Stability of Silver Nanoparticles in Aqueous and Organic Media

Patricia Tillmann, Chemistry, Western Washington University

NNIN REU Site: Materials Science Research Center of Excellence, Howard University
Principal Investigator: Dr. James Mitchell, Chemical Engineering, Howard University
Mentor: Dr. Jude Abanulo, Chemical Engineering, Howard University
Contact: jwm@msrce.howard.edu

Abstract:

Several chemicals have been used to research the stability of silver nanoparticles in aqueous and organic media for use in electrophoretic deposition and, ultimately, the fabrication of an infrared detector. Every chemical component in the electrophoretic medium must be compatible with the ultrapure reaction conditions required for the fabrication of the semiconductor infrared detector. Appropriate reagents must introduce no detrimental impurities and be easily removed by decomposition or volatilization. Moreover, the silver nanoparticles must be ultrapure.

In this experiment, silver nanoparticles are obtained commercially and an electrochemical synthesis is attempted [2]. To ensure the silver nanoparticles are the appropriate 10 nm size, particle-size distributions of some samples are obtained using the Zetasizer 3000. In addition, the relative abilities of ethylene glycol, water, sodium dodecyl sulfate, methanesulfonic acid, formic acid, and 1,1,1-trifluoro-2,4-pentanedione to stabilize silver nanoparticles are compared using UV-Vis spectrophotometry. These results, plotted in an absorbance vs. time graph, indicate that ethylene glycol and sodium dodecyl sulfate are the best stabilizing agents.

Introduction:

Silver is a versatile element with applications in the clothing [4], appliance [3], and semiconductor industries. It can be used to destroy bacteria [3, 4] or fabricate a nanocomposite IR detector. For the latter application, this paper reports the results of a ten week exploratory investigation to optimize conditions for preparing an electrophoretic deposition medium containing 5-10 nm silver particles.

Following deposition of silver onto a silicon substrate, a nanocomposite silver-silicon matrix is processed into an IR detector. Prior to deposition, using a stabilizing agent compatible with electrophoretic deposition and subsequent semi-conductor processing prevents the agglomeration of silver nanoparticles in the processing medium. The relative effectiveness of ethylene glycol, sodium dodecyl sulfate, methanesulfonic acid, formic acid, and 1,1,1-trifluoro-2,4-pentanedione to stabilize silver nanoparticles are compared.

Experimental Procedures:

Silver nanoparticle suspensions containing six stabilizing reagents and varying pHs were prepared. Samples containing the same initial loading of silver (%) were prepared from an original 10% w/v stock suspension (commercially obtained). Each sample contained an amount of stabilizer that produced an initial absorbance of 0.7 to 1.0. The stabilizing reagents include: formic acid, methanesulfonic acid, sodium dodecyl sulfate, 1,1,1-trifluoro-2.4-pentanedione, ammonium hydroxide (for a sample of pH 11), acetic acid (for a sample of pH 3), and ethylene glycol as the control.

To prepare the samples, an Eppendorff pipette was used to measure the appropriate amount of silver nanoparticle suspension. This amount was then added to the solution of water or ethylene glycol and a stabilizing agent to total 15 mL of suspension. Once prepared, 2-3 mL of a sample were transferred into a quartz cuvette using a polyethylene transfer pipette and tested using the UV-Vis. Following measurement of the initial absorbance, each suspension was periodically measured over a 1-2 week period.

Ten measurements were averaged to obtain results for a single day. During the measurement cycle, samples were stored in sealed vials and kept in a cool, dry, dark place until the next series of tests.

Results and Conclusion:

Particle-size distributions of several nanoparticle suspensions, determined by electrophoretic light scattering with a Zetasizer 3000, are shown in Figure 1. A slightly narrower distribution of particles over the same size range

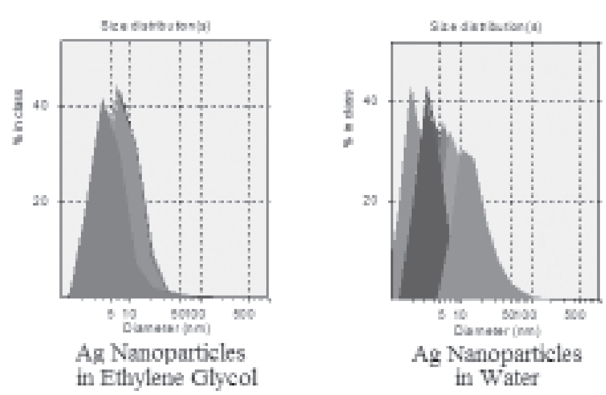

Figure 1: Size distributions of silver nanoparticles. Most silver nanoparticles are 5-10 nm in diameter.

exists in ethylene glycol. To determine the relative stability of the various silver nanoparticle media, a comparison of absorbance versus time at a constant wavelength was used. In the absence of the stabilizer chemically transforming silver metal particles into ionic forms or neutral absorbing chromophores, the decrease of the absorbance with time is dominated by the agglomeration and/or settling of silver nanoclusters from solution. Silver precipitates formed easily on the walls of vessels containing the least effective stabilizers. This provides a relative comparison of the stabilizing effect of various reagents.

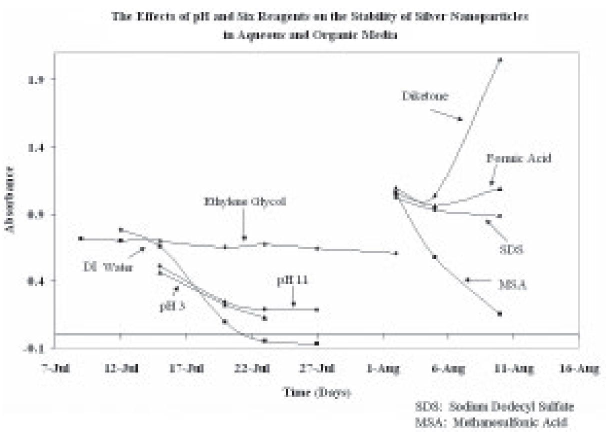

Figure 2: Ethylene glycol and SDS show the smallest decreases in absorbance over time and are the best stabilizers.

After 1-2 weeks of testing, Figure 2 shows ethylene glycol and sodium dodecyl sulfate are the most obvious and effective stabilizers of silver nanoparticles in aqueous and organic media. It is possible that ethylene glycol, the control, performed so well because another stabilizing agent is present in the solution. However, proprietary issues preclude analyses to document this.

Sodium dodecyl sulfate has previously been used to stabilize silver nanoparticles in aqueous solutions successfully [1] and these results are confirmed here. Unfortunately, the reagent does not meet our requirements. Results for the diketone (1,1,1-trifluoro-2,4-pentanedione) and formic acid require further investigation to verify or refute their validity. Within a few days, in the presence of methanesulfonic acid, absorbance decreases rapidly and silver particles precipitate. Other experiments can determine if the isoelectric point is reached, causing the destruction of electrostatic stabilization or if another explanation for this result is valid.

Future Work:

AFM images, as seen in Figure 3, are but one form of characterization necessary to validate or refute the above hypotheses. It is ideal to prepare silver nanoparticles in the lab to achieve complete control over the fabrication process. To efficiently perform the electrophoretic deposition, the pH at the isoelectric point of silver should be found. To make the fabrication process easier and purer, electrophoretic co-deposition of silver and silicon is ideal.

Acknowledgements:

I would like to thank Dr. James Mitchell, Dr. Jude Abanulo, Dr. Vilma Gultneh, Mr. Uche Nwodo, Mr. James Griffin, Dr. Otto Wilson, and my co-workers for their assistance and support. Finally, thank you to the NNIN and NSF for funding.

References:

[1] Mafune, F.; Kohno, J.K.; Takeda, Y.; Kondow, T. J. Phys. Chem. B, 2000, 104 (35), 8333-8337.

[2] Kortenaar, M.V. ten; Kolar, Z.I.; Tichelaar, F.D. J. Phys. Chem. B, 1999, 103, 2054-2060.

[3] http://www.samsung.com/ph/presscenter/samsunginthephilippines/productnews_20040608_0000058342.asp#

[4] http://www.essentialapparel.com/shopping/product/detailmain.jsp?itemID=1564&itemType=PRODUCT&iProductID=1564

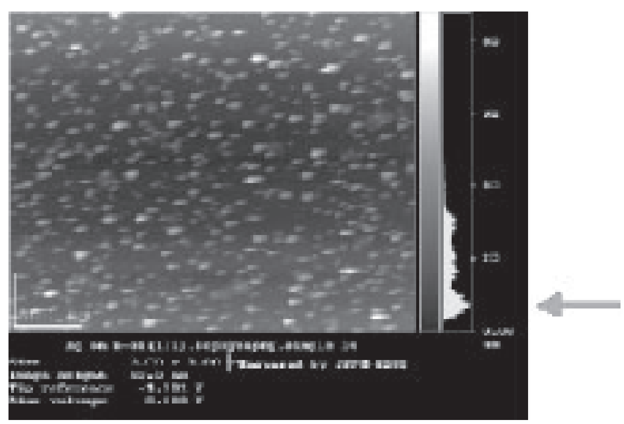

Figure 3: Silver nanoparticles are about 10 nm across and monodispersed.