

Morphological Design of Nanoparticle Assemblies: Application to Environmental Sensing

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Abstract

Silver nanoparticle deposition from suspension is proposed as a route for the morphological design of controllably disordered self-affine substrates for surface-enhanced Raman sensing of water pollutants. Ionic strength is used as a variable parameter to control the deposition process and, ultimately, the morphology of deposited substrates. The critical dependence of the enhancement factor on the substrate morphology is leveraged to develop sensors with tunable sensitivity. Fractal analysis is used to quantify deposit morphologies and to correlate these to enhancement factors afforded by the substrates.

1. Introduction

Development of sensors for the early detection of environmental pollution requires technologies with both fingerprinting capability and low detection limits. The remarkable sensitivity afforded by surface-enhanced Raman spectroscopy¹ (SERS) makes this vibrational technique especially attractive for such applications.^{2,3} Recent discovery of the single-molecule detection (giant SERS)

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¹ Jeanmaire, D. L.; Van Duyne, R. P. *J. Electroanal. Chem.* **1977**, *84*, 1; Albrecht, M. G.; Creighton J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5215.

² Chang, R. K.; Furtak, T. E. *Surface Enhanced Raman Scattering*; Plenum Press: New York, 1982.

³ Vo-Dinh, T. *Trends Anal. Chem.* **1999**, *17* (8-9) 557-582.

afforded by this technique has even further amplified the interest in possible uses of SERS for sensing applications⁴.

The SERS effect can be observed when analyte molecules are adsorbed on SERS-active substrates - specially-prepared surfaces of coinage metals. A wide variety of different enhancing substrates has been proposed since the discovery of the SERS effect more than twenty years ago. What all these systems have in common, however, is that their microstructure has a profound effect on their optical properties. On one hand, substrate morphology determines how high an enhancement of a Raman signal can be achieved; on the other hand it is the difficulty in fabricating reproducible substrates that is at the base of SERS irreproducibility, the Achilles heel of the technique.

Self-assembly of nanoparticles is one of new approaches to the reproducible SERS substrate fabrication that the rapidly developing field of nanoscale materials engineering has offered. 2D and 3D *ordered* SERS-active substrates have been assembled from metallic, polymeric, and hybrid particles. However, it is for *disordered* substrates that the highest enhancements (giant SERS) were achieved. Recently developed theory and experimental evidence point to the fact that only self-similar fractal surfaces can support the giant SERS⁵. While reports on the successful self-assembling nanoparticles into ordered array are abundant, no published data exists on controlling the degree of disorder (fractality) of nanoparticle-based SERS-active substrates. Therefore, to be able to leverage unique advantages that SERS based environmental sensors can offer, it is critical to develop reliable methods of fabricating *fractal* substrates *controllably* and *reproducibly*.

In this paper we consider the morphological design of SERS substrates using Ag nanoparticles deposited from suspension onto a solid support. Our approach is a subset of a more general framework for describing particle deposition. Within this framework, it is hypothesized that the structure of particle deposits can be predicted and controlled based on the solution chemistry, particle hydrodynamics, and surface chemistry of particles.^{6,7} Due the rich choice of particle transport mechanisms and interactions that can potentially be harnessed to deposit particles, the deposition process can be controlled to a greater extent,

⁴ Kneipp, K.; Wang, Y.; Kneipp, H.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Phys. Rev. Lett* **1996**, *76*, 2444.

⁵ Wang, Z.; Pan, S.; Krauss, T. D.; Du, H.; Rothberg, L. J. *P. Natl. Acad. Sci. USA* **2003**, *100* (15), 8638-8643.

⁶ Elimelech, M.; Gregory, J.; Jia, X.; Williams, R.A. *Particle Deposition and Aggregation*, Butterworth-Heinemann, 1995.

⁷ Wiesner, M. R. *J. Environ. Eng. ASCE* **1999**, *125* (12) 1124-1132.

and a wider range of morphologies can be created than can be achieved by strictly ballistic deposition as is the case of vacuum deposition. We implement this approach as an ionic strength controlled self-assembly of nanoparticles on a surface wherein the degree of disorder is controlled by varying the ionic strength of the solution. We extend previous studies of ionic strength dependent monolayer coverage of deposition surfaces by nanoparticles⁸, to explore the effect of the ionic strength on the microstructure of 3D deposits formed from nanoparticle suspensions.

2. Materials and Methods

2.1 Silver hydrosol preparation and fabrication of SERS-active Ag films

Suspensions of silver nanoparticles were prepared following the procedure described by Lee and Meisel⁹. Microscope slides (Gold Seal®, Becton, Dickinson and Co.) pre-cut to 1.27 cm × 4.62 cm size were cleaned using detergent, rinsed with deionized water, ultrasonicated (8890-DTH sonicator, Cole-Parmer) in methanol for one hour and then placed into 25% 3-aminopropyltrimethoxysilane (97% APTMS, Aldrich, cat. no. 281778) methanol solution for 24 hours for derivatization. Derivatized substrates were rinsed profusely in pure methanol and then stored in methanol until further use.

Deposition was carried out in two stages. First, a closely packed layer of silver particles was deposited on an APTMS-modified slide¹⁰. At this stage, APTMS-modified slides were rinsed in water and placed vertically into 20 mL borosilicate vials ("scintillation vials", cat. no. 03-337-15, Fisher Scientific) with silver hydrosol. Aggregation of suspension in the immediate vicinity of the derivatized slide initiated by residual physisorbed APTMS was indicative of poor rinsing and such slides were discarded. The aggregation could be recognized by darkening of the suspension, a gradual increase in transparency, and appearance of a lilac tint in the suspension. Prolonged generous rinsing was found to be necessary to avoid this phenomenon. After 24 hours of incubation in silver hydrosol, slides were rinsed with ultrapure water.

The second stage involved the deposition of silver particles at variable ionic strengths on horizontally positioned slides prepared during the first stage. To four 7.5 mL aliquots of hydrosol different amounts of 0.5 mol/L NaClO₄ solution and

⁸ Brouwer, E. A. M.; Kooij, E. S.; Wormeester, H.; Poelsema, B. *Langmuir* **2003**, *19* (19) 8102-8108.

⁹ Lee, P. C.; Meisel, D. (1982). *J. Phys. Chem.* **1982**, *86*, 3391.

¹⁰ Grabar, K. G.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735-743.

water were added to keep the total volume of 15 mL. Resulting suspension had the solid fraction of $1.5 \cdot 10^{-4}$ w/w, and ionic strengths of $2.1 \cdot 10^{-2}$ mol/L, $3.1 \cdot 10^{-2}$ mol/L, $4.4 \cdot 10^{-2}$ mol/L, and $5.4 \cdot 10^{-2}$ mol/L. The pretreated slides from the first stage were further cut to smaller pieces $1.27 \text{ cm} \times 1.27 \text{ cm}$ in size and placed on the bottom of eight (four ionic strengths in duplicate) 20 mL borosilicate glass vials. The vials were then filled with silver hydrosol of different ionic strengths and left for a certain period of time for Ag nanoparticles to deposit. The deposition time depended on the ionic strength and varied from several minutes in the case of the highest ionic strength to several days in the case of the lowest ionic strength.

2.2 Fractal Characterization of Ag Deposit Structure

Fractal dimensions of deposits can be calculated using the fact that the root-mean-square (RMS) roughness σ scales with image size L as

$$\sigma \propto L^H, \quad (1)$$

where the scaling exponent H relates to the fractal dimension D as^{11,12} (Mandelbrot 1983):

$$D = 3 - H, \quad (2)$$

Following the methodology proposed by Krim et al.¹³ RMS roughness was calculated based on a series of concentric AFM scans of deposited substrates. Five scans - $1 \mu\text{m}$, $2 \mu\text{m}$, $4 \mu\text{m}$, $8 \mu\text{m}$, and $16 \mu\text{m}$ in size were recorded and analyzed for each deposit. Fractal dimensions were computed using equations (1) and (2).

2.4 Acquisition of Raman Spectra

After the deposits were prepared, a thin layer of gold was sputtered on them, and SEM and AFM imaging was carried out. For SERS experiments, substrates were submerged for 2 hours in a $3.3 \cdot 10^{-8}$ mol/L aqueous solution of Rhodamine 6G, then rinsed with ultrapure water and dried. Rhodamine 6G is a dye that is frequently employed as a molecular probe in SERS experiments for calibration and testing purposes.

Raman spectra were collected with a Renishaw micro-Raman system 1000 spectrometer using 514.5 nm Ar laser line. Incident power of the Ar-ion laser was in the 5 mW - 8 mW range. Spot size for the 50x objective used was approximately $2 \mu\text{m}$. Spectra were recorded with the resolution of 2 cm^{-1} and a signal collection time of 10 s.

¹¹ Mandelbrot, B. B. *The Fractal Geometry of Nature*, Freeman, 1983.

¹² Vicsek, T. *Fractal Growth Phenomena*, World Scientific, 1992.

¹³ Krim, J.; Heyvaert, I.; Van Haesendonck, C.; Bruynseraede, Y. *Phys. Rev. Lett.* **1993**, *70* (1) 57-60.

3. Results and Discussion

3.1 Deposition of Ag nanoparticles

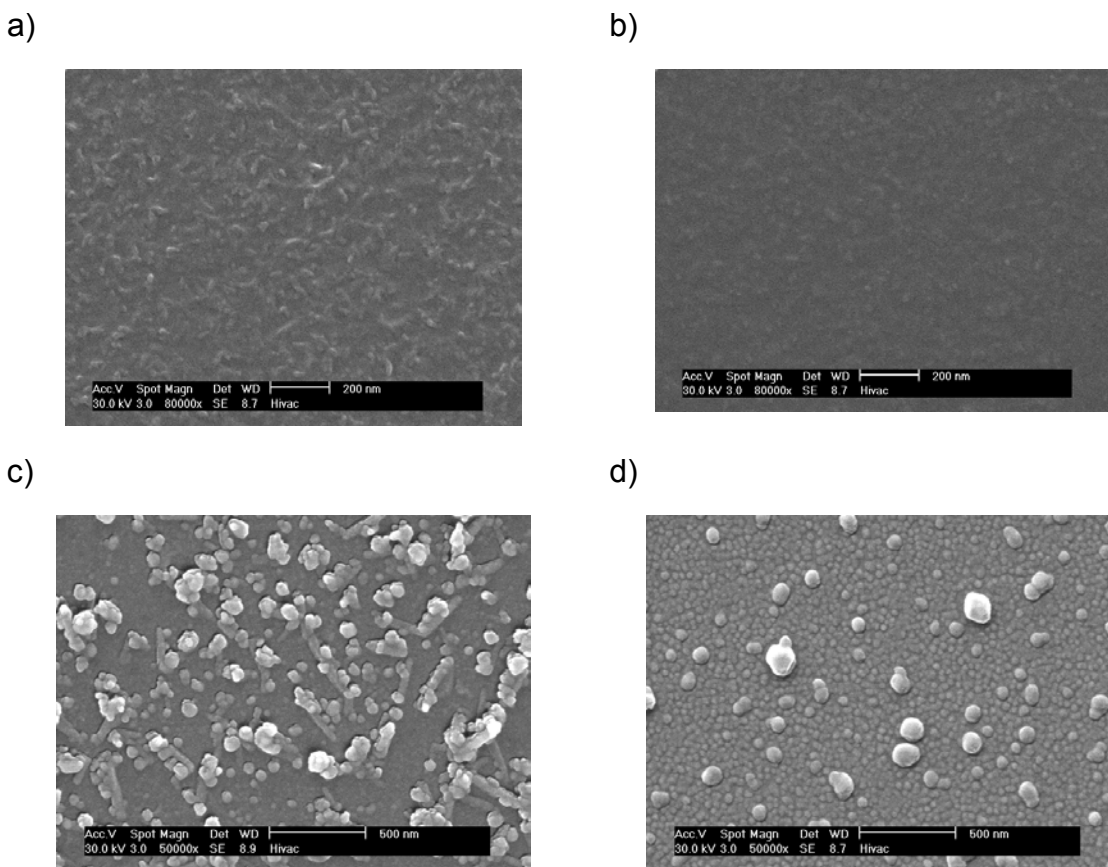


Figure 1. SEM micrographs of Ag nanoparticles deposited on vertically positioned APTMS-modified glass slides: a) clean glass slide, b) APTMS-modified glass slide, c) APTMS-modified glass after vertical immersion in Ag hydrosol for 26 hours, d) APTMS-modified glass after vertical immersion in Ag hydrosol for 70.5 hours, e) APTMS-modified glass after vertical immersion in stirred Ag hydrosol for 24 hours, f) APTMS-modified glass after vertical immersion in Ag hydrosol for 2 weeks (evaporation-induced deposition). Zeta scale is the same for all images.

In preliminary deposition experiments that involved non-diluted hydrosol at an ionic strength of $8.6 \cdot 10^{-3}$ mol/L, striped coverage patterns were occasionally observed (not shown). We attributed this to the non-homogeneity of glass slide surfaces. In all further experiments, SEM imaging was performed at this stage of SERS-active substrate preparation and slides with non-homogeneous coverage by Ag particles were discarded. Also, it was observed that attached to the slide surface were individual particles with almost no particle aggregates present at the surface. Thus, these preliminary experiments demonstrated that Ag particles

attach to APTMS-modified glass surface primarily as individual particles and that particle-APTMS interaction is favored over particle-particle interaction under the native ionic strength and solid fraction conditions.

Subsequent deposition experiments were carried out following the two steps procedure described in “Material and Methods” section. First, a layer of Ag particles was assembled on a surface of a glass slide.

3.1.1. Assemblage of the first layer of Ag particles

Figure 2 illustrates different stages of the preparation of silver deposits. Deposits formed when the glass was pretreated with the APTMS molecules was more regular than that on the clean glass (Figure 2a and Figure 2b) suggesting that the APTMS partially masks surface irregularities. Figures 2c and 2d illustrate the dependence of surface coverage by Ag particles on time. It was found that APTMS-modified slides had to be immersed in hydrosol for approximately 72 hours for the complete coverage to occur. Another interesting aspect of this dependence is that initially rods were overrepresented on the slide surface. At longer immersion time, smaller particles substituted rods at the surface and a dense, relatively defect-free layer of silver particles was formed on the surface.

This first step of covering APTMS-modified slides with a layer of Ag particles was undertaken for two reasons. First, as already mentioned, the quality of glass slides was monitored at this stage and all slides with apparently non-homogeneous surface chemistry were rejected. Second, having the initial substrate covered with a dense layer of Ag particles ensured that the structure of the deposit would be defined by interactions only between Ag particles.

3.1.2. Precipitation of Ag suspension under different ionic strength conditions

Figure 3 (a-d) portrays deposits formed at four different ionic strengths: a) $2.1 \cdot 10^{-2}$ mol/L, b) $3.1 \cdot 10^{-2}$ mol/L, c) $4.4 \cdot 10^{-2}$ mol/L, d) $5.4 \cdot 10^{-2}$ mol/L. As can be seen from these images, various degrees of aggregation in the settling suspension resulted in markedly different morphologies of deposited layers.

RMS roughness of the deposits as calculated by the AFM software was higher for deposits formed at higher ionic strengths. Under these conditions, repulsive electrostatic interparticle interactions are screened and aggregates with more open structure form in the suspended phase. As such aggregates settle, they are expected to form deposits with higher roughness than in the case of deposits formed from denser aggregates under lower ionic strength conditions.

3.2 *Fractal Analysis of Ag Deposits*

While results of roughness measurements were intuitive, calculations of the fractal dimension of deposits rendered an unexpected dependency of deposit scaling properties on the solution chemistry. Fractal dimension was found to increase with increasing ionic strength (Figure 5). Measurements of fractal dimensions of deposits formed at the lowest ionic strength had a relatively large

spread, which is reflected in the large error bar in Figure 5. However, for other ionic strengths, the tendency for the fractal dimension to increase with increasing ionic strength was clear. Thus, while for deposits formed at higher ionic strength the roughness was higher, it scaled slower with the size of the deposit.

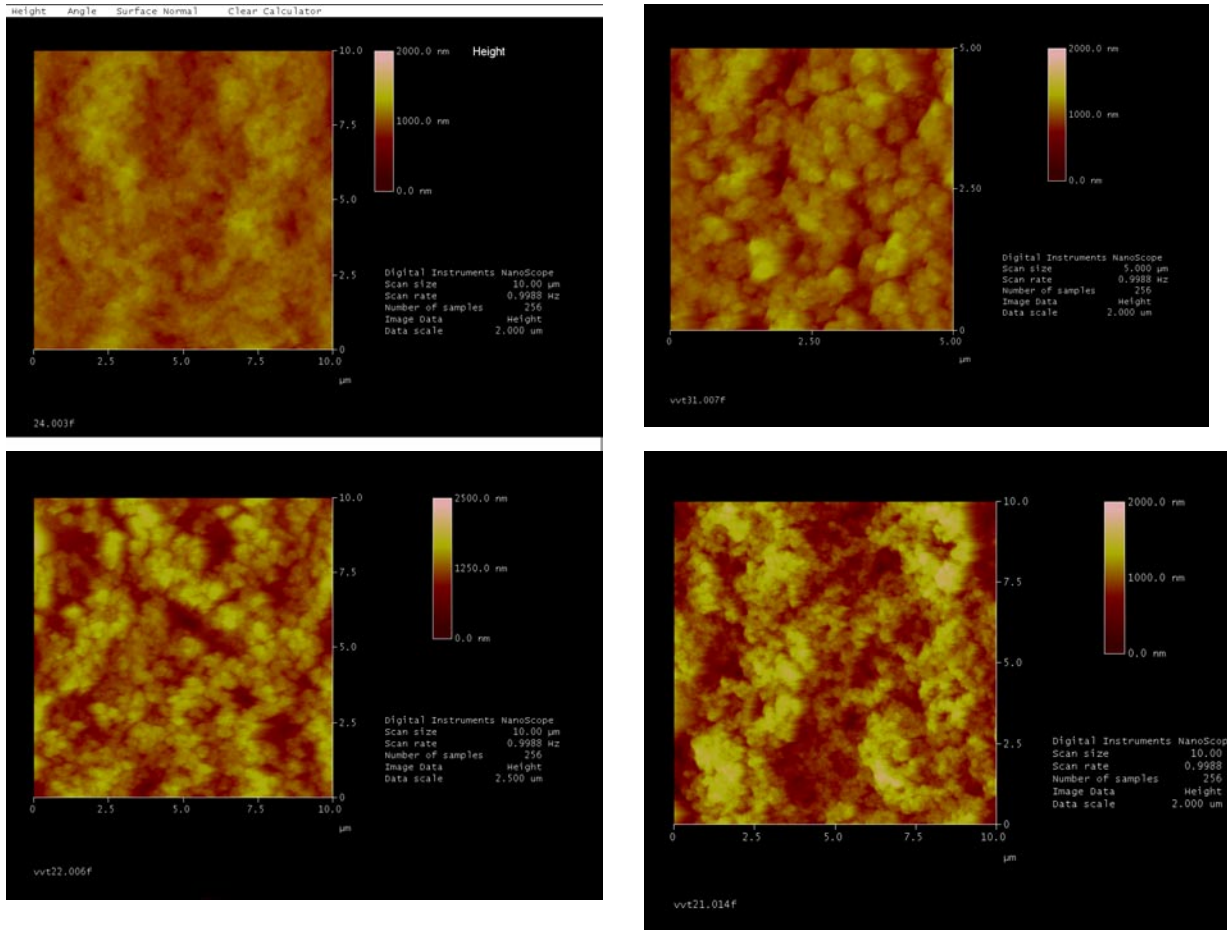


Figure 2. AFM images of Ag nanoparticle deposits formed on horizontally positioned APTMS-modified glass slides at different ionic strengths: a) $2.1 \cdot 10^{-2}$ mol/L, b) $3.1 \cdot 10^{-2}$ mol/L, c) $4.4 \cdot 10^{-2}$ mol/L, d) $5.4 \cdot 10^{-2}$ mol/L

This result may be explained in terms of different types of growth that result from aggregate deposition on surface. At lower ionic strengths, many smaller, more compact aggregates attach to already deposited aggregates resulting in a cluster-cluster aggregation at the surface. At higher ionic strength, however, large aggregates with a more open and fragile structure arrive at the surface and restructure upon deposition. It can be speculated that in the absence of fractal surface growth, resulting structures are porous yet the porosity does not scale as fast as it does in the case of surface growth from more compact clusters.

3.3 Enhancement Factor of SERS-substrates of different morphologies

Different locations on each substrate were probed with the 514.5 nm line of an Ar laser. Although the signal depended on the location, variations in intensity

within individual substrates were considerably smaller than between different substrates. Figure 6 illustrates SERS spectra of Rhodamine 6G adsorbed on Ag nanoparticle deposits formed at three different ionic strengths. Figure 7 depicts how intensities of three individual bands in the SERS spectrum depend on the ionic strength. The observed spectra demonstrate that the enhancement is a strong function of substrate morphology.

By comparing roughness measurements, results of fractal and multifractal analysis, and SERS results we can conclude that highest enhancements are supported by Ag deposits that are formed at medium ionic strengths from nanoparticle aggregates that do not restructure considerably upon deposition.

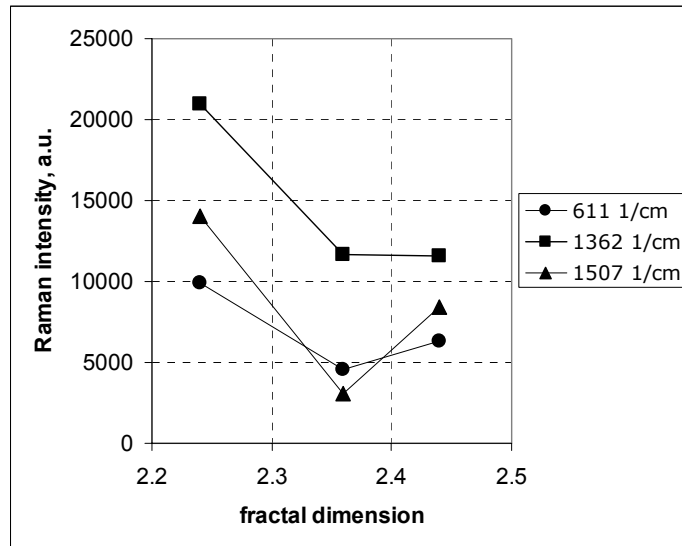


Figure 3. Intensity of four lines in SERS spectrum of Rhodamine 6G as a function of fractal dimension of SERS-active substrate.

4. Summary

In this paper we propose deposition of Ag nanoparticles from suspended phase onto a solid support as a route of morphological design of fractal SERS-active substrates. We demonstrate that it is possible to create Ag nanoparticle deposits with a range of morphologies using ionic strength as a control variable. Employing a combination of microscopic and spectroscopic characterization methods we show that the by varying the morphology of a SERS-active substrate, its enhancing properties can be tuned.

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