Airborne Synthesis and Application of a Novel Silver Sol for Sensitive and Reproducible FT-SERS Spectroscopy

Josefa R. Baena¹, Nicolae Leopold², Michael Haberkorn¹, Thomas Laurell³, Johann Nilsson³ and Bernhard Lendl¹

¹Institute of Chemical Technology and Analytics, TU Wien, Getreidemarkt 9-164/AC, A-1060 Wien, Austria http://www.iac.tuwien.ac.at/cavs/
²Universitatea Babes-Bolyai, Facultatea de Fizica, Kogalniceanu 1, 3400, Cluj-Napoca, Romania
³Department of Electrical Measurements, Lund University, PO Box 118, 221 00 Lund, Sweden

Introduction

We report a new simple and easy method for preparing stable, highly SERS-active silver colloids by reduction of silver nitrate with hydroxylamine. 

Advantages of this method are:
- Fast and easy preparation at room temperature
- High reproducibility and preparation success rate
- In situ synthesis and on line SERS measurement

Preparation of silver colloids

AgNO₃ (10⁻³ M) + H₂NOH / NaOH (1.5x10⁻³ M / 3x10⁻³ M)

Silver Colloid

Characterization of silver colloids

Figure 1. Extinction spectra of hydroxylamine reduced silver colloids, one day after preparation. 10 ml of hydroxylamine / NaOH were added (A) drop wise, (B) rapidly, to 90 ml silver nitrate. 10 ml silver nitrate were added (C) rapidly, (D) drop wise to 90 ml silver nitrate. 10 ml hydroxylamine / NaOH were added (A) drop wise, (B) rapidly, to 90 ml silver nitrate. 10 ml silver nitrate were added (C) rapidly, (D) drop wise to 90 ml hydroxylamine / NaOH.

Figure 2. (A), (B), (C), (D) TEM images of the hydroxylamine reduced silver colloids shown in Figure 1; (E) TEM image of a Lee-Meisel silver colloid.

In situ preparation and on line SERS measurement

Figure 3. (A), (B) FT-SERS spectra, using the 1064 nm laser line, of 2x10⁻⁴ M 9-aminoacridine adsorbed on hydroxylamine reduced and Lee-Meisel silver sol respectively. (C), (D) SERS spectra, using the 785 nm laser line, of 2.5x10⁻⁷ M 9-aminoacridine adsorbed on hydroxylamine reduced and Lee-Meisel silver sol respectively.

- For each excitation wavelength, 1064 or 785 nm, the spectrum of 9-aminoacridine obtained with the hydroxylamine reduced is mainly similar to that obtained with the Lee-Meisel silver sol.
- Small differences in the relative intensities can be attributed to different morphologies of the silver particles due to the different reduction procedures or to colloid age.
- The adsorption geometry of 9-aminoacridine to the hydroxylamine reduced or the Lee-Meisel silver colloid is the same.

Figure 4. FT-SERS spectra of 3.8x10⁻⁷ M crystal violet (A); 7x10⁻⁸ M rhodamine 6G (C), (D); 3.8x10⁻⁷ M methylene blue (E), (F). (A), (C), (E) employing the hydroxylamine reduced and (B), (D), (F) Lee-Meisel silver sol respectively.

- For each analyte the peak positions and relative intensities in the recorded spectra were found to be independent of the preparation method.
- Using the hydroxylamine reduced or the Lee-Meisel silver sol with different analytes under the same experimental conditions it was found that the signal to noise ratio for the same analyte differed in no more than a factor of two.

Figure 5. Experimental setup comprising a flow-through microdispenser coupled to an automated flow system, an ultrasonic levitator and a FT-Raman spectrometer.

- The particles size distribution of the silver particles can be easily adjusted in the range of 25 to 100 nm, as a function of the mixing order and rate of the reagents.
- By comparing the hydroxylamine reduced silver sol with the Lee-Meisel silver sol, it can be concluded that the employed analyte molecules adsorb in similar geometries and the SERS enhancement factor of the hydroxylamine reduced silver colloids is comparable to that obtained with the Lee-Meisel silver colloid.

Conclusions

Hydroxylamine reduced silver colloids:
- A new simple and easy method for preparing stable, highly SERS-active silver colloids.
- Fast preparation at room temperature.
- High reproducibility and preparation success rate.
- Possibility of in situ synthesis of the colloid and employment in on-line measurements.
- The particles size distribution of the silver particles can be easily adjusted in the range of 25 to 100 nm, as a function of the mixing order and rate of the reagents.
- By comparing the hydroxylamine reduced silver sol with the Lee-Meisel silver sol, it can be concluded that the employed analyte molecules adsorb in similar geometries and the SERS enhancement factor of the hydroxylamine reduced silver colloids is comparable to that obtained with the Lee-Meisel silver colloid.