However, this method has a limitation when it is extended to the separation of metal nanoparticles [7]. The density gradient ultracentrifugation rate (DGUR) separation

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1226-086X/$ – see front matter
http://dx.doi.org/10.1016/j.jiec.2013.11.059

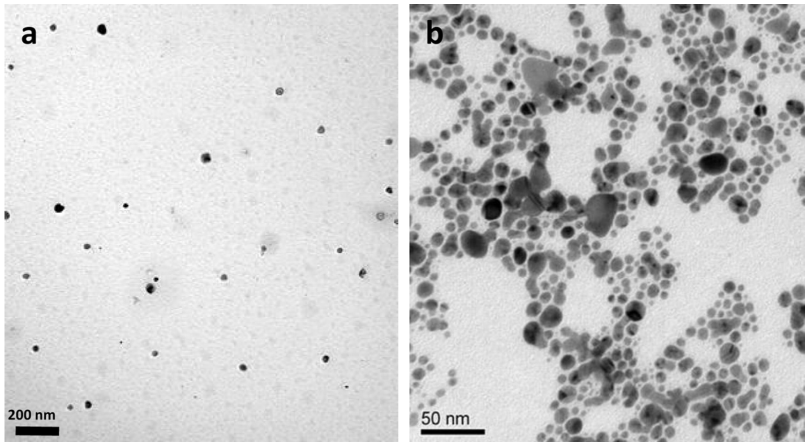

Fig. 1. TEM images of (a) fresh and (b) aged AgNPs (ABC Nanotech), which were stored under 10 °C for over 1 year.

technique can separate nanoparticles with higher densities than the gradient media itself. Recently, this technique has been employed as a general, nondestructive and scalable post-separation method to sort metal nanoparticles according to their size, shape, and chemical and structural differences in 10 min or even less [9–12].

Therefore, this provides a new opportunity for recycling and reusing the polydispersed aged-AgNPs as mono-dispersed fresh-AgNPs. In DGUR separation, the sample has a greater density than that of the highest density portion of the gradient. Because the centrifugal force can help particles to move radially away from the axis of rotation and can separate these particles by size and shape, the density of the fluid might effect on the separation efficiency [8]. Therefore, in this work, five separating fluids are tested to find the adaptable media for recycling aged-AgNPs via DGUR separation. The five media was selected according to simple criteria; eco-friendly and less-toxic chemicals. Glycerin is widely used in pharmaceutical formulations, and oligosaccharide (saccharide polymer) is used in food instead of sugar. Tween20 and Tween80 are a polysorbate surfactant whose relative non-toxicity allows it to be used as a detergent and emulsifier in pharmacological applications. Ethylene glycol is only weakly toxic, but generally used in centrifugal separation of biomaterials.

2. Experimental

Citrate-coated AgNPs as commercial materials was obtained from ABC Nanotech in Korea, and were also prepared by a chemical reduction method. As summarized in Table 1, we selected five solutions (glycerin, **G**; ethylene glycol, **E**; oligosaccharide, **O**; Tween20, **T2**; Tween80, **T8**) with suitable density distribution to prepare the density gradient, since these organics give appropriate viscosity and are inexpensive and environmentally friendly. In the typical procedure, density gradient solutions (10–90%) were prepared with deionized water. A step gradient was created directly in centrifuge tubes (50 mL Falcon tube) by adding layers with increasing density to the bottom of the tube. An aged-AgNP (200 ppm) was immediately layered on top of the five-layer density gradient prior to ultracentrifugation. The typical centrifugation condition was 10 min at 22,000 rpm (53,029 × g, SUPRA22, Hanil). The recovery ratio of AgNPs in five media was calculated from the concentration difference remaining in solution before and after centrifugation.

The morphological property of AgNPs was observed by transmission electron microscopy (TEM, JEM-1010, JEOL). The optical properties were characterized by UV–vis spectroscopy (UV-1800, Shimadzu). The concentration of the AgNPs sample fraction was analyzed by inductive couple plasma mass spectrometry (ICP-MS, Varian 820-MS, Variaon). The particle size distribution of AgNPs fraction after centrifugation was analyzed using ImageJ™ software (NIH) based on the TEM images.

3. Results and discussion

Fresh-AgNPs purchased from ABC Nanotech were initially under 40 nm in size, but their diameters were increased by aggregation and agglomeration, which was induced by the destabilizing effect such as occurring from storage conditions (i.e., pH, *T*, and light) [4–6]. Even though fresh-AgNPs were stored in a refrigerator under 10 °C and in a dark condition, the particle size distribution and aggregation feature of aged-AgNPs after 1 year might change, as shown in Fig. 2. While the aged-AgNPs were 40 nm in size, the polydispersity was increased by aggregation and Ostwald ripening between neighboring AgNPs [13]. Therefore, aged-AgNPs with polydispersity were not suitable for fabricating the target-oriented nanostructure and nanodevice.

In rate zonal centrifugation, the sample is applied in a thin zone at the top of the centrifuge tube on a density gradient. In isopycnic technique, the density gradient column encompasses the whole range of densities of the sample particles, and the sample is uniformly mixed with the gradient material. Because the isopycnic technique takes longer time to separate samples compared to the rate zonal technique, the rate zonal centrifugation is more effective separation method for nanoparticles with different size and shape.

DGUR separation used in this work was based on the fact that the particles of different sizes that move with different velocities in the medium provide a basis for particle separation into distinct bands. This method was successfully applied to achieve length separation of SWCNT [7,8] and size and shape separation of metallic nanoparticles [9–12]. Herein, particle velocity (ν) was calculated using the force balance between centrifugal force (F_c), buoyant force (F_b), and frictional force (F_f). The particle will be accelerated in a centrifugal field until the forces balance ($F_c + F_b = F_f$), and will subsequently become sediment with a constant velocity [3]. To increase the particle velocity, the density difference between the particles (ρ_p) and the fluid (ρ_f) should be large. In addition, it is known that viscosity generally amplifies the spatial separation between two particles that have different hydrodynamic behaviors [11]. Therefore, the density of the five media used here was 1.06–1.7 g/cm^3 and the viscosity ranged from 0.3 to 1.61 Pa s, due to ρ_p = 10.5 g/cm^3.