

# Coalescence of palladium nanoparticles assembled on carbon and SiC surfaces: STM and STS studies

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## Abstract

Pd nanoparticles assembled on carbon and carbon-terminated SiC substrates were prepared by reducing palladium ions in one step chemical reduction technique. Morphology, size distribution and coalescence of the nanoparticles were studied by scanning tunneling microscopy (STM). Smaller nanoparticles and higher coalescence events were observed for carbon substrates. The formation of Pd(111) terraces by coalescence of the nanoparticles was observed. Atomic diffusion induced by ambient exposure is proposed to explain the coalescence of the nanoparticles at the step edges of the Pd(111). Scanning tunneling spectroscopy (STS) results revealed the metallic contact between the nanoparticles and the absence of a thin non-metallic layer of residual impurities on the nanoparticle surface. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Palladium; Nanoparticles; Coalescence; Scanning tunneling microscopy

## 1. Introduction

The use of supported catalysts made of palladium are widely recognized in heterogeneous catalysis and recently with special attention in fuel cells research [1,2]. It is well known that the catalytic activity of metal dispersed catalysts is critically dependent on size and spatial dispersion of the particles. Therefore, the determination of coalescence effects which modify particle size and distribution on the support is very important. The influence of the support on the stability of the catalyst during the chemical reaction has motivated the study and use of carbon as support for Pd nanoparticles [3,4]. Efremenko and Sheintuch have found that Pd clusters are strongly bound to unsaturated and defect sites of activated carbon and that it has the strongest interaction with carbon than with any other support [3]. It is expected that for Pd nanoparticles self-assembled on carbon surfaces, the geometry of the nanoparticles array would be strongly influenced on the adhesion sites on the support.

In the study of surface structure of supported nanoparticles, size distribution, metal-induced changes of the support surface are very important. As the experimental identifications of those characteristics are very complicated for extremely small supported particles [5], the task remains open, limiting the application of supported catalysts [3]. In particular, if carbon is the support, transmission electron microscopy (TEM) has serious difficulties to analyse particles smaller than 4 nm [6].

To understand the properties of supported catalysts, the morphology, support–nanoparticle interaction, and electronic structure of metal nanoparticles, surface science techniques must be used. The scanning tunneling microscopy (STM) is possibly the most adequate technique to study the nanoparticles assembled on any substrate, because in STM there are not high energy excitations or applied forces that could modify the nanoparticle distribution. Moreover, the scanning tunneling spectroscopy (STS) in STM, is usually used to determine the local distribution of the surface energy states and the electronic structure of the surface.

In this work, palladium nanoparticles assembled on amorphous carbon and C-terminated SiC surfaces were

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analysed by scanning electron microscopy (SEM), STM and STS in order to study the effect of support substrates on size, dispersion and coalescence of nanoparticles in ambient condition.

## 2. Experimental

The samples investigated were grown by reducing the palladium metal ions on the substrate surfaces. In a typical synthesis process, carbon substrates (carbon coated microscopic grids) and 6 H-SiC wafers (epitaxially grown, CREE H0124-15) were immersed into 10 ml methanolic solution of PdCl<sub>2</sub> (Alfa Aesar, 99.9%; 0.033 mmol/50 ml of methanol) under mild agitation. Then, about 0.5 ml of aqueous solution of NaBH<sub>4</sub> (0.044 M) was added in a dropped wise. After the addition of the reducer (NaBH<sub>4</sub> solution), the carbon and SiC substrates were removed from the solution after 5, 10, and 20 min, and at 2, 5, 10, and 20 min intervals, respectively. The substrates were then dried in air at room temperature. The details of the growth technique will be discussed elsewhere. The samples prepared at different growth conditions are numbered from 1 to 7 as indicated in Table 1.

A JEOL JSM5300 SEM and a NanoScope E STM (Digital Instruments) operated in ambient conditions were employed for the topographic characterization of the samples. All the STM images presented in this work were taken in constant current (topographical) mode, using electrochemically etched W wires as probe-tips. For tunneling spectroscopy, mechanically sharpened Pt–Ir wire were used as tips. *I–V* data were collected following a common procedure: the feedback loop of the microscope that controls the vertical motion of the tip is interrupted momentarily and the bias voltage digitally ramped from an initial to a final pre-selected value, while the corresponding tunnel current is digitally sampled. The spectroscopic results presented in this work have been found to be reproducible for different nanoparticles and Pt–Ir tips.

## 3. Results and discussion

SEM micrographs of Pd nanoparticles deposited on amorphous carbon substrates revealed a surface covered by small particles whose size depended on the time of immersion in the reaction solution (Fig. 1). Small particles in range

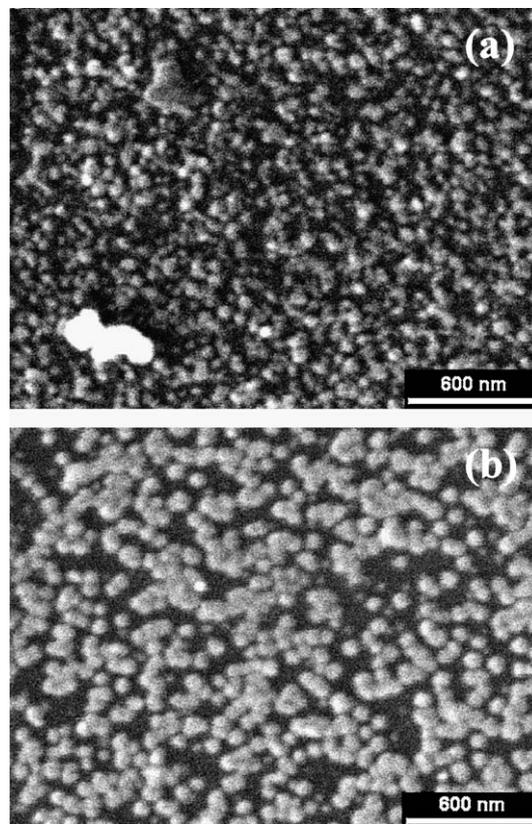


Fig. 1. SEM images of Pd nanoparticles formed on carbon substrates immersed for (a) 5 min and (b) 10 min in the reaction solution.

of 50–70 nm in diameter are observed for sample 1 and particles of approximately 80 nm in samples 2 and 3. Particle agglomeration can be observed in Fig. 1b, where the particles acquire a distribution similar to liquid droplets possibly influenced by an attractive interaction between them.

The STM images of the same samples revealed that the particles observed in SEM are really formed by an agglomeration of smaller Pd particles (nanoparticles). In fact, for all the samples prepared using carbon and SiC substrates, we observed nanoparticles-bunching as shown in the image in Fig. 2a. A more detailed study indicated that the Pd nanoparticles of sample 1 have a uniform size distribution with a mean diameter of the order of 6 nm (Fig. 2b), and the nanoparticles in samples 2 and 3 have a non-uniform size (Fig. 2c and d). Fig. 2c shows Pd nanoparticle distribution for sample 2, where we can observe some large nanoparticles possibly formed by the coalescence of smaller nanoparticles. Coalescence of small nanoparticles was also observed in sample 1, as indicated by an arrow in Fig. 2b. A similar distribution of the Pd nanoparticles was observed in the samples 2 and 3.

In all the samples large terraces were observed in some regions. Fig. 3 shows triangular-shape terraces found in the sample 1, where it is possible to observe nanoparticle agglomerations at the edges of the terraces. Large terraces without Pd nanoparticles were observed for the samples 2 and 3.

Table 1  
Designation of sample number according on their growth conditions

Sample number	Substrate	Time of immersion (min)
1	C	5
2	C	10
3	C	20
4	SiC	2
5	SiC	5
6	SiC	10
7	SiC	20

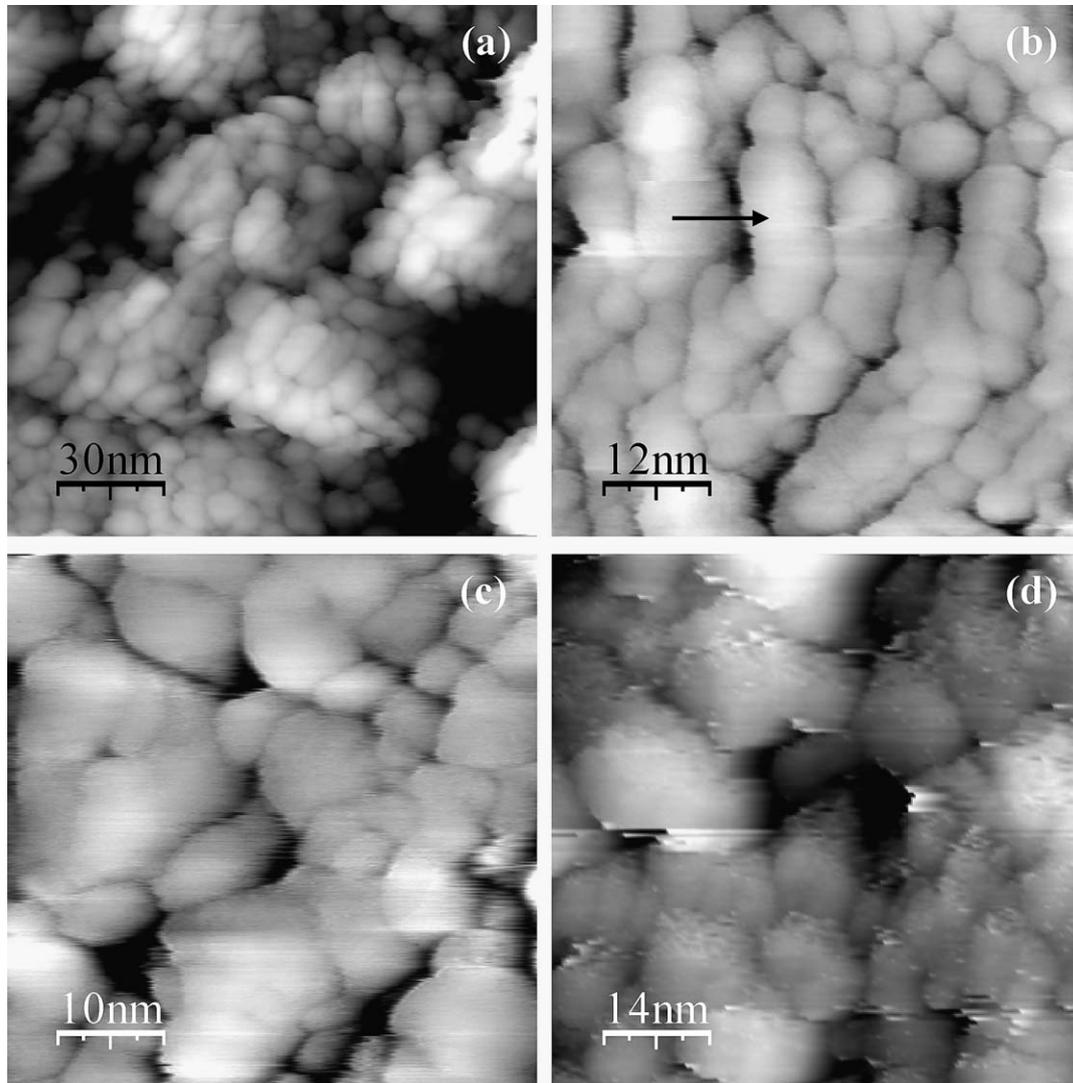


Fig. 2. STM images of the Pd nanoparticles (a) and (b) for the sample 1, (c) for the sample 2, and (d) for the sample 3. Tunneling parameters for (a–c) 350 mV and 1.5 nA, (d) 47 mV and 1.2 nA.

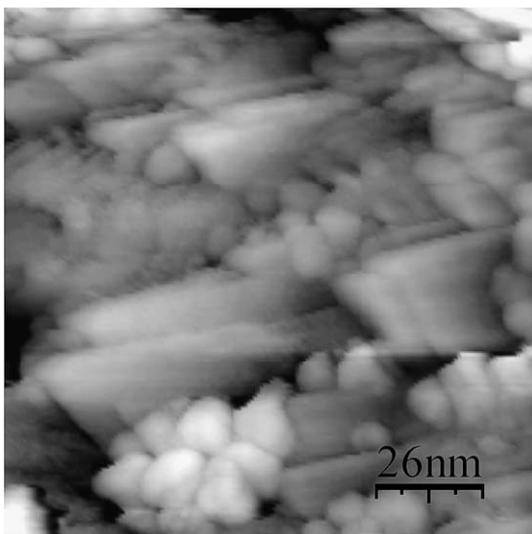


Fig. 3. A typical STM image of Pd nanoparticles forming triangular terraces, acquired at 350 mV and 1.3 nA.

SEM images of the samples prepared with SiC substrates revealed the presence of large particles with diameter of the order of 300 nm, Fig. 4. From the STM images of these samples, it was also possible to see that the particles consisted of smaller Pd nanoparticles. Fig. 5 shows the nanoparticle distributions for the samples 5 and 6. Only, a few nanoparticles with size smaller than 6 nm were found, and in general, Pd nanoparticles grown on SiC substrates had a larger size than that formed on amorphous carbon substrates (Fig. 2).

Coalescence of Pd nanoparticles on SiC substrates was also observed at lower degree than in carbon surfaces. The uniform size of the nanoparticles found in these samples (Fig. 5a and b) suggests that they were formed during synthesis, and not through coalescence of smaller particles as occurred in carbon surfaces (Fig. 2c and d). Formation of big particles of 300 nm (Fig. 4a and b) through agglomeration of small Pd particles in these samples probably can

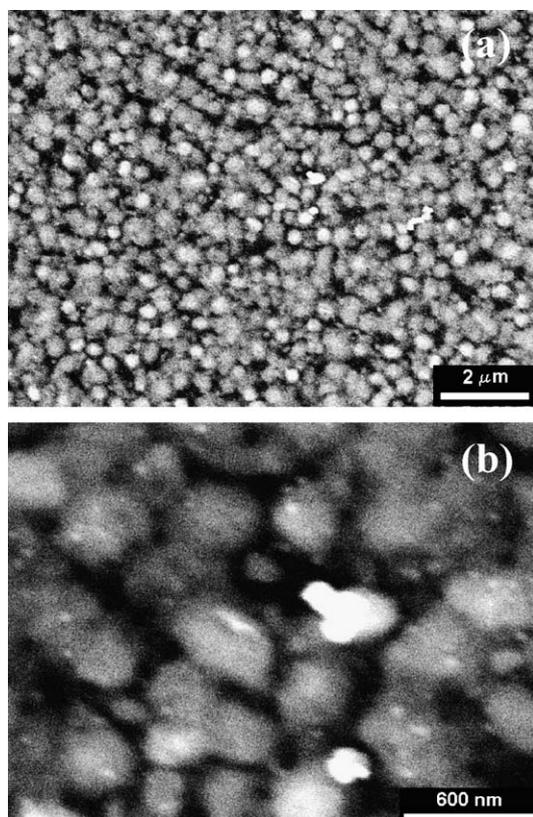


Fig. 4. SEM images of Pd nanoparticles observed in the sample 4. Similar particle distributions were observed in the samples 5–7.

be explained in terms of lower coalescence affinity of the small Pd particles.

Coalescence of Pd nanoparticles with terraces was observed only in some regions. Fig. 6a shows some triangular terraces formed with incorporated Pd nanoparticles at the apex and edges of the structures (indicated by arrows). The atomic structure of the triangular terraces (Fig. 6b) revealed a hexagonal geometry with atomic separation of  $2.6 \pm 0.2 \text{ \AA}$  that corresponds well with the value of  $2.77 \pm 0.04 \text{ \AA}$  reported for Pd(111) in Ref. [7]. We propose the formation of palladium terraces with (111) face as it is the most stable surface with lowest surface energy in the fcc-metals [8].

For the Pd nanoparticles, a high value of surface energy is expected when their size decreases, in a similar way that usually observed for other metal particles together with a reduction of their lattice parameters [9,10]. The high value of surface energy produces a reduction of the melting temperature and promotes the coalescence process in nanoparticles [11,12]. TEM experiments, however, show a lattice expansion of Pd nanoparticles when the size of the nanoparticles is reduced [13,14]. The compressive strain relaxation in the nanoparticles through the incorporation of impurities like carbon, oxygen and hydrogen reduces their surface energy as demonstrated by Lamber et al. [15].

The incorporation of impurities in the Pd nanoparticles in this study was highly probable. Our studies performed in

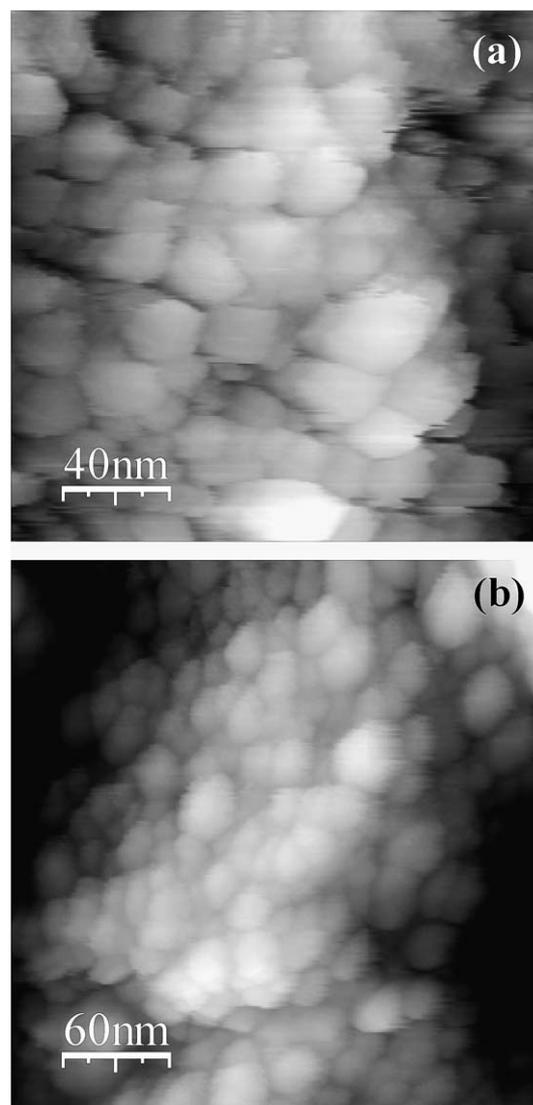


Fig. 5. STM images of the Pd nanoparticles formed in the samples (a) 5 and (b) 6. STM parameters for (a) 10 mV and 1.2 nA, (b) 750 mV and 1.3 nA.

air ambient surely were sensible to this effect and the adsorption of ambient gases on the particle surface cannot be discarded. Coalescence of Pd nanoparticles could be related with air adsorption, in a similar way that occurs with gold clusters on Au(111) [16], where isolated clusters of Au-adatoms are formed in air, reducing the size of the gold clusters with a mass flow limited by the generation of adatoms and vacancies at the step edges of the terraces. From Figs. 3 and 6a, we can see that our nanoparticles are localized near of the step edges and coalesce on the apex and edges of the triangular terraces. Moreover, the CO adsorption in Pd nanoparticles also induces coalescence and migration as has been reported by Jiang et al. [17]. Our observations suggest that the coalescence of Pd nanoparticles occurred after of the preparation of the samples and is promoted by air adsorbed or impurities incorporated in them.

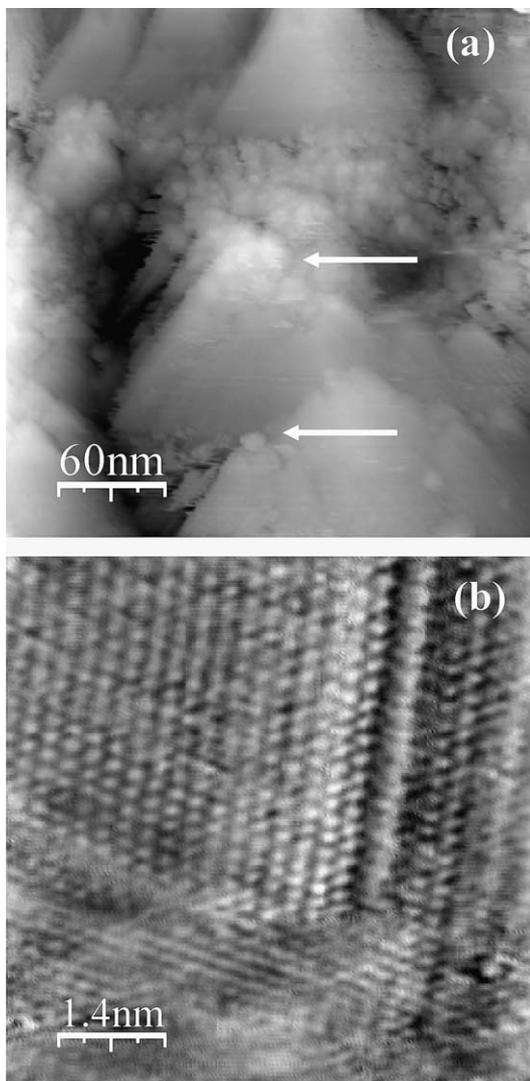


Fig. 6. STM images of (a) triangular terraces with Pd nanoparticles coalescence at their apex and edges, and (b) the atomic structure of the terraces. STM parameters: (a) 750 mV and 1.3 nA, (b) 14 mV and 5.6 nA.

Finally, STS spectra for different tip-particle separation of Pd nanoparticles were acquired. Fig. 7a shows the  $I$ - $V$  curves for some nanoparticles deposited on SiC substrates with a diameter of approximately 10 nm. Curves 1 and 2 correspond to sample 6 and the curves 3 and 4 correspond to sample 4, respectively. The curve 5 corresponds to sample 5. Close resemblance of the curves 2 and 4 indicates the reproducibility of the measurement for different Pd nanoparticles. The separation between the tip and nanoparticle was controlled with the tunnel-current set point and the sample bias in the STM. Very high values in tunnel resistance, or gap resistance, are observed for bias voltage in range of  $-500$  and  $500$  mV (curves 1–4 in Fig. 7a) for large tip-nanoparticle separation. For higher bias voltages, the exponential dependence of the tunnel current with the electron energy dominates the  $I$ - $V$  characteristic. In contrast, an Ohmic behavior was observed for lower tip-particle separations (curve 5). The normalized differential conductance

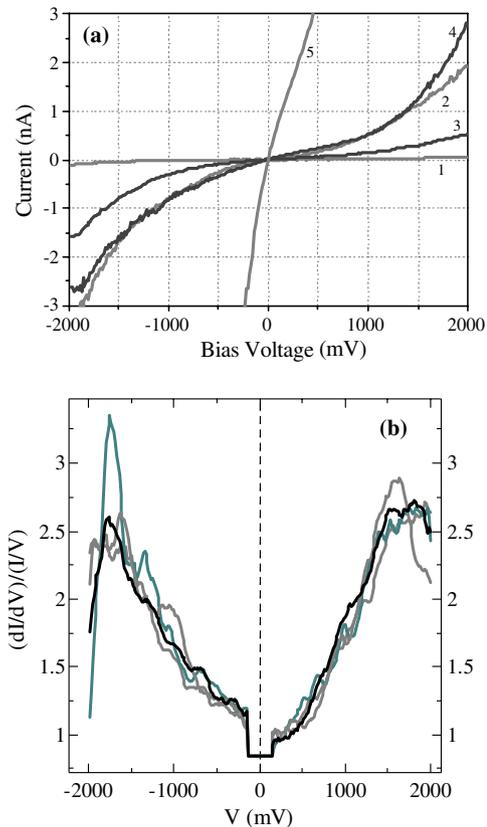


Fig. 7. (a)  $I$ - $V$  spectra acquired for the tip-nanoparticle separations determined by the tunneling parameters: (curve 1) 2100 mV and 1.3 nA; (curve 2) 700 mV and 1.5 nA; (curve 3) 692 mV and 613 pA; (curve 4) 700 mV and 1.5 nA; (curve 5) 70 mV and 1.2 nA. (b) The normalized differential conductance for the  $I$ - $V$  curves.

curves shown in Fig. 7b confirm the metallic behavior of the nanoparticles and eliminate the possibility of contamination of their surfaces by a thick non-metallic layer. Formation of only one air-monolayer is then expected for the coalescence phenomena. A non-metallic species/impurity adsorbed or absorbed on the surface of the nanoparticles in excess of some monolayer produces a barrier potential and can be easily detected with tunneling spectroscopy. Higher differential conductance values for the energy states of the conduction and valence bands are regularly recorded with STS in non-metals and semiconducting solids [18].

#### 4. Conclusions

Clean Pd nanoparticles assembled on carbon and carbon terminated SiC surfaces coalesce forming terraces of Pd(111) even in air ambient. Formation of smaller Pd nanoparticles along with higher coalescence effects are observed for the samples prepared using carbon substrates. The coalescence of Pd nanoparticles can produce bigger particles or participate in the growth of terraces. Atomic diffusion induced by air is proposed to explain the coalescence of the nanoparticles at the edge steps of the Pd(111) terraces.

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