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Insight into Nanoparticle Charging Mechanism in Nonpolar Solvents to Control the Formation of Pt Nanoparticle Monolayers by Electrophoretic Deposition

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ABSTRACT: We report on the formation of Pt nanoparticle monolayers by electrophoretic deposition from nonpolar solvents. First, the growth kinetics of Pt nanoparticles prepared by the reverse micelle technique are described in detail. Second, a model of nanoparticle charging in nonpolar media is discussed and methods to control the nanoparticle charging are proposed. Finally, essential parameters of the electrophoretic deposition process to control the deposition of nanoparticle monolayers are discussed and mechanisms of their formation are analyzed.

KEYWORDS: Frank van der Merwe layer-by-layer growth, 3D growth, Pt nanoparticles, nanoparticle monolayers, AOT reverse micelles, nonpolar suspensions, nanoparticle charging, electrophoretic deposition

INTRODUCTION

The preparation of nanoparticle monolayers is a subject of interest in many branches of research with a variety of potential applications in photonics, electronics, medicine, catalysis, and sensing.¹ Various techniques, such as Langmuir–Blodgett, evaporative self-assembly, ligand-mediated assembly or layer-by-layer deposition have been used to obtain nanoparticle monolayers.^{2–6} Recently, electrophoretic deposition using DC or AC electric fields has been employed to assist the monolayer formation.^{7,8} Electrophoretic deposition (EPD) of charged nanoparticles stands out as a technologically facile and highly scalable technique, which allows for the deposition of materials onto semiconductor wafers with large diameters.

EPD of different nanoparticle films from nonpolar solvents has been shown to provide substantial control over the deposition process.^{9–12} In nonpolar solvents, the EPD can be described as the motion of charged nano-objects in an electric field applied across an essentially stationary dielectric suspension. In contrast with more conventional polar solvents, the use of nonpolar solvents: (a) limits the current between the electrodes; (b) reduces the changes in the composition and conductivity of the medium due to the generation of charged species near the electrodes; and (c) suppresses electrochemical reactions at the electrodes. All this translates into great control of EPD on a monolayer scale and allows for the investigation of fundamental interactions between individual nanoparticles. Surfactants bound on nanoobjects not only protect nanoparticles from aggregation but also can induce nanoparticle

charging in nonpolar solvents, which makes the suspensions suitable for the EPD process.^{13–15} One of the frequently used surfactants in colloidal synthesis of nanoparticles is AOT.^{16–18} The preparation of colloidal suspensions of metal nanoparticles stabilized by AOT is a quick and relatively simple technique; these suspensions can be directly employed in electrophoretic deposition process.¹⁹

Platinum (Pt) is a precious metal with catalytic properties that are used in various branches of industry. Pt's ability to dissociate hydrogen is widely employed in catalysis or sensing applications. Hydrogen dissociation on a Pt surface is a bond-breaking process, which was intensively studied experimentally as well as theoretically.^{20,21} Hydrogen molecules are dissociated on the Pt surface and migrate into the Pt subsurface region to occupy interstitial sites.^{22,23} Pt in the form of nanoparticles adsorbs and desorbs hydrogen more effectively than Pt films or bulk materials because of their much larger surface area.²⁴ We have recently demonstrated that Schottky-diode structures consisting of Pt nanoparticles prepared by EPD on various n-type semiconductor substrates show superb sensing properties with one of the best parameters ever reported in the category of Schottky-based sensors.²⁵ These Schottky structures were shown to detect low concentrations of hydrogen in nitrogen down to 1 ppm with short response and recovery times and

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high sensitivity ratio.^{26–30} Moreover, they can be operated in a broad range of voltages down to 100 mV and thus have low power consumption. The superb sensing properties are given by (a) high quality Schottky barriers formed by Pt nanoparticles and the graphite contact, where the disorder induced gap states are suppressed in contrast with conventional contacts prepared by metal evaporation;³¹ (b) high absorption and desorption rates of hydrogen from Pt nanoparticles; and (c) elimination of instability of the Schottky interface caused by significant changes in Pt lattice constant under exposure to hydrogen. The fabrication of a Pt nanoparticle monolayer on a semiconductor substrate is essential to describe in detail the electric charge transport phenomena through the Pt nanoparticle/semiconductor Schottky diodes and to elucidate the sensing mechanism when these structures are exposed to hydrogen. In this Research Article, we report on the deposition of Pt nanoparticle monolayers by electrophoretic deposition from nonpolar solvents. We first describe the growth kinetics of AOT stabilized Pt NPs in isooctane. Then, we apply a theoretical model to describe how these nanoparticles acquire charge and propose methods to control their surface potential. Finally, we identify essential parameters of the EPD process to control the deposition of nanoparticle monolayers and analyze mechanisms of their formation.

MATERIALS AND METHODS

Pt nanoparticles dispersed in isooctane solution were prepared by the reverse micelle technique³² following the procedure described by Chen¹⁹ with moderate modifications. 0.1 M water solution of H_2PtCl_6 $\times$ 6 H_2O and 1 M water solution of hydrazine were prepared, and each solution was poured into a separate flask with 0.6 or 1 M AOT (sodium di-2-ethylhexylsulfosuccinate) solution in isooctane. Equal volumes of these solutions were mixed leading to the reduction of H_2PtCl_6 by hydrazine within the reverse micelles manifested by the solution color change from light yellow to dark brown. As a result, Pt nanoparticles embedded in reverse micelles of AOT dispersed in isooctane were obtained. To allow for the formation of nanoparticle monolayers by electrophoretic deposition, we employed a processing step that removed a portion of the surfactant molecules from the nanoparticle surface. This processing step consisted of a high-speed centrifugation leading to separation of nanoparticles, which formed a pellet on the bottom of Eppendorf tube. The supernatant was removed, and the pellet was redispersed in pure isooctane. All chemicals were purchased from Sigma-Aldrich and were used without further purification. AOT was dried at the temperature of 75 °C for 12 h to remove residual water.

The electrophoretic deposition technique was employed to deposit (sub)monolayers of Pt nanoparticles onto Si substrates. Epi-ready n-type Si wafers were cleaved to the size of 4 × 0.6 cm, cleaned in organic solvents, and mounted in a vertical parallel-plate configuration into a holder whose movement was controlled with stepper motors. The gap between the electrodes was kept at 5 mm. The electrodes were immersed into the suspension, and a DC bias was applied with a Keithley 6517A electrometer for a given period of time, after which the electrodes were extracted from the suspension. In some experiments, the electrodes were extracted in several steps, which allowed us to observe chronology of the monolayer formation. The deposition process was fully computer-controlled using LabView.

The size of the Pt nanoparticles was analyzed with a JEOL JEM 1400 transmission electron microscope (TEM) operating at 120 kV. UV–vis spectroscopy of the suspensions of Pt nanoparticles was conducted on Specord 210 Analytic Jena ultraviolet–visible spectrophotometer; the electrophoretic mobility and hydrodynamic diameter measurements were performed on a Malvern Zetasizer Nano ZS using dynamic light scattering (DLS). The surface topology and homogeneity of the electrophoretically deposited films of nano-

particles were characterized by scanning electron microscopy (SEM) using Hitachi 4800.

RESULTS AND DISCUSSION

The evolution of Pt nanoparticle formation was investigated in detail. The UV–vis spectroscopy of AOT-in-isooctane solution shows a broad absorption in the UV region below 250 nm (Figure 1). The edge of the AOT absorption correlates with the

Figure 1. (a) UV–vis absorption spectra of 0.6 M AOT suspension containing only H_2PtCl_6 precursor and (b, c) 0.6 M AOT suspension with Pt nanoparticles after the addition of hydrazine precursor. This figure shows (I) AOT-related broad absorption below ~ 240 nm, (II) the peak corresponding to Pt precursor at 262 nm, and (III) the broad tailed peak corresponding to the formation of Pt nanoparticles.

AOT concentration in the solution - the absorption edge moves to higher wavelengths with increasing AOT concentration. After the addition of the Pt precursor to the AOT-in-isooctane solution, a clearly observable peak at 262 nm appears. This peak vanishes rapidly when the AOT-precursor solutions (H_2PtCl_6 and hydrazine) are mixed together. This suggests a fast nucleation rate of Pt nanoparticles, which is further supported by the rapid intermicellar exchange rate estimated in the order of 10^5 – 10^7 $\text{M}^{-1} \text{s}^{-1}$ by Fletcher et al.³³

Figure 2 shows (a) the intensity of DLS versus hydrodynamic diameters of reverse micelles in 0.6 M solution of AOT in isooctane; (b, c) and aqueous precursor solutions injected to 0.6 M AOT-in-isooctane solution. When AOT is dissolved in a nonpolar continuous phase and its concentration is above the critical micellar concentration, reverse micelles are formed.³³ These micelles are referred as *dry reverse micelles*, since they contain only a trace amount of water.¹³ These water molecules were bound to the AOT molecules before they were dispersed in the continuous phase. The number of surfactant molecules forming a single dry reverse micelle is called the aggregation number and was found to be 21 for the AOT-isooctane system.¹⁶ In the DLS spectrum in Figure 2a, the peak with the maximum at 0.7 nm corresponds to dry reverse micelles. When water solutions of precursors are introduced into the system, the reverse micelles start to grow. Their size is controlled by the parameter ω_0 , which is given by the water-to-surfactant molar ratio. For $\omega_0 = 5$, the measured hydrodynamic diameters increase to 1.3 nm (Figure 2b, c). Other peaks in the DLS spectra in Figure 2 correspond to larger AOT aggregates. These peaks are suppressed or disappear after the precursor solutions have been mixed.

Figure 2. DLS intensity spectra showing how the size of reverse micelles evolves after the addition of precursor solutions to the system: (a) 0.6 M AOT in isooctane before addition of precursor solutions, (b) 0.1 M $\text{H}_2\text{PtCl}_6 \times 6\text{H}_2\text{O}$ added to the AOT-in-isooctane suspension, and (c) 1 M N_2H_4 added to the AOT-in-isooctane suspension.

corresponding to reverse micelles splits into two peaks. The first peak maintains its position and corresponds to empty reverse micelles (the reverse micelles without Pt nanoparticles), while the second peak gradually shifts to higher diameters with time and corresponds to the growing Pt nanoparticles. From 10 to 35 min, the nanoparticles grow slowly to their final average size of 7 nm. After 35 min, no further change in the spectra is observed. This is in accordance with the time dependent measurement of the UV-vis absorption of the final solution at a fixed wavelength of $\lambda = 300$ nm. In various Pt nanoparticle/surfactant systems, the tail intensity variation above 260 nm is related to the growth of Pt nanoparticles (Figure 1).^{34,35} When the precursors are mixed, the absorption rises with time. During the first 15 min, the nanoparticles form nuclei, which rapidly change their sizes. Between 15 and 35 min, the size of nanoparticles develops slowly. After 35 min, the value of absorption is saturated, and the growth process is terminated (Figure 4). The velocity of nanoparticle growth for lower AOT concentrations (<0.6 M) does not depend on the AOT concentration. Suspensions with higher molarities have significantly slower growth rates because of their much higher viscosity, which slows down the motion of nanoparticles and, thus, their intermicellar exchange rates. TEM images of Pt nanoparticles acquired after several hours from mixing of the precursor suspensions with 0.6 M AOT and 1 M AOT are shown in Figure 5. The average size of Pt nanoparticles prepared in 0.6 M AOT estimated from the TEM measurements was approximately 6.7 nm, which is in accordance with the hydrodynamic diameter measured by DLS after the growth has been finished.

The number of empty reverse micelles gradually decreases with time in favor of micelles with Pt nanoparticles, which grow in volume and acquire more AOT molecules for their stabilization. The DLS peak corresponding to these empty reverse micelles does not change its position (Figure 3), which indicates that the empty reverse micelles do not change their size during nanoparticle growth. The total number of empty reverse micelles per liter n_{rm} can be calculated using the molar concentration of the dissolved surfactant of c_{AOT} and the aggregation number $\bar{n}$:

$$n_{\text{rm}} = \frac{c_{\text{AOT}} N_{\text{A}}}{\bar{n}} \quad (1)$$

where N_{A} is the Avogadro constant. The calculated value of the total number of empty reverse micelles for the 0.6 M AOT suspension was $n_{\text{rm}} = 1.64 \times 10^7 \mu\text{m}^{-3}$. If we compare n_{rm} with the value of the total number of Pt nanoparticles $n_{\text{Pt}} = 9.4 \times 10^1 \mu\text{m}^{-3}$ calculated using the total weight of Pt dissolved in the suspension and assuming the nanoparticle diameter of 6.5 nm, we obtain that the number of empty reverse micelles is $\sim 10^5$ times larger than the number of Pt nanoparticles. All micelles in the suspension collide rapidly and exchange ions and surfactant molecules mutually. This is important for the understanding of nanoparticle charging and, thus, for the understanding of the EPD process itself. Schematic representation of colloid system containing Pt nanoparticles and empty reverse micelles, some of which are charged, is shown in Figure 6.

The ratio of the number of ionized empty reverse micelles n_{ion} to the total number of empty reverse micelles $\chi = n_{\text{ion}}/n_{\text{rm}}$ was calculated from the measured conductivity σ using the relation^{14,15}

The time evolution of the DLS spectra after mixing the precursor solutions is shown in Figure 3. Early after the mixing, the DLS spectrum consists of two peaks. The first peak at 1.3 nm corresponds to reverse micelles with Pt nuclei or Pt precursors, while the second peak at approximately 100 nm corresponds to AOT aggregates. With increasing time, the peak

Figure 3. Time evolution of the DLS intensity spectra of Pt nanoparticles after the mixing of precursor solutions prepared in 0.6 M AOT. Peak 1 corresponds to the empty reverse micelles and Peak 2 to the Pt nanoparticles. The peaks at larger diameters above 100 nm, which vanish with increasing time of the synthesis, correspond to bigger AOT aggregates.

Figure 4. (a) Time evolution of the UV-vis absorption of the suspension of Pt nanoparticles in 0.6 M AOT. The tail intensity variation above 260 nm is related to the growth of Pt nanoparticles. (b) Time evolution of the absorption at a fixed wavelength of $\lambda = 300$ nm shows different slopes: (1) a high slope during the first 15 min, during which the nanoparticle nuclei are formed, and the nanoparticles rapidly change their size; (2) a moderate slope between 15 and 35 min, during which the size of nanoparticles develops slowly; and (3) a saturation after 35 min when the growth process is terminated. These data are in accordance with the time evolution of the DLS spectra in Figure 3.

$$\sigma = \frac{e^2 n_{\text{ion}}}{6\pi\eta r_h} = \frac{e^2 \chi n_{\text{rm}}}{6\pi\eta r_h} \quad (2)$$

where e is the elementary charge, η is the dynamic viscosity of the solution and r_h is the hydrodynamic radius of empty reverse micelle. The measured conductivity for as prepared 0.6 M AOT suspension was $\sigma = 2.7 \mu\text{S/m}$ (see Table 1). The calculated value of χ was used for the calculation of the Debye length κ^{-1} , which is related to the thickness of a double layer formed by adsorbed ionized empty reverse micelles

$$\kappa^{-1} = \frac{1}{\sqrt{4\pi\lambda_B \chi n_{\text{rm}}}} \quad (3)$$

Figure 5. TEM image of Pt nanoparticles prepared in (a) 0.6 M AOT and (b) 1 M AOT.

where λ_B is the Bjerrum length which describes the distance of two objects of charge Z in media of relative permittivity ϵ_r , at which the electrostatic interaction energy is balanced by the thermal energy $k_B T$

$$\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad (4)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and ϵ_0 is the permittivity of vacuum. In isooctane, the value of Bjerrum length is $\lambda_B = 28.7$ nm, which is 2 orders of magnitude higher than for water (0.7 nm). Typical values of the Debye length κ^{-1} for the as prepared 0.6 M AOT suspensions calculated from the measured conductivities are $\kappa^{-1} \approx 50$ nm.

To understand how the removal of the charged empty reverse micelles during centrifugation affects the deposition process, the surface potential of a nanoparticle $\Psi(R)$, where R is the distance from the center to the surface of the nanoparticle, was calculated using equation derived by Cao.¹³ To estimate $\Psi(R)$ of a single Pt nanoparticle, a colloid system containing Pt nanoparticles together with empty reverse

Figure 6. Colloid suspension contains Pt nanoparticles in reverse micelles (NP) and empty reverse micelles, some of which are charged. The Pt nanoparticles in reverse micelles acquire charge due to the adsorption of the excess of positively (RM+, blue) or negatively charged reverse micelles (RM-, red), which leads to the formation of a charged layer around the Pt nanoparticle similar to double layer.

Table 1. Parameters of the 0.6M AOT Suspension before and after the Centrifugation^a

centrifugation status	σ [$\mu\text{S}/\text{m}$]	χ	κ^{-1} [μm]	ψ_R	$\psi(R)$ [mV]
as prepared	2.7	1.26×10^{-4}	0.05	1.51	38.7
supernatant	2.1	1.05×10^{-4}	0.06	1.63	41.7
pellet	0.2	1.07×10^{-4}	0.18	0.74	18.9

^aThe measured values of conductivity σ , the ratio of the number of ionized empty reverse micelles to the number of all micelles χ , inverse Debye length κ^{-1} , dimensionless surface potential ψ_R and the surface potential $\psi(R) = 25.6\psi_R$. For the calculations, we assumed that 96.5% of AOT empty reverse micelles remained in the supernatant and that 99% of nanoparticles were centrifuged to the pellet.

The total average charge carried by a single nanoparticle Z is then a difference of positively and negatively charged empty reverse micelles adsorbed on this nanoparticle (assuming that the empty reverse micelles carry the charge of $1e^{15}$ and the number of Pt nanoparticles per unit volume is n_{Pt}):

$$Z = \frac{n_+^{*A} - n_-^{*A}}{n_{\text{Pt}}} \quad (7)$$

Using eqs 5a, 5b, 6a, and 6b, eq 7 can be rewritten as

$$Z = \left(\frac{K_+(n_+^*)^2}{1 + K_+n_+^*} - \frac{K_-(n_-^*)^2}{1 + K_-n_-^*} \right) \frac{1}{n_{\text{Pt}}} \quad (8)$$

Around the charged nanoparticle, in equilibrium, the charged empty reverse micelles are gathered due to balancing electrostatic forces and thermal diffusion. Therefore, the concentration of ionized empty reverse micelles n_+^* and n_-^* depends on the distance from the center to the surface of spherical nanoparticle R . The concentration of ionized empty reverse micelles n_+^* and n_-^* in terms of the bulk concentration n_+ and n_- is given by the Boltzmann distribution

$$n_+^* = n_+ \exp\left(-\frac{e\psi(R)}{k_B T}\right) = n_+ \exp(-\psi_R) \quad (9a)$$

$$n_-^* = n_- \exp\left(\frac{e\psi(R)}{k_B T}\right) = n_- \exp(\psi_R) \quad (9b)$$

where

$$\psi_R = \frac{e\psi(R)}{k_B T} \quad (10)$$

is the dimensionless particle potential, n_+ and n_- are the bulk concentrations of positively and negatively charged empty micelles, respectively, and the ratio between the thermal energy and elementary charge is $k_B T/e = 25.6$ mV. Because of the practical absence of free ions in nonpolar solvents, we can assume that $n_+ = n_-$, and $n_+ + n_- = n_{\text{ion}}$. Then the fraction of positively (or negatively) ionized empty reverse micelles χ_{ion} can be written as

$$\chi_{\text{ion}} = \frac{n_+}{n_{\text{ion}}} = \frac{n_-}{n_{\text{ion}}} \quad (11)$$

It is obvious that $\chi = 2\chi_{\text{ion}}$. The average charge carried by a single nanoparticle can be then expressed using eqs 8, 9a, 9b, 10, and 11

$$Z = \left(\frac{K_+ n_{\text{ion}}^2}{e^{2\psi_R} + K_+ \chi_{\text{ion}} n_{\text{ion}} e^{\psi_R}} - \frac{K_- n_{\text{ion}}^2}{e^{-2\psi_R} + K_- \chi_{\text{ion}} n_{\text{ion}} e^{-\psi_R}} \right) \frac{\chi_{\text{ion}}^2}{n_{\text{Pt}}} \quad (12)$$

If a spherical nanoparticle is assumed, the electric potential ψ_R is obtained from nonlinear Poisson–Boltzmann equation

$$\nabla^2 \psi_R = \kappa^2 \sinh \psi_R \quad (13)$$

with the approximate solution for uniformly charged sphere based on Sader³⁶

micelles was assumed. Some of these empty reverse micelles are charged and these charged reverse micelles gather around the Pt nanoparticles. The volume concentration of positively (or negatively) charged micelles around the nanoparticles is n_+^* (or n_-^*), out of which n_+^{*A} (or n_-^{*A}) are adsorbed on these nanoparticles and n_+^{*F} (or n_-^{*F}) are free. Assuming that the number of charged empty reverse micelles is small and that majority of them are adsorbed on the nanoparticle surface, the equilibrium between adsorption and desorption can be described as follows:

$$\frac{n_+^{*A}}{n_+^*} = K_+ n_+^{*F} \quad (5a)$$

$$\frac{n_-^{*A}}{n_-^*} = K_- n_-^{*F} \quad (5b)$$

where K_+ and K_- are the correlation coefficients of the equations above. The total number of charged empty reverse micelles is the sum of adsorbed and free ones:

$$n_+^* = n_+^{*F} + n_+^{*A} \quad (6a)$$

$$n_-^* = n_-^{*F} + n_-^{*A} \quad (6b)$$

$$\frac{Z\lambda_B}{R} = \psi_R(1 + \kappa R) - \frac{\left(2 \sinh\left(\frac{\psi_R}{2}\right) - \psi_R\right)^2 (\kappa R)^2}{4 \tanh\left(\frac{\psi_R}{4}\right) - \left(2 \sinh\left(\frac{\psi_R}{2}\right) - \psi_R\right) \kappa R} \quad (14)$$

with the relative error predicted to be less than 1% over the whole range of κR for surface potential not exceeding 200 mV.³⁶ The combination of the approximate solution (eq 13) with eq 11 gives the final relation for the surface potential $\Psi(R)$ for a single nanoparticle:

$$\psi_R = \left(\frac{K_+ n_{rm}^2}{e^{2\psi_R} + K_+ \chi_{ion} n_{rm} e^{\psi_R}} - \frac{K_- n_{rm}^2}{e^{-2\psi_R} + K_- \chi_{ion} n_{rm} e^{-\psi_R}} \right) \frac{\chi_{ion}^2 \lambda_B}{n_{pt} R (1 + \kappa R)} + \frac{\left(2 \sinh\left(\frac{\psi_R}{2}\right) - \psi_R\right)^2 (\kappa R)^2}{\left[4 \tanh\left(\frac{\psi_R}{4}\right) - \left(2 \sinh\left(\frac{\psi_R}{2}\right) - \psi_R\right) \kappa R\right] (1 + \kappa R)} \quad (15)$$

The electric surface potential Ψ_R for given parameters was found numerically using Matlab. The following values of correlation coefficients K_+ and K_- were chosen: $K_+ = 10^2 \mu\text{m}^3$ and $K_- = 10^{-5} \mu\text{m}^3$ in accordance with the previously reported data for the AOT-dodecane system.¹³ For the calculations, we assumed a suspension of Pt nanoparticles in 0.6 M AOT, where 96.5% of the empty reverse micelles were removed with the supernatant removal after the centrifugation and that 99% of the Pt nanoparticles were centrifuged into a pellet.

Table 1 summarizes parameters of the 0.6 M AOT suspension before and after the centrifugation. We can see that the conductivity calculated from the eq 2 is the lowest for the pellet dissolved in pure isooctane. The reason is that majority of ionized empty reverse micelles were removed after the centrifugation cycle by the removal of the supernatant. The values of χ shown in Table 1 are nearly identical, which indicates that the equilibrium between the ionized empty reverse micelles and uncharged empty reverse micelles is maintained after the centrifugation. The suspension of Pt nanoparticles contains $n_{pt} = 9.4 \times 10^1 \mu\text{m}^{-3}$ Pt nanoparticles and $n_{rm} = 1.64 \times 10^7 \mu\text{m}^{-3}$ empty reverse micelles, which means that there are approximately seven positively and seven negatively charged reverse micelles per one Pt nanoparticle ($\chi = 1.26^{-4} \times 10^{-4}$).

The dependence of the calculated surface potential $\Psi(R)$ on the concentration of empty reverse micelles for our suspension is shown in Figure 7. This figure shows $\Psi(R)$ for two suspensions: the as prepared suspension and the supernatant after one-cycle of centrifugation. We can see that the calculated surface potentials for both suspensions have maximum for a certain concentration of empty reverse micelles. This maximum corresponds to the state when the surface of the Pt nanoparticles is saturated with charged empty reverse micelles and thus optimal conditions for nanoparticle charging are reached. The surface potential $\Psi(R)$ decreases for lower values of the concentration of empty reverse micelles because there is less charged empty reverse micelles to adsorb on the nanoparticle surface. This behavior was also experimentally observed; after one-cycle centrifugation, where the amount of

Figure 7. Dependence of the calculated surface potential Ψ_R on the total number of empty reverse micelles n_{rm} for the suspension before centrifugation and the supernatant.

empty reverse micelles in suspension is significantly decreased, the measured value of ζ -potential decreased. The lowering of the surface potential $\Psi(R)$ in the opposite case, that is, when the concentration of the empty reverse micelles is higher, corresponds to the screening of nanoparticle surface by oppositely charged empty reverse micelles in the charged layer comprised of ionized empty reverse micelles. In the supernatant, only a small fraction of Pt nanoparticles exist, that is, saturation of the nanoparticle surface occurs at lower concentrations of empty reverse micelles.

First, the as prepared, noncentrifuged, suspensions of Pt nanoparticles were deposited. Deposition of these suspensions generally results in the formation of 3D aggregates (Figure 8a). These 3D aggregates were formed during the deposition process, since the DLS spectra before and after EPD showed only the peaks corresponding to individual Pt nanoparticles and empty reverse micelles. When Pt nanoparticles are immobile on the surface and their electrostatic repulsion is low, newly arriving Pt nanoparticles are not allowed to find a position with the lowest energy on the substrate surface and form a 3D aggregate. In suspensions with a large concentration of empty reverse micelles, the surface mobility of Pt nanoparticles may be also decreased by the formation of a compact layer of empty reverse micelles. The deposition of aggregates could be assigned to the distortion of the layer of charged empty reverse micelles around the nanoparticle in the electric field similar to the mechanism, proposed by Sarkar for the aggregation of particles in the proximity of electrodes in polar solvents.³⁷ When the concentration of the charged empty reverse micelles in the suspension is high, the layer of charged empty micelles created around the Pt nanoparticles is thin. When the nanoparticles move in the electric field, the fluid dynamics and the applied electric field distort the charged layer envelope, thinner in the front and thicker in the rear. Then in the proximity of the electrode, the next incoming nanoparticle can interact with the tail of the charged layer of the nanoparticle closer to the electrode and deposit selectively on the top of the preceding nanoparticle, creating a 3D deposit (Figure 8a). Moreover, a large number of charged empty reverse micelles are deposited on the substrate surface. These empty reverse

Figure 8. SEM images demonstrate the importance of the surfactant removal and of the parameters of the EPD process for the monolayer formation on the negative electrode: (a) 3D growth was observed when as-prepared suspensions with a large amount of the surfactant are deposited, (b) almost a full monolayer was deposited when 97.4% of the supernatant was removed from the suspension, and a low electric field of 5 V/cm was applied, (c) 3D growth due to field-induced aggregation was observed when 97.4% of the supernatant was removed and a high electric field of 200 V/cm was applied, and (d) large aggregates were formed in the suspension and deposited onto the substrate when more than 98% of supernatant was removed regardless the applied electric field.

micelles also hinder the nanoparticle arrangement into 2D layers. To observe the deposited layers by SEM, the empty reverse micelles and the AOT molecules that are weakly bound to the Pt nanoparticles had to be washed in a polar solvent.

To avoid the 3D layer formation and to obtain well-defined 2D layers without the excess of the surfactant, we applied a one-cycle or two-cycle centrifugation procedure during which a different amount of the supernatant was removed, and the pellet was redispersed in pure isooctane. Through this procedure, a portion of the charged empty reverse micelles was removed from the suspension together with the supernatant. As a consequence, the charge carried by the Pt nanoparticles was altered and so was the mobility. Figure 9 shows how the ζ -potential of the Pt nanoparticles changed with the amount of the supernatant removed in the centrifugation process. The ζ -potential was calculated by Hückel equation since the ratio of the particle radius and Debye length is small ($R\kappa \approx 0.1$), that is, the Debye length κ^{-1} is large when compared to the radius of Pt nanoparticle R . Before centrifugation, the Pt nanoparticles had a positive charge and deposited on the negative electrode. After the one-cycle centrifugation during which approximately 85% of the supernatant was removed, the Pt nanoparticles gained both positive and negative charges and deposited on both electrodes. After the two-cycle centrifugation during which approximately 97% of the surfactant was removed, the Pt nanoparticles gained a negative charge and deposited preferentially on the positive electrode. This suggests that the original charge of Pt nanoparticles is negative. These conditions proved ideal for the deposition of a Pt nanoparticle monolayer (Figure 8b). When more than 98% of the supernatant was removed, the remaining amount of AOT became insufficient for nanoparticle stabilization. Subsequently, the Pt nanoparticles started to aggregate in the suspension. Peaks corresponding to large

Figure 9. ζ -Potential distribution before and after centrifugation. Before centrifugation, the ζ -potential is positive. With increasing number of centrifugation cycles, that is, the amount of removed empty reverse micelles, the value of ζ -potential decreases and changes from positive to negative.

aggregates appeared in the DLS spectra, while the peaks corresponding to empty reverse micelles and individual nanoparticles disappeared. Large aggregates were found on the substrate after EPD (Figure 8d).

Another prerequisite for the controlled deposition of a monolayer of Pt nanoparticles is the application of relatively low electric fields. Higher electric fields allow for higher substrate coverage, but initiate field-induced aggregation of nanoparticles, which results in the deposition of large aggregates on the substrate (see Figure 8c). A chronology of

Figure 10. Chronological growth of a monolayer of Pt nanoparticles deposited onto Si substrate from the 0.6 M AOT suspension at 5 V/cm after the two-cycle centrifugation. The deposition times were (a) 10, (b) 30, (c) 60, (d) 90 min. When the first monolayer is almost complete (c), the growth of islands of the second nanoparticle layer is observed (d).

the development of a monolayer of Pt nanoparticles with the applied electric field of 5 V/cm is shown in Figure 10. The hydrodynamic radius of Pt nanoparticles measured by DLS was in accordance with the size of the deposited nanoparticles, as observed by SEM. This suggests that the Pt nanoparticles were dispersed as individual nanoparticles in the suspension and that during EPD they also moved in the electric field as individual nanoparticles toward the electrode. After 10 min (Figure 10a), single nanoparticles, dimers, or small islands were observed on the substrate. As the deposition time increases, the small islands grow (Figure 10b) until majority of voids in the monolayer are filled (Figure 10c). When the first monolayer is almost complete, the growth of islands of the second nanoparticle layer is observed (Figure 10d). The process of filling of this second layer is similar to the formation of the first layer; smaller 2D islands are formed on the first monolayer, and they grow with increasing time. This behavior is characteristic for the layer-by-layer or Frank-van der Merwe growth mechanism. The analogy between the EPD process and the growth of epitaxial films by molecular beam epitaxy can be drawn.^{38,39} In the nucleation phase, the nanoparticles are highly mobile. The interaction between individual nanoparticles leads to the formation of critical 2D nuclei with substantially lower mobility. Further development of the nuclei into larger 2D islands is diffusion limited; the nanoparticles are either deposited directly in the proximity of the existing islands, or more likely, the nanoparticles are deposited on the substrate randomly, but they undergo a lateral motion and find a position with the lowest energy at the island edge. Even though the deposition of almost a full monolayer was achieved (Figure 10c), the nanoparticle film lacked a long-range ordering. This lack of long-range ordering was induced by a relatively large degree of polydispersity in size and shape of the Pt nanoparticles synthesized within AOT reverse micelles at low AOT concentrations.

To estimate the average time it takes for a single nanoparticle to travel along the gap between the electrodes, the electrophoretic mobility was measured. The electrophoretic mobility is defined as

$$\mu_E = \frac{v}{E} \quad (16)$$

where v is the drift velocity of a dispersed nanoparticle and E is the electric field strength. The electrophoretic mobility of Pt nanoparticles in the 0.6 M suspension measured after two centrifugation cycles was $0.05 \mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}$. Let us assume the parallel plate configuration with a spatially and temporally constant electric field between the electrodes in a 5 mm distance. In the electric field of 5 V/cm, the negatively charged nanoparticle drift velocity is $0.25 \mu\text{m}/\text{s}$, and the nanoparticle traverses the gap between the electrodes in 5.5 h. Since the longest deposition time was 90 min, only a part of Pt nanoparticles reaches the electrode within the deposition time. Moreover, only a small fraction of the nanoparticles that reach the electrode is incorporated into the growing nanoparticle layer. The remaining nanoparticles stay in the suspension when the electrodes are pulled out. The density of nanoparticles that form a monolayer on the electrode is approximately $2.2 \times 10^{12} \text{ cm}^{-2}$ (assuming the full monolayer). The concentration of Pt nanoparticles in the 0.6 M suspension is approximately $3.4 \times 10^{14} \text{ cm}^{-3}$. It follows that the deposition of a monolayer of Pt nanoparticles consumes only $\sim 0.6\%$ of Pt nanoparticles in the suspension. It means that only a small fraction of Pt nanoparticles is deposited from the suspension and, as a consequence, the suspension can be used multiple times to deposit a monolayer. This fact was proved experimentally—repetitive EPD with fixed parameters from the same suspension led to the same results.

To obtain a higher degree of ordering, we prepared Pt nanoparticles in 1 M AOT with a spherical shape (Figure 5). With the same centrifugation and deposition parameters

Figure 11. Chronological growth of a monolayer of Pt nanoparticles with uniform shapes deposited onto Si substrate from the 1 M AOT suspension at 5 V/cm after the two-cycle centrifugation. The deposition times were (a) 10, (b) 40, (c) 60, (d) 90 min.

(96.5% of the supernatant removed, the applied electric field of 5 V/cm, and various deposition times), we deposited monolayers with domains of hexagonally packed nanoparticles. The hexagonal packing is the ideal packing of spherical nanoparticles and has been demonstrated on various systems.^{10,38–41} Figure 5 and Figure 12 shows, that the nanoparticle shape is responsible for the quality of packing. The spherical nanoparticles of spherical shape obtained by 1 M synthesis easily incorporate into the ordered array than in comparison with the 0.6 M Pt nanoparticles with nonuniform shape and high polydispersity. The growth mechanism is similar to the growth mechanism of the film deposited from the 0.6 M AOT suspension except for the fact that isolated nanoparticles are almost absent during the formation of a monolayer (Figure 11). The nanoparticle adhesion to the substrate is weak, which leaves the nanoparticle enough freedom to diffuse to the most energetically favorable position in the monolayer. With increasing time, the nanoparticle islands show tendency to connect by forming thin chains. Formation of this network is probably driven by electric field gradients coming from the geometric structure of Pt islands.

Figure 12 illustrates that the monolayer is composed of several hexagonally packed domains which merged during the monolayer formation. The long-range periodicity is perturbed by occasional presence of larger Pt nanoparticles. These larger nanoparticles are present in the center of the domains while smaller and more mobile nanoparticles assemble around them.

CONCLUSIONS

AOT-stabilized Pt nanoparticles were prepared by the reverse micelle technique in isooctane and their growth kinetics was investigated in detail. Optical measurements using dynamic light scattering technique showed that the empty reverse micelles, which do not contain Pt nanoparticles, coexist with the AOT-stabilized Pt nanoparticles in the suspension. Some of

Figure 12. Highly magnified SEM images of Pt nanoparticles prepared in (a) 0.6 M AOT, and (b) 1 M AOT. For 1 M AOT a long-range ordering within hexagonally packed domains, outlined in white, is perturbed by voids and irregularly sized nanoparticles.

the empty reverse micelles are charged and these charged empty reverse micelles are responsible for the charging of Pt nanoparticles in the solution. The charge carried by Pt

nanoparticles can be controlled by varying the amount of empty reverse micelles in the solution. Control of the amount of empty reverse micelles was achieved using the one-cycle or two-cycle centrifugation procedure, during which a certain amount of supernatant containing empty reverse micelles was removed. The measured data of ξ -potential were in accordance with the proposed theoretical model of nanoparticle charging. Electrophoretic deposition of the suspensions with controlled surface potential of nanoparticles allowed us to identify the mechanisms of their incorporation into 2D or 3D films. Electrophoretic deposition with low voltages allowed for the growth of nearly complete monolayers with the domains of hexagonally packed nanoparticles on Si substrates.

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Notes

The authors declare no competing financial interest.

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