# Packing Density Parameters of Palladium Nanoparticle Monolayers Fabricated *via* Spin-Coating Electrostatic Self-Assembly

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Spin-coating electrostatic self-assembly (SCESA) is utilized to fabricate a single layer of carboxylic-acid-coated Pd nanoparticles (NPs) (D ≈ 5 nm) on an oppositely charged surface. The packing density of a NP monolayer formed on a rotating solid substrate (3000 rpm) was examined with regards to various parameters, including the particle concentration, the pH, and the ionic strength of the solution. Initially, the packing density grew exponentially with increases in the particle concentration, up to a maximum value (of $8.4 \times 10^{11}/cm^2$) at 1.2 wt%. The packing density was also found to increase drastically as the pH decreased and the ionic strength of the solution increased; these trends can be attributed to a reduction in the interparticle repulsions among the NPs in the solution and on the substrate. The best result of this study was achieved in a 1.2 wt% solution at pH 8; under these conditions, an NP monolayer with the highest density (namely, $1.6 \times 10^{12}/cm^2$) was obtained.

**Key Words :** Pd nanoparticle, Monolayer, Packing density, Spin-coating electrostatic self-assembly

## Introduction

The precise positioning of functionally distinct nanoparticles (*NPs*) during the integration of organic and inorganic materials into hybrid optoelectronic structures appears to be an essential prerequisite for the realization of high-performance electronic and optical devices.[1-3] Numerous attempts have been made to fabricate uniform 2D *NP* monolayers by using diverse techniques such as self-assembly,[4,5] electrophoretic deposition,[6] the Langmuir-Blodgett method,[7] electrostatic interactions,[8] and DNA hybridization.[9] In general, immobilization by means of solution-dip self-assembly is accomplished via surface modification of a substrate with functional groups (*e.g.*, thiol, pyridyl, amino, and carboxyl groups) that are used to attract *NPs* onto various oxide surfaces; for instance, the electrostatic attraction between oppositely charged entities has also been exploited for the immobilization of negatively charged gold NPs on a poly(ethyleneimine)-modified substrate.[10] To date, however, there has been no recognizable breakthrough in the preparation of large laterally extended *NP* monolayers, which are necessary for the development of high-tech nanoparticle-based memory[11] and light-emitting diode (LED) devices.[1]

Over the last several years, spin coating electrostatic self-assembly (*SCESA*) method[12,13] has been successfully applied as a highly efficient fabrication technique for a variety of well-ordered heterostructured multilayer thin films on a solid substrates. Moreover, we demonstrated that this method could be well adopted for the immobilization of acid-functionalized NPs (*i.e.* CdSe, $D \approx 6$ nm) in a single layer on an amino-terminated self-assembled monolayer.[14] The morphology of this spin-assembled *NP* monolayer (*i.e.*, *surface roughness and domain feature*), was revealed by means of atomic force microscopy (AFM).

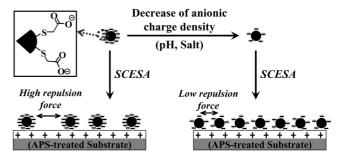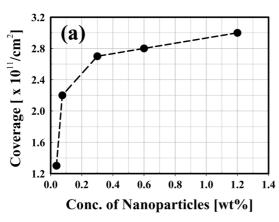As described previously,[14] the NP density of the mono-



**Figure 1**. Pictogram of the increasing NP density, which results from the minimization of the repulsion forces between NPs adsorbed on a substrate.

layer was found to reach an upper limit (namely, $3.0 \times 10^{11}/cm^2$) despite the increase in the particle concentration (see also the updated results in Figure 2) and the multiple coating steps. The main source of this density limit was the repulsion forces among the identically charged particles adsorbed on the substrate. Thus, in the present work we examined control parameters that could minimize the repulsion forces among nanoparticles in solution and on the substrate, to ultimately increase the density of the monolayer, as revealed in the pictogram of Figure 1. The two parameters, namely the pH value and the salt concentration in the NP solution were mainly investigated with regards to the enhancement of the particle density, which was evaluated using field emission scanning electron microscopy (FE-SEM).

## Results and Discussion

Here, the density of the NP monolayers deposited on a silicon substrate by SCESA was investigated as a function of the particle concentration, the pH value, and the ionic strength. The density was estimated from FE-SEM monolayer images as the number of the NPs per unit area.
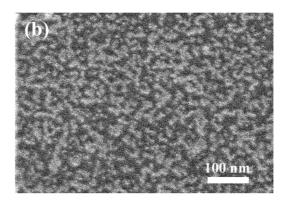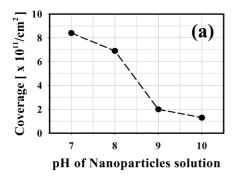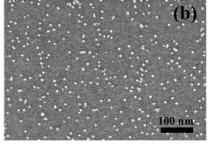
**Figure 2**. a) Plot of the NP density versus the concentration (ranging from 0.04 to 1.20 wt%). b) FE-SEM images of the NP monolayer obtained at 1.20 wt%.
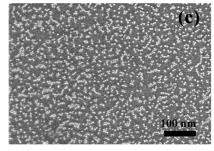


**Figure 3**. a) Plot of the NP density versus the pH value (varied from 7.0 to 10.0). b) and c) FE-SEM images of the NP monolayers obtained at pH 10.0 ($1.3 \times 10^{11}$/cm$^2$, b) and 7 ($8.4 \times 10^{11}$/cm$^2$, c).

Firstly, the influence of the concentration on the density of the NP monolayer self-assembled on an amino-functionalized silicon surface was investigated by varying the concentration of mecaptoacetic-acid-modified Pd NPs (MAA_Pd NP, pH = 9) from 0.04 to 1.20 wt% (see Figure 2). The NP density increased very rapidly up to a particle concentration of 0.30 wt% and then continued to augment exponentially, thereby reaching to a maximal value (of $3.0 \times 10^{11}$/cm$^2$) at 1.2 wt% (see Figure 2a). The formation of small NP aggregate domains at this concentration can be observed from the FE-SEM images, in which the white spots represent the NPs (Figure 2b).

Here, we hypothesized that the repulsion forces between the charged NPs in the monolayer would be the main cause for the NP density limit, which could not be exceeded despite the concentration growth. The first approach to minimize the repulsion forces was to reduce the population of the free carboxylic anions on the NP surface by lowering the pH. As expected, the density of the spin-assembled NP monolayer increased significantly when the pH was lowed from 10.0 to 7.0 in a 0.1 wt% solution, as can be seen in Figure 3a, which shows a plot of the number of NPs/cm$^2$ versus pH. Lowering the pH value from 10.0 to 7.0 caused a sevenfold increase in the density (from $1.3 \times 10^{11}$ to $8.4 \times 10^{11}$/cm$^2$), which was confirmed using FE-SEM studies (see Figures 3b and 3c). Further lowering of the pH was not possible, because the NPs became unstable in the buffered

solution, and precipitated as a result of aggregate formation.

Another alternative way to minimize the interparticle electrostatic repulsion would be to increase the ionic strength in the solution, which would introduce salt ions into solution that would screen the Coulombic interactions between NPs with the identical surface charges.[15] It was found that the particle density strongly increased (from $0.2 \times 10^{12}$ to $1.0 \times 10^{12}$/cm$^2$, when the ionic strength was raised (to 0.1 M NaCl) in a 0.1 wt% NP solution (pH = 9, data not shown here). This was the highest concentration at which the homogeneity of the NP solution was stably preserved during
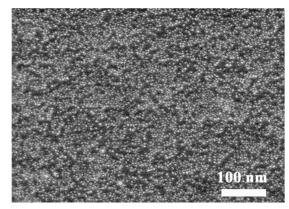


**Figure 4**. FE-SEM image of a NP monolayer spin-assembled from a 1.2 wt% MAA-Pd solution at pH 8.

the preparation procedure.

After all these efforts to optimize the preparation conditions, we finally obtained an NP monolayer with the maximum density observed until now (namely, $1.6 \times 10^{12}/cm^2$); this monolayer was obtained at a concentration of 1.2 wt% (at pH 8) by means of SCESA (see Figure 4). As described previously,[14] the AFM image of a spin-assembled NP monolayer highlights the excellent quality of that monolayer, and reveals a very smooth surface over an area of 500 × 500 $nm^2$ with a root-mean-square (rms) roughness of 0.390 nm.

## Conclusion

The optimal conditions for fabricating a MAA_Pd nanoparticle monolayer on a silicon substrate (D ≈ 5 nm) - with a particle density of at least $4.5 \times 10^{12}/cm^2$ – were examined by varying the particle concentration, pH, and ionic strength. Such a high particle density is known to be essential for the realization of high-performance memory devices. The NP density increased exponentially with increasing the particle concentration up to a maximum value (*i.e.*, $0.84 \times 10^{12}/cm^2$) at a concentration of 1.2 wt%.

The preparation conditions for obtaining a higher NP density were improved by minimizing the interparticle repulsions as a result of lowering the pH and increasing the ionic strength in the solution. A sevenfold increase in the NP density (from $1.3 \times 10^{11}$ to $8.4 \times 10^{11}/cm^2$) was observed when the pH value was lowered from 10.0 to 7.0. Moreover, the particle density also increased (from $0.2 \times 10^{12}$ to. $1.0 \times 10^{12}/cm^2$), when the ionic strength was raised by varying the NaCl concentration to 0.1 M (this was found to be the maximum concentration, at which a homogeneous NP dispersion could be obtained). The best NP-monolayer density obtained in our study, was $1.6 \times 10^{12}/cm^2$; this density was achieved via SCESA in a 1.2 wt% solution at pH 8. Another new concept for minimizing the interparticle repulsions via the surface modification of the NPs with a mixed solution of ionically and nonionically tailed surfactants is now under investigation.

## Experimental Part

**Materials.** Silicon wafers (n-type, 100) were obtained from Siltron Inc. Korea, and cut into 20 mm × 20 mm squares. Mercaptoacetic acid (97%) and tris(hydroxymethyl)aminomethane (99.8%) were obtained from Aldrich and used without further purification. 3-Aminopropylmethyldiethoxysilane (technical grade) was purchased from Degussa and distilled before the use. Toluene was distilled from sodium, and all the other solvents used in this work were HPLC quality. Ultrapure water, which was employed for all experiments and cleaning steps, was obtained by using an ion-exchange and filtration unit (Milli-Q, Millipore GmbH) to give a resistivity above 18.0 MΩ·cm.

**Surface Modification of the MAA_Pd NPs.** The substitution of trioctylphosphine (TOP) by MAA on the surface of the Pd NPs (which were synthesized by using the method proposed by Hyeon *et al.*[16]) was performed based on Nie's report.[17]

Briefly, TOP-coated Pd nanoparticles (10 mg) were dispersed in toluene (10 mL); this dispersion was heated to 110 °C. Subsequently, MAA (20 M, 1.4 mL) was added with a drop speed of 1 mL/h, and the mixture was stirred for 3 hours (at 110 °C). The MAA-substituted Pd nanoparticles were then isolated by centrifugation (at 4000 rpm), and washed five times with chloroform (10 mL) to remove the remaining MAA and TOP. Then, the MAA_Pd NPs were dispersed in a tris(hydroxymethyl)aminomethane (TRIS) buffer (0.1 M), the pH of which has been adjusted to 7-10. This NPs solution was filtered - through 0.2-$\mu$m-pore filter- before use.

**Aminopropylsilanized Silicon Substrate.** Aminopropylsilanized (APS) silicon substrates were used for the adsorption experiments. These substrates were cleaned by ultrasonication in a mixture of $H_2SO_4/H_2O_2$ (7:3), heated in a mixture of $H_2O/H_2O_2/NH_3$ (5:1:1) (at 80 °C for 1 h), and then thoroughly washed with ultrapure water. After that, they were sequentially immersed (for 2 minutes) in pure methanol, a methanol/toluene (1:1) mixture, and pure toluene. Then, the silicon substrates were directly transferred to a 5% solution of APS in toluene-in which they were kept for 15 hours under a dry-nitrogen atmosphere- and dipped for 2 minutes in a sequence of solvents including pure toluene, a toluene/methanol (1:1) mixture, methanol, and ultrapure water in an ultrasonicator. Finally, the substrates were immersed in a 0.1 N HCl solution to achieve the protonation of the amino groups.[18]

**Preparation of MAA-Pd Monolayers Based on the Spin-Coating Electrostatic Self-Assembly Method.** The preparation of MAA-CdSe monolayers by means of the *SCESA* method is described in literature.[14] Firstly, MAA-Pd (*ca.* 0.5 mL) in TRIS buffer solution (≈ 1 mg/mL, pH = 9) were poured onto a substrate, which was then spun (at a speed of 3000 rpm) for 20 s. Then, deionized water (1 mL of) was added, and the spinning procedure was repeated to remove the weakly bound MAA-Pd nanoparticles from the surface. The washing steps were repeated three times.

**Measurement.** FE-SEM images were obtained using an S-4500 (HITACHI).

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