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Kinetics of silver nanoparticle deposition onto poly(ethylene imine) modified mica determined by AFM and SEM measurements

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ABSTRACT

A stable silver nanoparticle sol was synthesized via the reduction of silver nitrate using sodium borohydride in the presence of polyvinyl alcohol serving as the stabilizing agent. Bulk characteristics of this sol involved the solid weight content, the extinction spectrum, diffusion coefficient (hydrodynamic diameter) measured by dynamic light scattering (DLS) and the electrophoretic mobility. The average diameter of silver nanoparticles measured by scanning electron microscopy (SEM) and atomic force microscopy (AFM) was 19 and 18 nm, respectively. On the other hand, the hydrodynamic diameter of particles, determined via the diffusion coefficients measurements was 25 nm, being fairly independent of ionic strength. The electrophoretic mobility measurements revealed that the zeta potential of nanoparticles increased with the ionic strength, from −43 mV for $I = 10^{-4}$ M to −12 mV for $I = 3 \times 10^{-2}$ M. Using the sol, the kinetics of silver particle deposition on mica modified by a PEI sublayer was studied under diffusion-controlled transport conditions. The surface concentration of particles was determined by a directly enumeration using AFM and SEM technique. The measurements were performed for various ionic strengths ranging from 10^{-4} to 3×10^{-2} M. Both the kinetics of particle deposition (for the time reaching 24 h) and the maximum surface concentration were determined. It was found that for higher ionic strength the maximum coverage exceeded 0.2, and the monolayers were uniform in a macroscopic scale. It was also proven that the monolayers were stable over a prolonged time period. The kinetic data were quantitatively interpreted in terms of the random sequential adsorption (RSA) model using the effective hard particle concept. It was concluded that by applying the self-assembling process exploited in our work, uniform silver particle monolayers of controlled density can be produced in a reliable way.

1. Introduction

Noble metal nanoparticles (NPs), especially silver, have attracted considerable interest due to their significant potential applications in the areas of nanotechnology [1], catalysis and medicine. For example silver nanoparticles have been used as an antimicrobial agent for years [2], long before the appearance of antibiotics.

Silver nanoparticles of various shape and size can be produced by the chemical reduction of silver nitrate using: citrate [3], hydrazine [4], sodium borohydride [5], formaldehyde [6] and b-D-glucose [7]. Stabilization of silver particle sols can be achieved using surfactants [8] or neutral polymers [9]. On the other hand, the size of silver particles can be regulated by choosing the appropriate concentration of the metallic salt, varying reaction temperature or reaction time [10] and related factors such as the weight ratio of stabilizer/silver nitrate [6,9].

The bulk properties of silver sols can be routinely determined using the conventional dynamic light scattering (DLS) [11] and microelectrophoretic mobility measurements [12]. The sol concentration in the bulk can be precisely determined using the UV–vis spectroscopy, or by the dry weight method [13]. The size distribution and the number of silver particles as well as their arrangement on solid substrates can be monitored using the transmission electron microscopy (TEM) [14], scanning electron microscopy (SEM) [15] or the atomic force microscopy (AFM) working in the intermittent contact mode [16].

AFM offers many advantages in characterization the sub-, mono- and multi-layer formed by particles. In most cases this technique provides important information such as particle shape, surface area, roughness, electrical property and chemical composition. Moreover, AFM can characterize the particles in different environment including air or liquid. The sample preparation for this method is easier in comparison to e.g. SEM. Samples can be

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conductor, semiconductor or insulator. The AFM technique can be used for the determination of the diameter of particles in the broad range of sizes and shapes and the broad range of particle coverage.

Using SEM one can measure the particles down to nanometers size but only under vacuum conditions. On the other hand, the sample preparation is complicated and long-lasting process, especially in case of nonconductive samples. They are therefore usually coated with an ultrathin coating of electrically conducting material, commonly gold, chromium or tungsten deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation and thus time of sample preparation increased additionally. Furthermore, the sample drying and coating of electrically conducting material can affect the deposited particle configuration as well as their apparent sizes [17,18].

In QCM method the force is determined rather than the mass of adsorbed layer. As a result the signal depends not only on the mass of adsorbed particles but also on the structure of the adsorbed layer and its hydrodynamic resistance. Therefore, the amount of adsorbed particles alone cannot be uniquely determined, and tedious calibration procedures are needed. Last but not least, the substrate surfaces are practically limited to silver coated quartz plates [19].

Reflectometry is applied to characterize single and multi-layer structures and coatings. However, this indirect optical method is expensive and provides information averaged from broad area of surface. The studies of local micro- or nano-structures deposited particle sub- or mono-layers are complicated and often leaded to errors in characterization of adsorbed layers.

After a throughout bulk characterization, silver particle sols can be used for preparation of films on solid/liquid interfaces to achieve new functionalities. When they are assembled into a close-packed structure, their optical properties will change due to the interaction of the particles local electric fields [20]. Therefore, such two-dimensional Ag structures are attractive especially in the development of micro electronic and optical devices [21], biomedical labeling [22] and silver enhancement Raman spectroscopy [23].

However, in many cases, methods based on self-assembly of nanometer-scale silver particles are sophisticated and require expensive apparatus and procedures, e.g., vacuum sputtering and evaporation [24], chemical vapor deposition, photochemical reduction, chemical bath deposition (in situ reduction), etc. [25].

It seems that the simplest and most flexible method of producing homogeneous silver films of controlled properties is self-assembly from stable aqueous silver sols under the diffusion-controlled transport condition. Such a process allows one to produce homogeneous monolayers over macroscopic areas with the coating density controlled by the ionic strength, pH, bulk concentration of the suspension or adsorption time.

Despite the significance of the silver film preparation by the self-assembly method, there are few studies in literature that report kinetics of silver particle deposition at surfaces modified by a chemical coupling agents. Kim et al. [26] studied the adsorption and aggregation from aqueous silver sol onto a poly(4-vinylpyridine) (P4VP) using QCM, AFM and Raman scattering spectroscopy. The authors determined the particle surface concentration (particles per $\mu m^2 = \mu m^{-2}$) as a function of time (min) for a linear regime, where the surface blocking effects were negligible. The maximum coverage of particles was 472 μm^{-2} (determined by the AFM and QCM), which corresponds to particle coverage equal to 23%. However, the kinetics of nanoparticles deposition was monitored for a short deposition time only (up to 6 h) and no further information about the adsorption conditions, i.e., concentration of silver sol, ionic strength and pH as well as the stability of adsorbed silver sublayer were given. Also, no theoretical model describing the kinetics and mechanism of particle deposition was proposed.

Park et al. [27] reported deposition of silver nanoparticles (prepared by reduction of $AgNO_3$ using the sodium citrate with no addition of a polymer) on glass slides modified with silane compounds having bifunctional moieties. This process was studied using the UV–vis adsorption spectroscopy and the AFM. No physicochemical information on silver nanoparticle properties i.e., their polidispersity, stability, size, zeta potential as well as on substrate zeta potential (glass coated by silane) and deposition conditions were given.

Bandyopdhyay et al. [28], using the QCM technique, studied deposition of silver particles on the 4-carboxythiophenol (4-CTP)-covered Al and Au, respectively. However, the silver sols were polydisperse (bimodal) with two maximum peaks occurring at 10 and 38 nm. Furthermore, there was no information on particle transport conditions and the physicochemical parameters of the deposition procedure (pH, ionic strength) and all experiments were performed for short deposition time only, i.e., up to 60 min. Also, no quantitative interpretation of the results obtained was undertaken. It was only stated that the maximum coverage of Ag nanoparticles was close to 10%.

Therefore, the main goals of this work is to measure the kinetics of silver particle deposition on mica modified by PEI, in particular to determine the role of the ionic strength in this process. Because of the use of direct observation methods, the particle surface concentration can be determined in an absolute way, without using any adjustable parameters. This allows one to verify the validity of known theoretical approaches to describe the kinetics of nanoparticle deposition, which has significance for basic science. Apparently, this kind of studies has not been attempted before in the literature.

Our study has also practical implication because it allows one to work out a quantitative procedure for preparing silver nanoparticle films of high coverage and controlled structure.

2. Experimental

2.1. Materials

The precursor used to synthesize the colloidal silver was silver nitrate (Chempur). The sodium borohydride (granules, 99% metal basis) and poly(vinyl alcohol) (PVA), (80%, hydrated, M_w = 9000–10,000 Da) were purchased from Sigma–Aldrich. Sodium chloride (Fluka) was a commercial product and was applied without further purification.

Natural ruby mica sheets supplied by Continental Trade Ltd., Poland were applied as the substrates for polyelectrolyte adsorption. Thin sheets were freshly cleaved and used in experiments without any pre-treatment.

Platinum holders used for SEM measurements consisted of borosilicate glass (0.7 ± 0.1 mm), chromium layer (2.5 ± 1.5 nm) and platinum layer (250 ± 50 nm) were purchased from *arrandee* Precious Metal Coated Substrates, Germany. The Pt substrates were cleaned in acetone and isopropanol for 30 min and annealed in flame for 30 s directly before measurement.

The poly(allylamine hydrochloride) (PAH) having molecular weight of 70,000 Da was purchased from Sigma–Aldrich, and used exclusively for the Pt holder surface modification. PAH solution of concentration equal to 100 ppm was prepared in ionic strength $I = 10^{-2}$ M and pH 4.

The poly(ethylene imine) (PEI), having an average molecular mass of 75,000 Da was purchased from Polysciences, Inc., and was used for mica surface modification. PEI solution of concentrations equal to 2 ppm was prepared in ionic strength 10^{-3} M and pH 4. Working with solutions of very low polyelectrolyte concentrations requires special care to avoid PEI depletion caused by adsorption at cell and glassware walls. This was achieved by conditioning all