# MONOLAYERS OF PLATINUM NANOPARTICLES PREPARED BY DIP-COATING

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## Abstract

Platinum is a transition metal known for its catalytic properties, which are further enhanced when employed in a nanoparticle form. We have recently shown that a monolayer of Pt nanoparticles deposited on semiconductor substrates forms high quality Schottky diodes, which were used in sensitive hydrogen sensors with a detection limit of 1 ppm of $H_2$ in $N_2$. Preparation of ordered monolayers of Pt nanoparticles is essential for the understanding of the behaviour of such an interface. To obtain a hexagonal closed-packed nanoparticle array, we prepared Pt nanoparticles stabilized by oleylamine and oleic acid with a narrow size distribution and uniform shapes. A monolayer prepared by dip-coating of Si substrate in the suspension containing Pt nanoparticles showed hexagonal arrangement within separate domains with the surface coverage up to 90%. The increase of the surface coverage with increasing withdrawal speed of the dip-coating process was observed.

**Keywords:** Pt nanoparticles, oleylamine, dip coating, self-assembly

## 1.    INTRODUCTION

Pt is a transition metal well-known for its superb catalytic properties. In the nanoparticle form, these catalytic properties are further enhanced by their large active surface. We have recently developed hydrogen sensors based on the graphite/semiconductor Schottky diodes, where the sensing properties were achieved by the deposition of a Pt nanoparticle monolayer between the semiconductor and graphite [1-6]. The principle of this sensor is as follows: hydrogen molecules are dissociated into single atoms which adsorb on the metal/semiconductor interface and lower the Schottky barrier. This systematic reduction of the Schottky barrier causes the increase of current, which is thus related to the hydrogen concentration. The variation of the Schottky barrier height is generally described by two mechanisms: (a) a fraction of single hydrogen atoms is stored in Pt nanoparticles and forms Pt hydride, which causes lowering of the work function of Pt nanoparticles resulting in the decrease of the Schottky barrier height [7]; (b) a fraction of hydrogen atoms is adsorbed on the semiconductor surface - hydrogen atoms are polarized and create a dipole layer which reduces the Schottky barrier [8].

Until now we prepared the layers of Pt nanoparticles by electrophoretic deposition from their nonpolar colloid suspension stabilized by AOT surfactant. AOT is suitable for the electrophoretic deposition because it induces particle charging [9], which helps nanoparticles to move in the applied electric field during the electrophoretic deposition process. Although we have prepared monolayers with a high coverage, these monolayers lacked long-range ordering because of the size and shape polydispersity of the AOT-based Pt nanoparticles. To describe this system in detail, it is essential to prepare monolayers with a high degree of arrangement. Pt nanoparticles synthetized in the presence of oleylamine and oleic acid show a narrow distribution of sizes and uniform shapes [10]. We prepared these nanoparticles and deposited their monolayers on Si substrates by dip-coating.
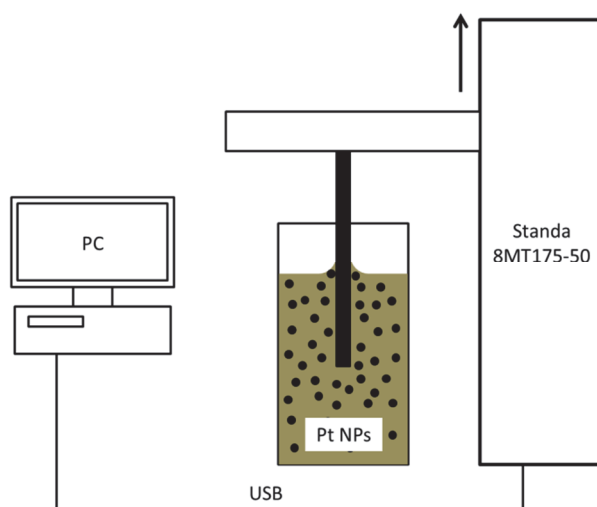
**Fig. 1** Schematic representation of the setup for dip-coating. Substrate is clamped to the holder which is attached to computer-controlled stepper motor

## 2.     MATERIALS AND METHODS

### 2.1.   Preparation of Pt nanoparticles

The suspensions of Pt nanoparticles were prepared by following the procedure described by Wang et al. [10]. 0.2 g of platinum(II) acetylacetonate ($Pt(acac)_2$) was mixed with 1-octadecene (10 ml), oleic acid (1ml), and oleylamine (1ml). The suspension was boiled in Argon atmosphere for 30 min with gradual increase of temperature to 120°C. Within this time, the suspension turned from pale yellow to light brown. During the next 30 min of gradual increase of the temperature to 200°C, the suspension changed color to dark brown. The resulting suspension was further treated by the centrifugation process: 12 ml of the suspension was mixed with 30 ml of ethanol and centrifuged. The pellet was redispersed in another 40 ml of acetone and stored for further use. Before the experiment, Pt nanoparticles were centrifuged one more time and redispersed in n-hexane.

### 2.2.   Preparation of a monolayer

Dip coating was performed on the system using a holder to which n-type epiready (100) Si substrates were attached. The movement of the holder was controlled with a stepper motor. The velocity of the motion in vertical direction was fully computer-controlled using LabView. Before dip-coating, the Si substrates were cleaved to the size of 4 × 0.6 cm and cleaned in organic solvents. After the cleaning procedure, the substrates were mounted to the holder and immersed into the suspension containing Pt nanoparticles. When the samples were extracted from the suspension, they were let dry in air.

The size of the Pt nanoparticles was analyzed with JEOL JEM 1400 transmission electron microscope (TEM) operating at 120 kV. The size distribution of Pt nanoparticles was calculated from the thresholded TEM images in the ImageJ software. The electrophoretic mobility and hydrodynamic diameter measurements were performed on a Malvern Zetasizer Nano ZS. The surface topology and homogeneity of the deposited films of nanoparticles were examined by scanning electron microscopy (SEM) in Hitachi 4800. For the estimation of the coverage, the procedure including the thresholding of SEM images in ImageJ and the integration of pixels in Matlab were employed. The dependence of the coverage on the withdrawal speed was fitted in Origin.
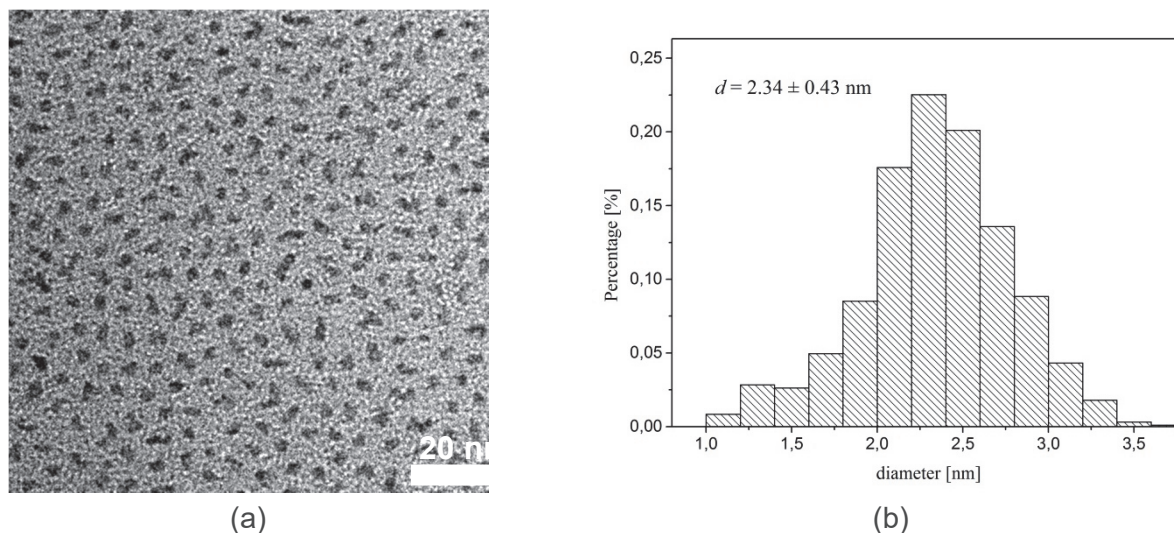
**Fig. 2** (a) TEM images of nanoparticles prepared in the presence of oleic acid and oleylamine. The white bar represents 20 nm. (b) Distribution of sizes estimated from the analysis of TEM images

## 3.    RESULTS AND DISCUSSION

For the TEM measurements, a dilute suspension was dropped onto the copper grid and let dry. The TEM image of Pt nanoparticles (**Fig. 2a**) shows that the nanoparticles have nearly spherical shape with a minority having an elongated rod-like shape. The size of Pt nanoparticles obtained from the analysis of TEM images is 2.34 ± 0.43 nm (**Fig. 2b**). The measured size from TEM image correlates with the size measured by DLS (**Fig. 3**). A moderately higher value of the diameter measured by DLS is probably given by the thickness of the capping agent surrounding the platinum nanoparticle.
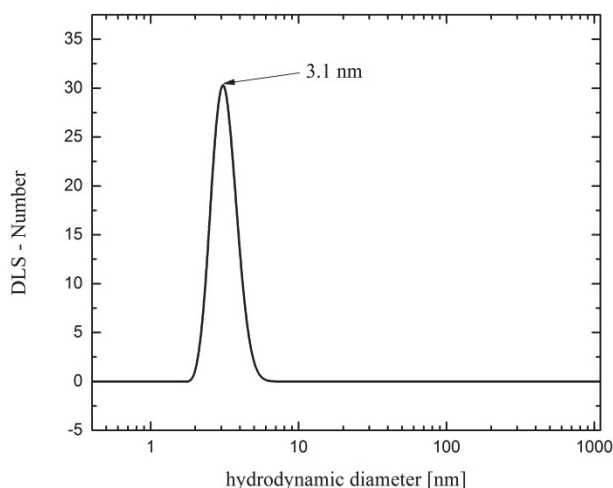


**Fig. 3** DLS spectra shows the peak corresponding to the nanoparticles of the size of 3.1 nm

The monolayers obtained by the dip-coating method are shown in **Fig. 4**. The nanoparticles are hexagonally arranged within separate domains, which is typical for the deposition of spherical nanoparticles by the dip-coating process [11]. The spacing between the nanoparticles in the monolayer is approximately 2 nm, which is the distance comparable with the chain length of the molecule of oleylamine (~2.3 nm [12]). Because the size of the Pt nanoparticles is comparable with the interparticle distances, they have a large space to move and assemble into ordered arrays, when compared with the formation of Pt nanoparticles prepared in AOT

colloid suspensions (interparticle distances ~ 1 nm, nanoparticle diameter ~ 8 nm) studied in our group previously. At low withdrawal speeds, the monolayer was formed by discrete 2D islands separated by voids. Higher withdrawal speeds led to the filling of these voids and the monolayer became more compact. At the fastest withdrawal speeds (> 0.3 mm/s), the formation of the second layer was observed.
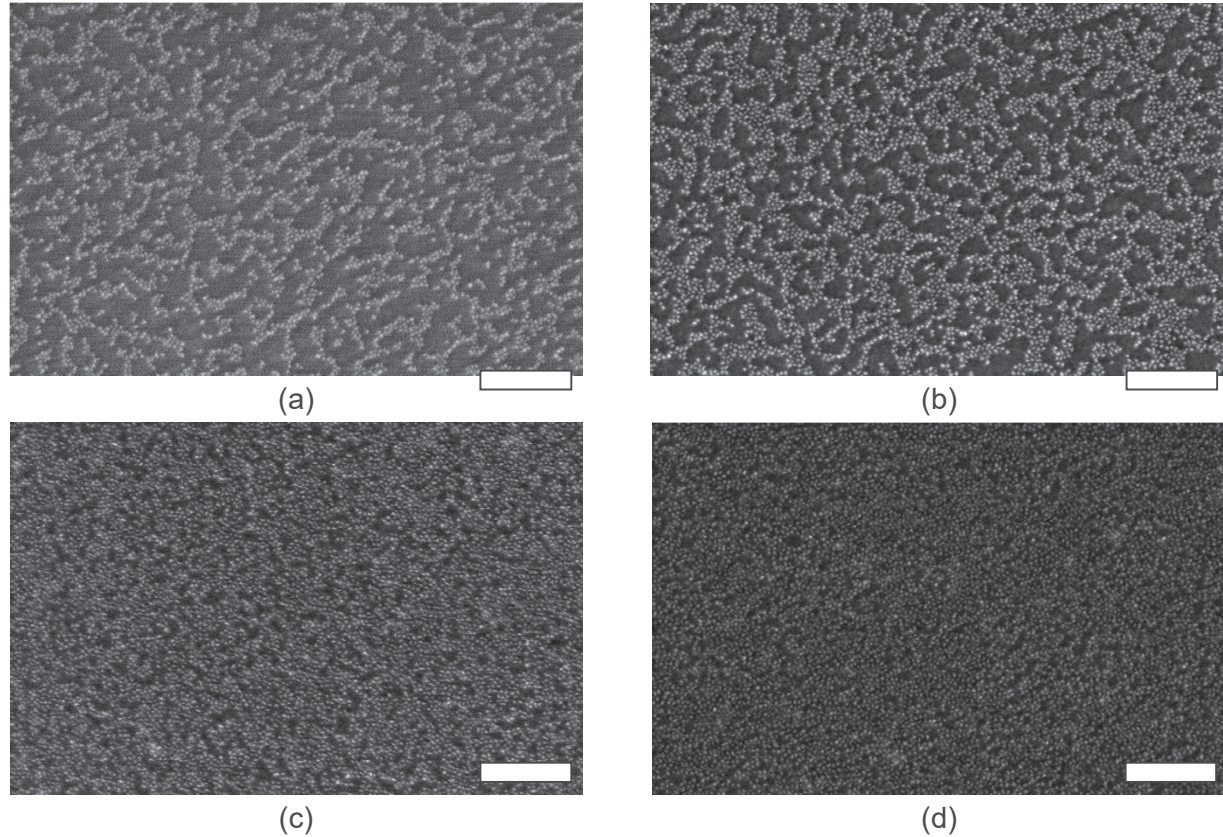


(a)

(b)

(c)

(d)

**Fig. 4** SEM images of monolayers prepared by dip-coating with various withdrawal speeds: (a) 0.1 mm/s; (b) 0.2 mm/s; (c) 0.3 mm/s; (d) 0.5 mm/s. The white bar represents 100 nm

We also studied the dependence of the coverage on the withdrawal speed while other parameters of the dip-coating (the submersion time, the solution composition, the concentration and temperature, and the substrate cleaning procedure) were fixed. If the substrate moves upwards at the velocity $v$, a liquid is entrained by the substrate. The reason for entraining is the viscosity of the liquid $\eta$ where molecules close to the substrate follow the substrate motion and entrain their neigbours. Opposite forces to the viscous force are gravitational force and surface tension [13]. The equillibrium among these forces leads to the formation of a meniscus. The suspension above the meniscus forms a thin film. The evaporation of this film leads to the nanoparticle selfassembly via attractive capillary immersion forces.

In **Fig. 5**, the dependence of the coverage $S$ on the withdrawal speed $v$ estimated from SEM figures is shown. The increasing coverage with the increasing withdrawal speed was observed. This dependence was found to be $S \approx \sqrt{v}$. This dependence is typical for high withdrawal speeds and high suspension viscosities, where the relation between the thickness of the deposited layer and the withdrawal speed is derived from balancing the viscous drag $\eta v / h$ and the gravity force $h \rho g$ [14]:

$$h = \sqrt{\frac{\eta v}{\rho g}} = C \sqrt{v} \qquad (1)$$

where $\eta$ is the viscosity of the liquid, $\rho$ is the liquid density, $g$ is the gravitational acceleration and $C = \sqrt{\eta/\rho g}$.
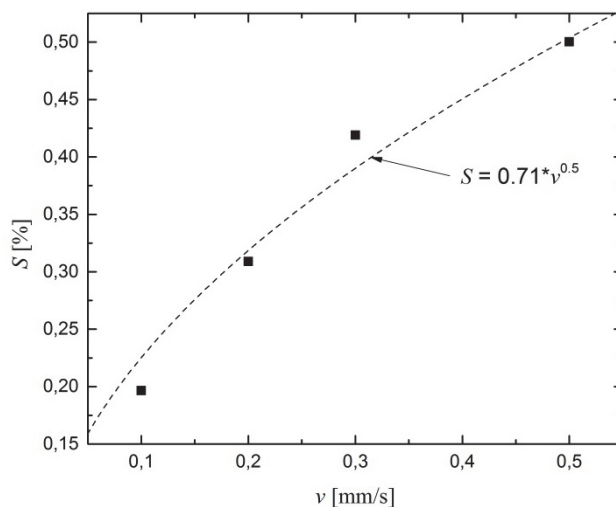


**Fig. 5** Dependence of the coverage $S$ on the withdrawal speed $v$ estimated from SEM images. The data were fitted by the equation (1)

## 4.    CONCLUSION

The synthesis of Pt nanoparticles in the presence of oleic acid and oleylamine produced nanoparticles with the size of approximately 2.3 nm with polydispersity less than 20%. These nanoparticles were successfully assembled to a monolayer with hexagonal arrangement within separate domains. A high coverage was achieved, which makes these layers promising for the preparation of Schottky barriers with a well-defined Pt nanoparticle interlayer. The increase of the withdrawal speed led to higher coverages. At the withdrawal speed of 0.5 mm/s almost a full monolayer was obtained and small islands of the second layer appeared.

## REFERENCES

[1]    CERNOHORSKY O., ZDANSKY K., ZAVADIL J., KACEROVSKY P., PIKSOVA K. Palladium nanoparticles on InP for hydrogen detection. Nanoscale Research Letters, 6(1), 2011, pp 410.

[2]    GRYM J., et al. Electrophoretic Deposition of Metal Nanoparticle Monolayers from Nonpolar Solvents for Hydrogen Sensing. Key Engineering Materials, 654, 2015, pp 213-217.

[3]    YATSKIV, R., et al. Transport properties of metal-semiconductor junctions on n-type InP prepared by electrophoretic deposition of Pt nanoparticles. Semiconductor Science and Technology, 29(4), 2014, pp 045017.

[4]    ZDANSKY K., CERNOHORSKY O., YATSKIV R. Hydrogen sensors made on InP or GaN with electrophoretically deposited Pd or Pt nanoparticles. Acta Physica Polonica-Series A General Physics, 122(3), 2012, pp 572.

[5]    ZDANSKY K., et al. Graphite Schottky Barriers on n-InP and n-GaN with deposited Pd, Pt or Bimetallic Pd/Pt Nanoparticles for H2 Sensing. Proceedings on Nanocon conference, Brno, 2011.

[6] ZDANSKY K., et al. Electrophoresis deposition of metal nanoparticles with reverse micelles onto InP. International Journal of Materials Research, 100(9), 2009, pp 1234-1238.

[7] HÜBERT T., et al. Hydrogen sensors - A review. Sensors and Actuators B: Chemical, 157(2), 2011, pp 329 - 352.

[8] VAN der BIEST O.O., VANDEPERRE L.J. Electrophoretic Deposition of Materials. Annual Review of Materials Science, 29(1), 1999, pp 327-352.

[9] CAO H., et al. Regulation of charged reverse micelles on particle charging in nonpolar media. Phys. Chem. Chem. Phys., 15, 2013, pp 12227-12234.

[10] WANG C., et al. Synthesis of Monodisperse Pt Nanocubes and Their Enhanced Catalysis for Oxygen Reduction. Journal of the American Chemical Society, 129(22), 2007, pp 6974-6975.

[11] WANG Y., ZHOU W. A review on inorganic nanostructure self-assembly. Journal of nanoscience and nanotechnology, 10(3), 2010, pp 1563-1583.

[12] MORDIKOUDIS S., LIZ-MARZÁN L.M. Oleylamine in nanoparticle synthesis. Chemistry of Materials, 25(9), 2013, pp 1465-1476.

[13] MALEKI M., et al. Landau-Levich menisci. Journal of colloid and interface science, 354(1), 2011, pp 359-363.

[14] BRINKER C., et al. Fundamentals of sol-gel dip coating. Thin Solid Films, 201(1), 1991, pp 97-108.